



Competitive extraction of multi-component contaminants in water by Carboxen–polydimethylsiloxane fiber during solid-phase microextraction

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Abstract

A headspace analysis for groundwater contaminated with BTEX (benzene, toluene, ethylbenzene, and xylenes) was employed to investigate the feasibility and limitations of Carboxen–PDMS (polydimethylsiloxane) fiber during SPME (solid-phase microextraction). Although the response of the Carboxen–PDMS fiber was much higher than that of conventional PDMS fiber, a reduction of the extracted amount was also observed under multi-component conditions due to competitive replacement. The general affinity of analytes to the fiber was high in the order xylene > ethylbenzene > toluene > benzene. The behavior of the Carboxen–PDMS fiber was examined more precisely at constant compositional ratio, because the analysis of contaminants using Carboxen–PDMS fiber was reported to be possible at known composition. The relative affinity of each component was shown to differ according to the total amount of analytes. Furthermore, the extracted amounts of benzene and toluene did not show a consistent tendency as the concentration of each component increased. These results indicate that caution should be exercised if Carboxen–PDMS fibers are used for the analysis of BTEX in groundwater samples.

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1. Introduction

BTEX (benzene, toluene, ethylbenzene, and xylenes) are readily soluble components in petroleum; they are contaminants in groundwater due to leakage from underground storage tanks and are of great concern. Characterization of gasoline-contaminated groundwater requires a large number of sam-

ples and appropriate analytical procedures to verify low levels of organic contaminants. Therefore, various analytical methods have been suggested for the quantification of BTEX in groundwater.

Solid-phase microextraction (SPME) has been widely accepted as an innovative technique for the determination of organic pollutants in environmental matrices [1]. Analytes are absorbed into or adsorbed onto the SPME fiber in the aqueous solution or in the headspace over the solution, and then directly desorbed from the SPME fiber within the GC injector at high temperature. Because extraction and con-

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centration of analytes can be achieved at the same time without solvent, SPME can minimize loss of organic compounds during the simplified sample preparation process. In addition, it has been shown to be very sensitive to BTEX in water with detection limits in the sub-ng/ml level for both headspace and direct extraction application [2]. Headspace solid-phase microextraction (HS-SPME) has the advantage of reducing interference from complex constituents in water samples. In addition, high resolution and low cost can be obtained through HS-SPME in comparison to conventional headspace methods or purge-and-trap methods.

Polydimethylsiloxane (PDMS) has been used mostly as the coating material of fused-silica fiber in SPME. Several different kinds of coating materials have been introduced to enhance the selectivity and sensitivity [1,3]. Because Carboxen has a high capacity for volatile organic compounds, the first attempt to combine Carboxen with SPME was reported by Chai and Pawliszyn in 1995 [4]. They reported that a 100- μm PDMS fiber showed better response than a Carboxen fiber of unknown thickness, while the Carboxen coating had extracted a larger quantity of the target organic compounds than a Carboxen B coating. Eventually, a new 75- μm Carboxen–PDMS mixed coating fiber was designed to increase the efficiency of SPME using Carboxen, and was commercialized in 1997 by Supelco [5]. Popp and Paschke proved that the Carboxen–PDMS had an even better extraction capability than the PDMS fiber, though repeatability was slightly worse and equilibrium time was prolonged [6]. There are several more studies that have reported the advantages of Carboxen–PDMS fiber [7,8].

Recently, the limitations of Carboxen–PDMS fiber in quantification have become more apparent. Black and Fine [9] found that the response of the internal standards, deuterated methyl *tert.*-butyl ether (MTBE) and *tert.*-butyl alcohol (tBA), dropped by more than 65–90% when total aromatic compounds in groundwater increased from 0.18 to 1.8–18 mg/l. These results were compared with the static headspace sampling method, which showed that the normalized peak area of internal standards did not drop below 80% as the total aromatic content increased. They concluded that the application of

Carboxen–PDMS fiber for MTBE and tBA quantification in groundwater gave no advantage when the sample contained more than 1 ppm of total aromatic hydrocarbons such as BTEX and trimethylbenzenes (TMBs). Murray [10] also observed the competitive displacement of volatile organic sulfur compounds in Carboxen–PDMS fiber during the gas phase analysis. These results demonstrate the limitations of Carboxen–PDMS fiber for the quantitative analysis of multi-component samples.

It is important to understand the difference in extraction mechanism between Carboxen–PDMS fiber and PDMS fiber to explain these phenomena. Adsorption is the governing extraction mechanism in a mixed coating, which has porous solid as the primary extraction phase like PDMS–DVB (divinylbenzene), Carbowax–DVB, Carbowax–TR (template resin–DVB with uniform pore sizes) and Carboxen–PDMS, while absorption occurs in PDMS fiber. In an adsorption process, surface sites, where adsorption can take place, restrict the total extraction amount, and a molecule with higher affinity for the surface can replace a molecule with lower affinity. Gorecki et al. [11] tried to establish a theoretical description for porous polymer coatings based on the Langmuir isotherm model. However, this model cannot be applied to Carboxen–PDMS fiber, because the pores in Carboxen are so small that capillary condensation as well as simple adsorption can occur.

Although the effects of other analytes were quantified for fuel oxygenate (MTBE, tBA) [9] and volatile organic sulfur compounds [10] during Carboxen–PDMS fiber extraction, the performance of the fiber has not been characterized for BTEX which belong to the most abundant volatile organic contaminants in water and air. Several studies have applied Carboxen–PDMS fiber to the analysis of BTEX in headspace or gas phase without considering the interference caused by the existence of other contaminants [12–14]. These papers showed high sensitivity and efficiency of SPME with Carboxen–PDMS fiber for BTEX analysis compared to other sampling methods.

This study was designed to investigate the limitations and feasibility of BTEX extraction from contaminated groundwater using Carboxen–PDMS fiber for effective site assessment.

2. Experimental

2.1. Material and methods

Benzene, toluene, ethylbenzene, and *p*-xylene were obtained from Aldrich or Merck. Standard stock solutions of multi-component mixtures and each single component were prepared by spiking each component in HPLC-grade methanol. For multi-component standard solution, benzene, toluene, ethylbenzene, and xylene were added together to methanol at the same molar ratio. The standard stock solution was mixed with deionized water to prepare contaminated water samples at various concentrations (0.001, 0.002, 0.004, 0.01, 0.02, 0.03, 0.04, 0.07, 0.1, 0.15, 0.2 mM). A manual sampling holder for SPME equipped with a 75- μ m Carboxen–PDMS fiber (Supelco, Bellefonte, PA, USA) was used. A 100- μ m PDMS fiber was also used for comparison. Before the experiment, the fiber was conditioned at 280 °C for Carboxen–PDMS and 250 °C for PDMS. A 10-ml sample was prepared immediately before use and thoroughly mixed before the extraction. Extraction time profiles for each multi- and single-component sample were checked to determine an appropriate extraction time. The HS-SPME procedure was conducted for 30 min in a 20-ml screw-top vial equipped with a PTFE-coated silicone septum. During the extraction, the sample was stirred at 300 rpm using a magnetic spin bar and the extraction temperature was maintained at 25 °C. After the extraction, the SPME fiber was removed from the vial and immediately inserted into the GC injector and desorbed for 2 min. Each experiment was repeated three times.

2.2. Instrumentation

A Hewlett-Packard HP 6890 GC system with a split-splitless injector and a flame ionization detection (FID) system was used for analysis. Analytes were separated with a 30 m \times 0.25 mm HP-1 capillary column. Carrier gas was He and column flow was maintained at 1 ml/min. Initially, the oven temperature was held at 40 °C for 5 min, and then increased to 100 °C at 4 °C/min, and held at 100 °C for 5 min. The temperature of the injector was

300 °C for the Carboxen–PDMS fiber and 250 °C for the PDMS fiber. The temperature of the detector was 300 °C.

3. Results and discussion

The extraction time profiles were investigated to determine the time required to attain steady-state. As shown in Fig. 1, steady-state was achieved before 30 min for both multi- and single-component extraction using 75- μ m Carboxen–PDMS fiber. In the multi-component system, the extracted amount of benzene and toluene slightly decreased with time while a small increase was detected for ethylbenzene and xylene. This is probably due to the molecular replacement in Carboxen–PDMS fiber as a consequence of a high initial rate of adsorption of benzene and toluene but higher affinity for ethylbenzene and xylene. Though Li et al. [12] reported the apparent extraction peak time at 15 min during multi-component extraction in the gas phase using 75- μ m Carboxen–PDMS fiber, that kind of tendency was not observed in headspace extraction. For 100- μ m PDMS fiber, the extraction time profile was similar to that for a 75- μ m Carboxen–PDMS fiber obtained from single-component mixtures. The difference between multi- and single-component extractions was not observed for 100- μ m PDMS fiber. Therefore the extraction was conducted for 30 min according to the GC operation procedure.

The response of 75- μ m Carboxen–PDMS fiber was compared with that of 100- μ m PDMS fiber for BTEX at 0.1 mM. In the sample contaminated with a single component, the amount extracted by Carboxen–PDMS was much higher than for PDMS (Fig. 2). This result is compatible with the studies by Popp and Paschke [6] and Gaines et al. [7]. However, a reduction of peak area for each component was observed with the multi-component contaminated sample extracted with Carboxen–PDMS. In contrast, absorption on the PDMS fiber was not affected by other components, as expected. In spite of the peak area decrease, Carboxen–PDMS fiber extracted more analytes than PDMS in the multi-component system (Fig. 2).

The effect of sample composition on extraction by

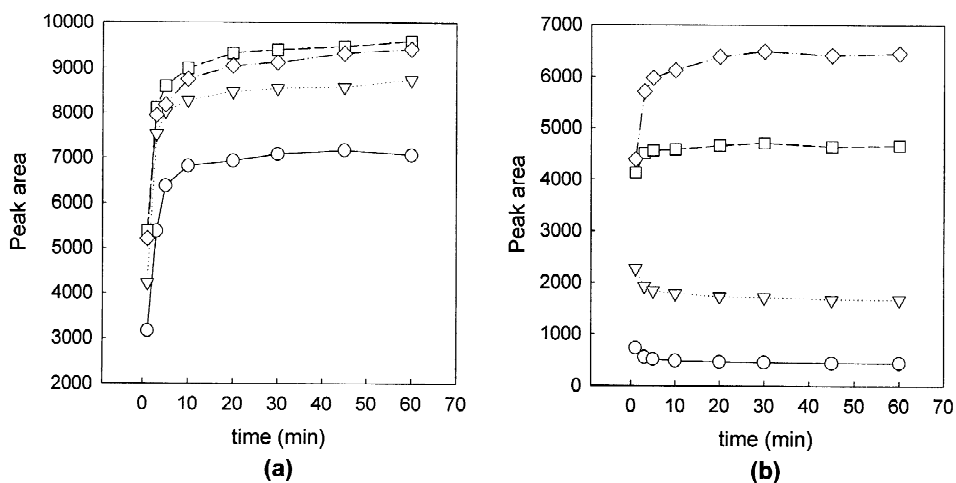


Fig. 1. Extraction time profiles for 75- μ m Carboxen-PDMS fiber at 0.1 mM. (a) Single-component extraction, (b) multi-component extraction. ○, Benzene; ▽, toluene; □, ethylbenzene; ◇, *p*-xylene.

Carboxen-PDMS was investigated more precisely over a wide range of concentrations. It seems that the interaction between analytes and Carboxen-PDMS fiber follows the general adsorption behavior when a single-component exists, while the PDMS fiber has linear correlation with analytes because of an absorp-

tion effect. Fig. 3 shows how the presence of interfering compounds can affect the extraction. Therefore, the single-component standard is not valid for the analysis of multi-component mixtures as mentioned by Murray [10]. The reduction caused by interference with other components was different for individual components, and was greatest for benzene. The affinity of xylene was higher than that of others but also decreased in the multi-component system. From these results, we could estimate the affinity sequence for different analytes for Carboxen-PDMS fiber: the order was xylene, ethylbenzene, toluene, and benzene. Gorecki et al. [11] characterized the effect of benzene on methyl isobutyl ketone (MIBK) and MIBK on benzene for both PDMS-DVB and Carbowax-DVB fiber. They found that the affinity of benzene was higher than that of MIBK.

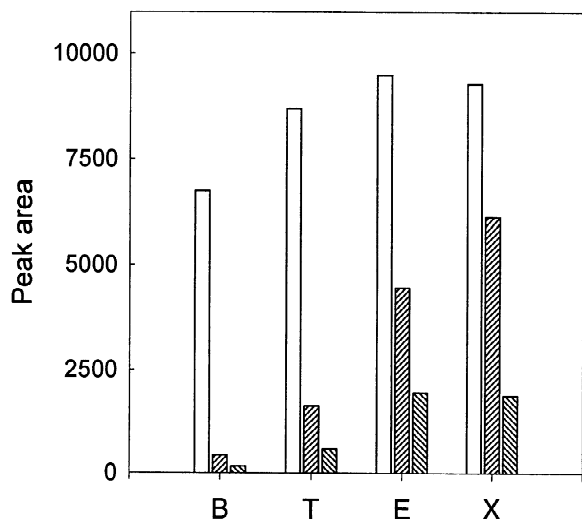


Fig. 2. Effect of fiber coatings and composition on the extracted amount at 0.1 mM; □, 75- μ m Carboxen-PDMS fiber, single-component extraction; ▨, 75- μ m Carboxen-PDMS fiber, multi-component extraction; ▩, 100 μ m PDMS fiber, single- and multi-component extraction.

There are several factors that affect the analyte selectivity of SPME fiber. For example, molecular mass and size of analyte, boiling point and vapor pressure of analyte, polarity of analyte and fiber, functional groups on analyte and fiber, and concentration range are major influencing factors [5].

Black and Fine [9] investigated the effect of BTEX and TMBs on MTBE and tBA for Carboxen-PDMS fiber, and explained the decrease in MTBE and tBA as replacement of polar compounds by less polar compounds. However, since BTEX are all non-polar aromatic compounds, the selectivity ob-

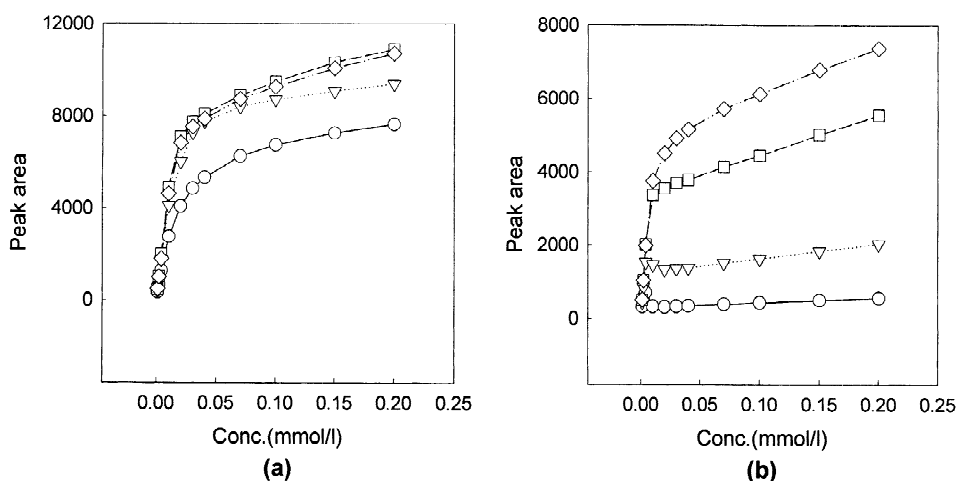


Fig. 3. Effect of composition on the extracted amount for 75 μm Carboxen–PDMS fiber. (a) Single-component calibration, (b) multi-component calibration. ○, Benzene; ▽, toluene; □, ethylbenzene; ◇, *p*-xylene.

served in this study cannot be ascribed to polarity differences. Although benzene is only slightly less polar than other components, its affinity was much lower than others.

Murray [10], who examined the interfering effect of volatile organic sulfur compounds such as methanethiol (MeSH) and 2-propenyl isothiocyanate (PITC) in the gas phase with Carboxen–PDMS fiber, pointed out that the compounds with higher molecular masses can displace those with lower molecular

masses as a consequence of competition for active sites on the fiber surface. Fig. 4a illustrates the relationship between the amount extracted and the molecular mass of analyte at 0.2 mM. For the single-component extraction, the response of each component was almost proportional to the molecular mass. The deviations from linearity were not significant. Though the Carboxen–PDMS fiber has been proved to be effective for light analytes in a gas phase, it seems that higher molecular mass is pre-

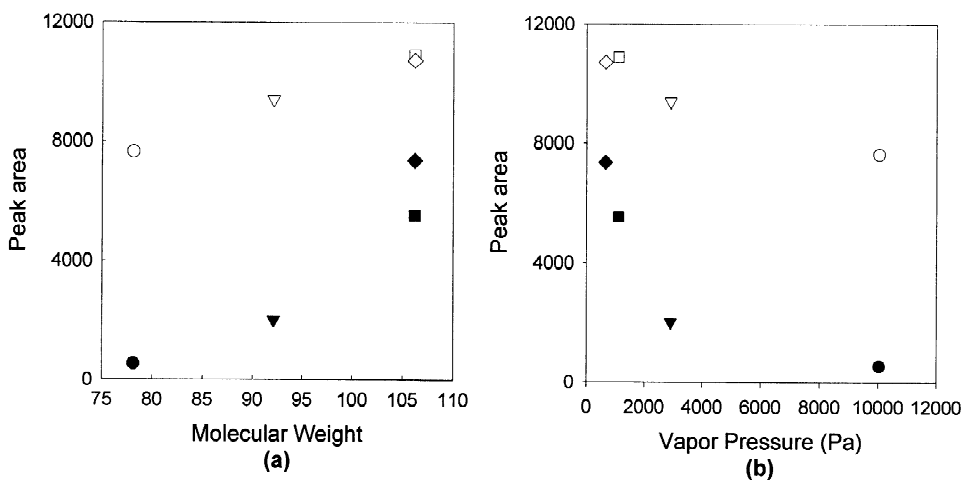


Fig. 4. Effect of molecular mass and vapor pressure on the amount of analyte extracted by the Carboxen–PDMS fiber at 0.2 mM. ○, Benzene; ▽, toluene; □, ethylbenzene; ◇, *p*-xylene. Open symbols: single-component extraction; closed symbols: multi-component extraction.

ferred over the extractable range, C_2 – C_{12} . For the multi-component extraction, the slope of the response curve was similar, but ethylbenzene and xylene, for which the molecular mass is the same, showed different affinities while the total extracted amount in a single component was almost the same. Therefore, the molecular mass alone is insufficient to explain the selectivity. As the vapor pressure of xylene is lower than that of ethylbenzene, this parameter might also influence selectivity in multi-component systems (Fig. 4b). It might be possible that both molecular mass and vapor pressure could affect the competitive extraction of analytes by the Carboxen–PDMS fiber.

From Fig. 5, which illustrates each analyte in-

dividually from Fig. 3b, we found unexpected unique characteristics of benzene and toluene during multi-component extraction using Carboxen–PDMS fiber. At the beginning, the extracted amount of benzene and toluene increased sharply, and then decreased back to some degree, and finally increased again. Because this phenomenon was not observed during single-component extraction, it was inferred that the competition with other compositions caused the problem. But this competitive replacement has no consistent tendency and differs from ordinary adsorption behavior. As a result, it seems that the total amount of analytes plays an important role in adsorption of Carboxen–PDMS fiber. For example, for benzene, the initial increase probably corresponds

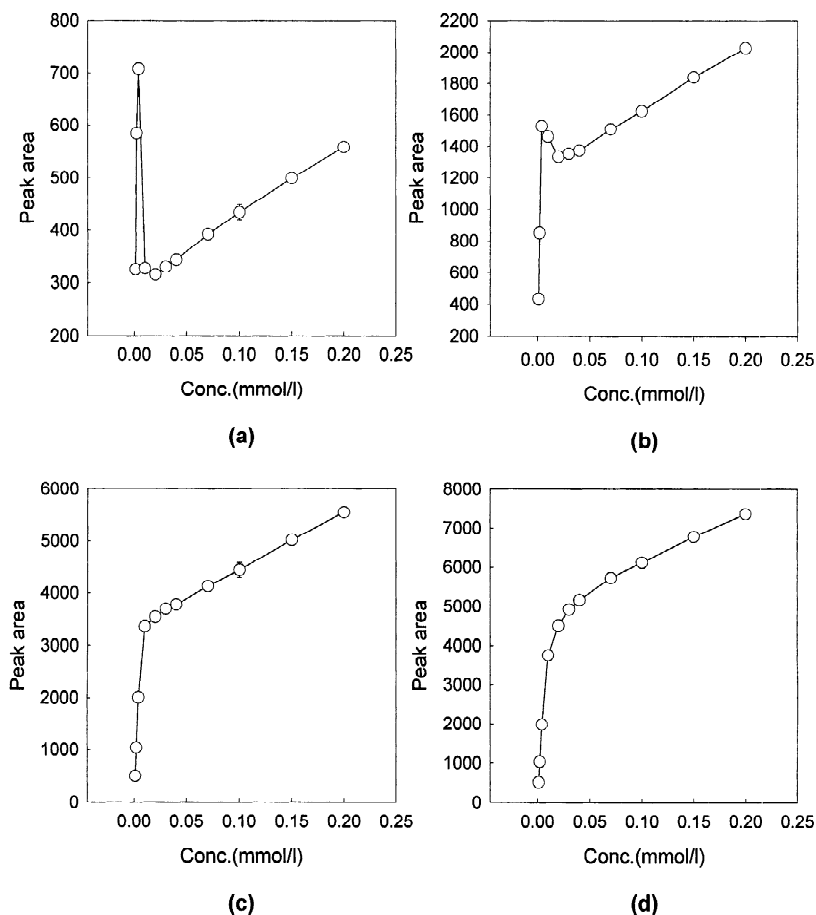


Fig. 5. Behavior of each component in multi-component calibration. (a) Benzene, (b) toluene, (c) ethylbenzene, (d) *p*-xylene.

to a scenario where there are still a significant number of active sites available for adsorption. At the higher concentrations of the mixture, the number of available sites decreases rapidly; therefore molecules start to compete for them. Since benzene has the lowest affinity to the coating, it is replaced by the other BTEX molecules, and its peak area goes down. At even higher concentrations, capillary condensation is most probably responsible for the observed increase in benzene peak area. The differences between the shapes of the curves can be easily attributed to the different affinities of the molecules towards the coating. Fig. 6 reveals that the relative affinity was changed according to the total concentration of analytes, even though analytes in the sample were maintained at the same molar ratio. At low concentrations, all analytes were extracted with similar efficiency, but the relative amounts of benzene or toluene decreased as concentration increased. Restriction of effective surface site and influence of capillary condensation may not be significant at low concentration range. Therefore, not only compositional change but also the amount of analytes can

affect the competitive displacement in Carboxen–PDMS fiber. It makes the use of Carboxen–PDMS fiber for quantitative analysis difficult even when the relative proportions of analytes are known. As suggested by Black and Fine [9], the effectiveness of Carboxen–PDMS fiber can only be realized when the concentration of the analyte is at a low level and interfering compounds are absent. To identify the advantages and limitations of the Carboxen–PDMS fiber, adsorption characteristics need to be investigated further.

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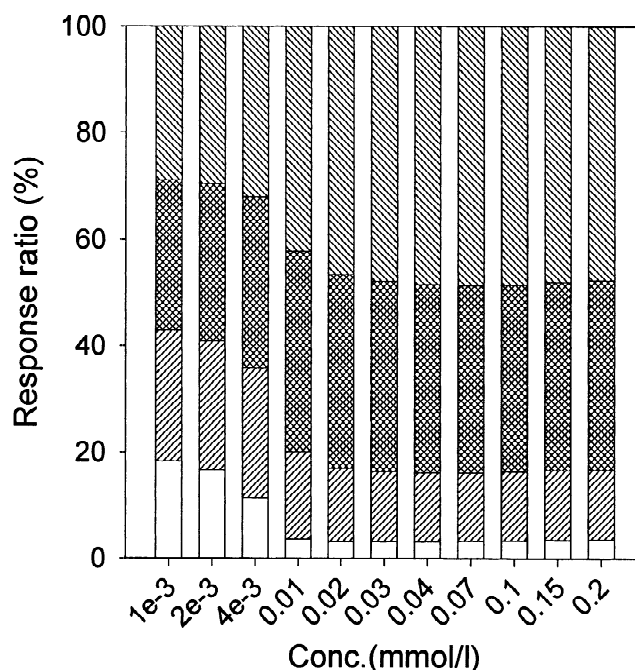


Fig. 6. Relative amounts of analytes extracted at various concentrations. □, Benzene; ▨, toluene; ▩, ethylbenzene; ▤, p-xylene.

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