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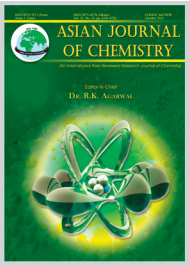

Use of 1-Adamantanecarboxylate as Desorbing Displacer for Eluting Solutes Retained with the Sorbent of β-Cyclodextrin Bonded Silica in Coupling Solid Phase Extraction with Micellar Electrokinetic Chromatography

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Use of 1-adamantanecarboxylate as desorbing displacer for eluting solutes retained with the sorbent of β-cyclodextrin bonded silica in coupling solid phase extraction with micellar electrokinetic chromatography was studied. The sorbent showed strong capacity of retaining 4-*tert*-butylphenol and 2,2-di(4-hydroxyphenyl)propane spiked in double-distilled water. Using the desorbing displacer of 1-adamantanecarboxylate was more effective in eluting 4-*tert*-butylphenol and 2,2-di(4-hydroxyphenyl)propane retained from the β-cyclodextrin bonded silica sorbent in the solid phase extraction cartridges than common organic solvents. The eluate collected can be directly introduced to micellar electrokinetic chromatography for separation. The results of evaluation on analytical performance of coupling the solid phase extraction with micellar electrokinetic chromatography have been presented.

Key Words: Solid phase extraction, β-Cyclodextrin bonded silica, Displacer, 1-Adamantanecarboxylate, Micellar electrokinetic chromatography.

INTRODUCTION

Micellar electrokinetic chromatography (MEKC), one of the common formats of capillary electrophoresis, has gained popularity in analytical separation of neutral compounds as well as charged ones[1]. Separation in micellar electrokinetic chromatography is based primarily on the partitioning of the solutes between the micellar phase and the aqueous phase. This technique shows advantages of high separation efficiency, short analysis time, easy operation and low operation cost.

Sample preparation is an essential step of chemical measurement processes in general. It is even more crucial in capillary electrophoresis owing to a number of factors including very small sample loading volume, low sensitivity of on-capillary detection systems and strong influence of the sample matrix components. One way of avoiding or minimizing these inherent difficulties and their strong effects on the quality of analytical results is by considering sample preparation a key part of capillary electrophoresis process[2].

Extraction has been widely used for off-capillary sample preparation in micellar electrokinetic chromatography[3]. In general, extraction serves as two functions of concentration and clean-up in sample preparation in micellar electrokinetic chromatography. Extraction usually results in considerable concentration effect of analytes and reduction of interference from sample matrix in complex samples. On-capillary coupling solid-phase extraction with micellar electrokinetic chromatography is usually difficult due to less effective desorption of retained solutes from the sorbents, very small sample volume loading and incomparability of eluates to micellar electrokinetic chromatography. On-capillary coupling liquid-liquid extraction is also rare in use because solvents employed in liquid-liquid extraction are usually of low conductivity and lead to interruption of the current during micellar electrokinetic chromatography process[4]. We reported some strategies for coupling liquid-liquid extraction with micellar electrokinetic chromatography[4,5]. However, solid-phase extraction, mainly owing to their avoidance of toxic and flammable solvents, has been frequently employed in off-capillary mode for sample preparation in micellar electrokinetic chromatography[6-10].

Sample preparation in separation of environmental pollutants of phenols by micellar electrokinetic chromatography has been reported with the use of many kinds of solid phase extraction sorbents[3,6,11]. But these common sorbents showed only moderate selectivity to phenols. Recently, a more selective sorbent, based on β-cyclodextrin-bonded silica (CDS), to phenols has been reported[12-14]. β-Cyclodextrins can selectively

form inclusion complexes with certain molecules, it offered a range of separation methods for those compounds[13,15,16]. Moreover, the β-cyclodextrin-bonded silica has been used as solid phase extraction materials for phenols by chromatographic methods[12,14,17-19].

Displacement has been a well-known chromatographic mode[20-23]. However, use of displacement in solid phase extraction eluting step was surprisingly scarce[24,25]. Although displacement is not suitable to generate discrete solute zones in chromatogram development, it is likely to reduce eluting volume for retained desired solutes in solid phase extraction and to improve concentration limits of detection for these solutes with use of appropriate displacers. In this paper, we described the use of 1-adamantanecarboxylate as desorbing displacer for eluting solutes retained with the β-cyclodextrin-bonded silica in coupling solid phase extraction with micellar electrokinetic chromatography. The modeling solutes used in this work were common phenol pollutants, bisphenol A (2,2-*bis*-(4-hydroxyphenyl) propane, BPA) and 4-*tert*-butylphenol (4-tBP).

EXPERIMENTAL

Micellar electrokinetic chromatography experiments were performed on a CE-L1 instrument (CE Resources Pte, Singapore) equipped with a linear UVIS 200 detector (Alltech, Deerfield, IL, USA). Electropherograms were recorded with the CSW software (Data Apex, Prague, Czech Republic). Fused-silica capillaries of 61 cm total length and 50 cm effective length (375 μm O.D. and 50 μm I.D.) used in the micellar electrokinetic chromatography experiments were purchased from Yongnian Optical Fiber Factory (Hebei, China). Solid phase extraction cartridges were homemade by packing 25 mg of β-cyclodextrin-bonded silica in each medical syringe tube. A Y002.30 vacuum pump (Shanghai Medical Instrument Plant, China) was used to provide a negative pressure to facilitate sample eluting process. Nylon filters with pore size of 0.45 μm were obtained from Quandao Technical Company (Shanghai, China). Fluorescence spectra were recorded with an RF-5301 PC,Spectrofluorophotometer (Shimadzu, Japan).

1-Adamantanecarboxylic acid and 4-*t*-butylphenol (4-tBP) were products of Aldrich (Milwaukee, MI, USA). Methanol, acetonitrile, sodium dihydrogenphosphate and disodium hydrogenphosphate dodecahydrate of analytical grade and 2,2-di(4-hydroxyphenyl) propane (BPA) of chemical pure grade were purchased from SCRC (Shanghai, China). Sodium dodecyl sulfate (SDS) and hydrochloric acid of analytical grade were obtained from Shanghai Haoshen Chemical Reagent (Shanghai, China). β-Cyclodextrin was purchased from Sigma (St. Louis, MO, USA). Silica gel (10 μm in diameter) used in synthesis of β-cyclodextrin bonded silica (CDS) was purchased from Qingdao Sea Chemical Plant (Qingdao, China). The β-cyclodextrin-bonded silica was synthesized in our laboratory according to the method reported by Feng *et al.*[14].

Stock solutions of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane (1000 mg L^{-1}) were prepared in methanol. The working solution of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane was prepared before use by mixing 1 mL of each of the phenolic solutions and being diluted to 2.00 mg L^{-1} with double-distilled water. Sample solutions used for solid phase extraction were prepared by 50-fold dilution of the working solution with double-distill water. 1-Adamantanecarboxylate solution of 50 mM was prepared by dissolving 1-adamantanecarboxylic acid in 100 mM sodium hydroxide and then adjusting pH to 7 with hydrochloric acid. All reagents were used without further purification.

Solid phase extraction procedure: Before use, the cartridges were conditioned with 4 mL of methanol and then 4 mL of double-distilled water at a flow rate of 2 mL min^{-1}. During the conditioning step and the following extraction process, the cartridges were not allowed to dry. Sample solutions (50-fold dilution of the working solution) of 150 mL were then loaded onto the solid phase extraction cartridges and 3 mL of otherwise specified eluting solution was employed to elute the solutes. Concentration of solutes in the eluates was then measured by micellar electrokinetic chromatography with the capillary electrophoresis system, which is described in detail below.

Micellar electrokinetic chromatography operating procedures: To prepare running buffer for the micellar electrokinetic chromatography, 20 mM sodium dodecyl sulfate was dissolved in 25 mM phosphate buffer (pH = 8.0) and then the solution was mixed with acetonitrile at a ratio of 95:5 (v/v). New capillaries were rinsed with 0.1 M NaOH for 10 min, double-distilled water for 5 min and the run buffer for 10 min in order. Sample introduction was made by applying pressure of 0.30 psi for 10 s. Voltage of 20 kV with normal polarity (the positive electrode at the injection end) was applied for the micellar electrokinetic chromatography separation. On-column UV detection was conducted at 214 nm in the micellar electrokinetic chromatography experiments. Temperature was maintained at 25 ºC for the micellar electrokinetic chromatography experiments.

RESULTS AND DISCUSSION

Breakthrough curves: To evaluate the sample loading capacity of a sorbent for interesting solutes, the breakthrough volume (Vb) is an important characteristic parameter, which can be established from the breakthrough curves[26,27]. Thus, we constructed the breakthrough curves of the β-cyclodextrin-bonded silica for 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane. Solutions of each of the phenols at 2 mg L^{-1} in double-distilled water were used in order to provide a reasonable detector response and 60 mL of each solution was allowed to pass the cartridges with the aid of vacuum at a flow rate of 1 mL min^{-1}. About every 2 mL of solution was collected and then determined by micellar electrokinetic chromatography. The results are shown in Fig. 1. The breakthrough volumes of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)-propane were found to be 12 mL and 25 mL, respectively, indicating the effective retention of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane on the β-cyclodextrin-bonded silica.

Comparison of eluting procedures with and without displacer: Among the various steps in the whole solid phase extraction procedure, elution is the most essential one since it determines whether the solutes retained on the sorbent could

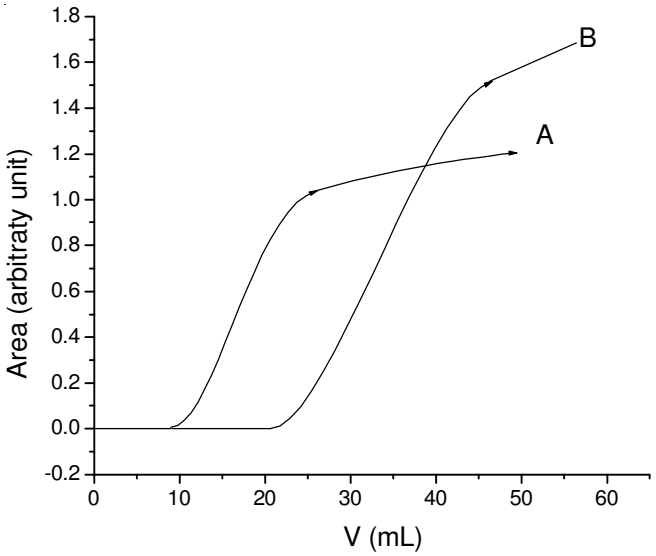

Fig. 1. Breakthrough curves of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane. Loading sample solution: each of the phenols at 2 mg L^{-1} in water. Each solution of 60 mL was allowed to pass the cartridges with the aid of vacuum at a flow rate of 1 mL min^{-1}. A: breakthrough curve of 4-*tert* butylphenol, B: breakthrough curve of 2,2-di(4-hydroxyphenyl)propane

be recovered efficiently. A good eluting solution should be able to remove the retained solutes from the sorbent effectively and selectively. Close investigation was carried out to obtain a rapid effective eluting procedure. To evaluate eluting procedure, 10 mL of working solution containing 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane at 2 mg L^{-1} was first loaded onto the solid phase extraction cartridges and then different solutions were tested for eluting effectiveness. It was found that 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane could not be eluted with 5 mL of methanol-water (v/v = 2:3) and the same solutes only partly eluted with 5 mL of acetonitrile-water (v/v = 2:3). These results indicated that methanol and acetonitrile were not effective solvents for eluting the two solutes. It was much likely due to the fact that inclusive interaction of the solvent molecules with the cavity of the cyclodextrin is rather weak. Adamantane is known to have a strong tendency to interact with the cavity of the cyclodextrin[13,28-30]. 1-Adamantanecarboxylate has been demonstrated as the solute-competitive mobile phase additive in HPLC of enantiomeric separation with β-cyclodextrin stationary phase[23]. As mentioned above, 2,2-di(4-hydroxyphenyl)propane could hardly be eluted effectively by methanol and acetonitrile due to the strong inclusion interaction on the β-cyclodextrin-bonded silica, 1-adamantanecarboxylate, however, could strongly compete with 2,2-di(4-hydroxyphenyl)propane for β-cyclodextrin and might displace 2,2-di(4-hydroxyphenyl)-propane effectively out of the cavity of the cyclodextrin. Thus, it is decided to test 1-adamantanecarboxylate as a displacer to elute the solutes of 2,2-di(4-hydroxyphenyl)propane and 4-*tert* butylphenol. The comparison of the eluting effectiveness of acetonitrile and 1-adamantanecarboxylate for 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane is given in Fig. 2. It can be seen in Fig. 2(a) that the maxima on the two eluting curves for 4-tBP occurred corresponding to about 1 mL eluting volume for both acetonitrile and 1-adamantane-carboxylate based eluting systems. In Fig. 2(b) the maximum on the eluting curve for acetonitrile based eluting system corresponded to about 1 mL and the maximum on the eluting curve for 1-adamantanecarboxylate based eluting system corresponded to about 2 mL. However, at any given volume within 5 mL, the 1-adamantanecarboxylate based eluting system showed higher eluting efficiency for both 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane than the acetonitrile based one, that is, the eluting curves using 1-adamantanecarboxylate were above the eluting curves using acetonitrile. Comparison of the recoveries of the two model solutes using 3 mL eluting solution with and without the displacer is given in Table-1.

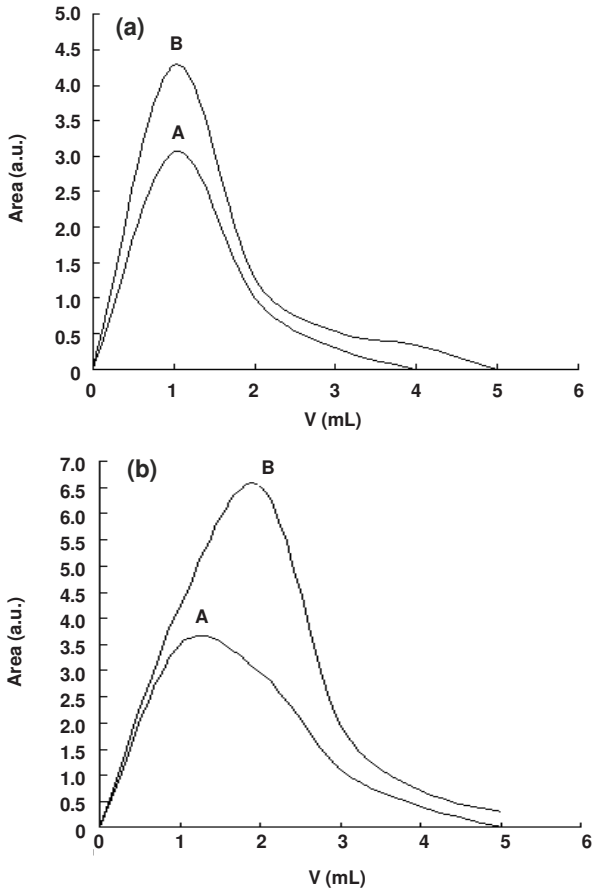

Fig. 2. Comparison of eluting effectiveness of acetonitrile and 1-adamantanecarboxylate for 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane. (a) Comparison of eluting effectiveness of acetonitrile and 1-adamantanecarboxylate for 4-*tert* butylphenol. A: eluting with acetonitrile-water (v/v = 2:3), B: eluting with 50 mM 1-adamantanecarboxylate. (b) Comparison of eluting effectiveness of acetonitrile and 1-adamantanecarboxylate for 2,2-di(4-hydroxyphenyl)propane. A:eluting with acetonitrile-water (v/v = 2:3), B: eluting with 50 mM 1-adamantanecarboxylate

TABLE-1
COMPARISON OF THE RECOVERIES OF THE TWO MODEL SOLUTES USING 3 ML ELUTING SOLUTION WITH AND WITHOUT THE DISPLACER

	Recovery (mean + RSD[a]) (%)	
	4-tBP	BPA
40 % Acetonitrile	59(9.6)	42(10)
1-Adamantanecarboxylate	71(12)	73(11)

[a]Mean and RSD were calculated for triplicate experiments

The fluorescence spectra (Fig. 3) of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane were measured under different conditions to get insight into the displacement of 1-adamantanecarboxylate for the cavity of β-cyclodextrin to the solutes. Comparing trace A with trace B in the Figs. 3(a) and 3(b), it is obvious to see that the presence of β-cyclodextrin enhanced fluorescence intensity of both 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane at 305 nm significantly. Such enhancement on fluorescence intensity could be explained as the result of change of the solutes from aqueous surrounding to hydrophobic surrounding after inclusion of the solutes into the cavity of β-cyclodextrin. Introduction of 1-adamantanecarboxylate led to decrease in fluorescence intensity represented by trace C relative to trace B. It was due to displacement of 1-adamantanecar-boxylate for the cavity of β-cyclodextrin to the solutes through competitive interaction between 1-adamantanecarboxylate and the solutes with β-cyclodextrin.

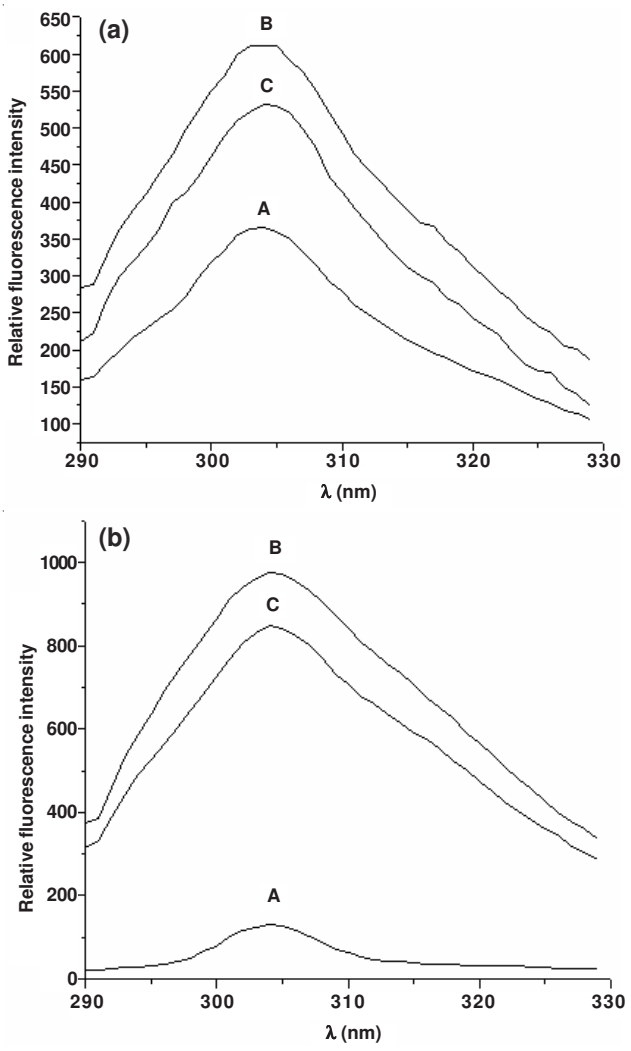

Fig. 3. Fluorescence spectra of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane measured under different conditions. Excitation wavelength: 276 nm. (a) A: 4-*tert* butylphenol at the level of 100 μg L^{-1} in water; B: 0.3 mM β-cyclodextrin added in the solution for A; C: 0.2 mM 1-adamantanecarboxylate added in the solution for B. (b) A: 2,2-di(4-hydroxyphenyl)propane at the level of 100 μg L^{-1} in water; B: 0.3 mM β-cyclodextrin added in the solution for A; C: 0.2 Mm 1-adamantanecarboxylate added in the solution for B

The phenomena observed here were analogous to those typically found in studying the competing chemical equilibria of the inclusion systems of β-cyclodextrin and two competing solutes. The proposed mechanism of the displacement of eluting the two solutes with 1-adamantanecarboxylate in the solid phase extraction procedure could be well supported by the results of the fluorescence studies.

Analytical performance of coupling the solid phase extraction with micellar electrokinetic chromatography: To examine the effects of 1-adamantanecarboxylate in eluate on the micellar electrokinetic chromatography separation of 4-tBP and BPA, the electropherograms of 4-tBP and BPA obtained for the working solution without the solid phase extraction procedure and the dilute sample solution after the solid phase extraction procedure are presented in Fig. 4 for comparison. It can be seen that 1-adamantanecarboxylate showed very low mobility (much shorter migration time) as a large peak on trace B in Fig. 4. 1-Adamantanecarboxylate in eluate had no interfering effects on the separation of 4-tBP and BPA and no adverse effects on separation efficiency of the micellar electrokinetic chromatography separation system. To prepare the sample for trace B, 150 mL of sample solution of 4-tBP and BPA (each 40 μg L^{-1}) was forced to pass the solid phase extraction cartridges and then the cartridges were eluted with 3 mL of 50 mM 1-adamantanecarboxylate, finally the eluates were collected and measured by the micellar electrokinetic chromatography. The sample for trace A was the working solution (each 2 mg L^{-1}) without the use of the solid phase extraction procedure. The analytical performance of the solid phase extraction procedure is summarized in Table-2. A great advantage of using the eluting solution of 1- adamantane-

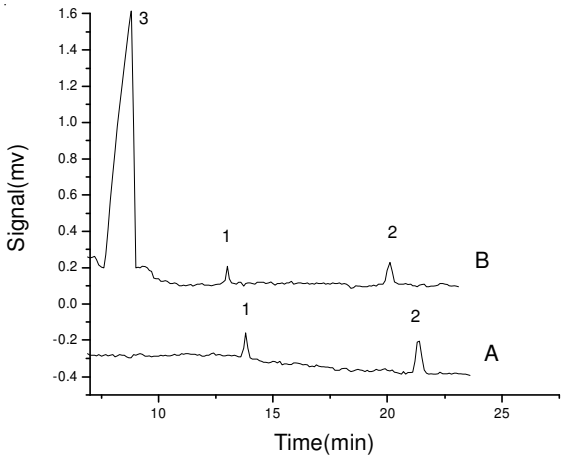

Fig. 4. Comparing electropherograms of 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane obtained in the micellar electrokinetic chromatography for the working solution without the solid phase extraction procedure and the dilute sample solution after the solid phase extraction procedure. Running buffer: 20 mM sodium dodecyl sulfate in 25 mM phosphate buffer (pH = 8.0) containing 5 % acetonitrile (v/v). Capillaries: total length of 61 cm and effective length of 50 cm (375 μm O.D. and 50 μm I.D.). Sample introduction: 0.30 psi for 10s. Separation voltage: 20 kV with normal polarity (the positive electrode at the injection end). Detection: at 214 nm. Temperature: at 25 ºC. A: electropherogram obtained with working solution (each 2 mg L^{-1}). B: electropherogram obtained with the dilute sample solution (each 40 μg L^{-1}) after the solid phase extraction procedure. Peak identification: **1**: 4-*tert* butylphenol; **2**: 2,2-di(4-hydroxyphenyl)propane. **3**: 1-adamantanecarboxylate

TABLE-2
ANALYTICAL PERFORMANCE OF COUPLING THE SPE WITH MEKC

	4-tBP	BPA
RSD (n = 5, 2 mg L^{-1}) Migration time (%)	1.5	1.7
Peak height RSD (%)	2.8	3.6
Peak area RSD (%)	1.9	3.8
Concentration factor[b] (RSD, %, n = 5, 40 μg L^{-1})	35(13)	36(10)
Concentration factor[c] (RSD, %, n = 5, 40 μg L^{-1})	32(14)	34(12)
LOD (mg L^{-1}, S/N = 3)	0.025	0.020

[b]Concentration factor (in terms of peak height) = [(peak height obtained after SPE procedure)/(peak height obtained with working solution)] × dilution factor; [c]Concentration factor (in terms of peak area) = [(peak area obtained after SPE procedure)/(peak area obtained with working solution)] × dilution factor

carboxylate is that the collected eluate can be directly introduced to micellar electrokinetic chromatography for separation. Unlike some organic eluting solvents, exchanging the organic solvents for the micellar electrokinetic chromatography running buffer before sample introduction is not required. The concentration factors for 2,2-di(4-hydroxyphenyl)propane and 4-*tert* butylphenol were 36 and 35 in terms of peak height and 34 and 32 in terms of peak area, respectively.

Conclusion

Evaluation on use of 1-adamantanecarboxylate as desorbing displacer for eluting solutes retained with the selective sorbent of β-cyclodextrin-bonded silica in coupling solid phase extraction with micellar electrokinetic chromatography was performed. The β-cyclodextrin-bonded silica showed strong capacity of retaining 4-*tert* butylphenol and 2,2-di(4-hydroxyphenyl)propane spiked in double-distilled water. The concentration factors for the two solutes were greater than 30-fold. The solution of 1-adamantanecarboxylate has been proven to be effective for eluting the solutes retained by the β-cyclodextrin-bonded silica through inclusion and may be used for eluting other solutes retained with the β-cyclodextrin-bonded silica by similar mechanism of inclusion complexation. The eluate collected can be directly introduced to the micellar electrokinetic chromatography for separation. Coupling solid phase extraction with micellar electrokinetic chromatography effectively exploits the advantages of both solid phase extraction and micellar electrokinetic chromatography, one for sample preparation and the other for separation. Such a coupling method can be potentially used for concentration enhancement and sample clean-up and expansion of application of micellar electrokinetic chromatography to separation of neutral compounds at low concentration levels in real samples, such as some pollutants in environmental water samples.

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