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Preparation and application of the sol–gel-derived acrylate/silicone co-polymer coatings for headspace solid-phase microextraction of 2-chloroethyl ethyl sulfide in soil

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Abstract

Three types of novel acrylate/silicone co-polymer coatings, including co-poly(methyl acrylate/hydroxy-terminated silicone oil) (MA/OH-TSO), co-poly(methyl methacrylate/OH-TSO) (MMA/OH-TSO) and co-poly(butyl methacrylate/OH-TSO) (BMA/OH-TSO), were prepared for the first time by sol–gel method and cross-linking technology and subsequently applied to headspace solid-phase microextraction (HS-SPME) of 2-chloroethyl ethyl sulfide (CEES), a surrogate of mustard, in soil. The underlying mechanisms of the coating process were discussed and confirmed by IR spectra. The selectivity of the three types of sol–gel-derived acrylate/silicone coated fibers was studied, and the BMA/OH-TSO coated fibers exhibited the highest extraction ability to CEES. The concentration of BMA and OH-TSO in sol solution was optimized, and the BMA/OH-TSO (3:1)-coated fibers possessed the highest extraction efficiency. Compared with commercially available polyacrylate (PA) fiber, the sol–gel-derived BMA/OH-TSO (3:1) fibers showed much higher extraction efficiency to CEES. Therefore, the BMA/OH-TSO (3:1)-coated fibers were chosen for the analysis of CEES in soil matrix. The reproducibility of coating preparation was satisfactory, with the RSD 2.39% within batch and 3.52% between batches, respectively. The coatings proved to be quite stable at high temperature (to 350 °C) and in different solvents (organic or inorganic), thus their lifetimes (to 150 times) are longer than conventional fibers. Extraction parameters, such as the volume of water added to the soil, extraction temperature and time, and the ionic strength were optimized. The linearity was from 0.1 to 10 μg/g, the limit of detection (LOD) was 2.7 ng/g, and the RSD was 2.19%. The recovery of CEES was 88.06% in agriculture soil, 92.61% in red clay, and 101.95% in sandy soil, respectively.

Keywords: Sol–gel; Polyacrylate; Solid-phase microextraction; 2-Chloroethyl ethyl sulfide

1. Introduction

Chemical warfare agents (CWAs) pose a serious and credible threat to civilian and military populations owing to the demonstrated toxicity of such compounds and the relative ease with which they may be used. In recent years, there has been a growing interest in the analysis of CWAs and their related compounds in complex environmental samples. This is mainly because of the coming into force of the Chemical Weapons Convention (CWC), which prohibits the development, production, stockpiling and use of CWAs. Analysis of CWAs and their related compounds may play a key role in the verification of the treaty. One of the most widely used chemical warfare agents has been bis(2-chloroethyl)sulfide, better known as sulfur mustard agent. It is a vesicant or blistering chemical warfare agent, for which there is still no effective therapy. Because of the potential health hazards and legal issues associated with the use of actual chemical warfare agents, 2-chloroethyl ethyl sulfide (CEES), which is structurally similar to mustard agent but less toxic and less of an environmental hazard than mustard, is commonly used as the surrogate of mustard by most researchers [1,2].

Detection of mustard and its simulant CEES is challenging because they are semivolatile liquid under ambient conditions, can easily hydrolyze in water and soil, and can

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be strongly adsorbed to many surfaces. The most widely employed technique for the analysis of mustard and its simulant CEES in environmental, biological and decontamination samples has been capillary gas chromatography [3], gas chromatography-mass spectrometry [4,5], ion trap mass spectrometer [6,7], etc. Owing to the complexity of environmental samples, sample pretreatments, such as extraction, preconcentration and clean-up steps, are often required to improve the sensitivity. Solid-phase microextraction (SPME), introduced by Pawliszyn and co-workers [8], is an inexpensive, time-efficient, and solvent-free sample preparation technique. It has been developed and successfully used to rapidly and simply complete sampling in field and laboratory settings for numerous types of compounds. Recently, SPME has been successfully used for relatively safe sampling and analysis of extremely dangerous compounds such as CWAs or their degradation products in air [9,10], natural water [11,12] and soil [13–15]. Smith and co-workers developed a headspace SPME and gas chromatography-mass spectrometry (GC–MS) method for the detection of mustard in an agriculture soil [4]. The commercially available polyacrylate (PA) fiber was selected for study, and the LOD of mustard in soil was 237 ng/g. Moreover, they used SPME under field conditions to sample VX contamination on clothing materials, and analysis was completed under field conditions as well [14]. In addition, the SPME–GC–MS sampling and analysis method was also employed in bis(diisopropylaminoethyl)disulfide (a degradation product of the nerve agent VX) analysis in soil [15]. Analyst safety is enhanced by the alkaline hydrolysis of VX in the soil sample and the intent to determine the presence of VX through the identification of the resulting VX degradation product bis(diisopropylaminoethyl)disulfide.

SPME is based on the partitioning of analytes between the stationary phase immobilized on a fused silica fiber substrate and the sample matrix, therefore, the key part of the SPME device is the fiber coating. Besides the commercially available SPME fibers, some new types of fibers such as non-polar silica particles bonded with C_8, C_{18} [16], inorganic carbopack [17], gold [18], pencil lead [19], graphite [20], activated charcoal [21], filter paper [22], poly(3-methylthiophene) [23], nafion perfluoriated resin [24], polyimide [25], polypyrrole [26], anodized aluminum wire [27], molecularly imprinted polymer (MIP) [28], and alkyldiol-silica (ADS) particles [29] have also been developed by several research groups. However, most of these fibers are normally prepared by mere physical deposition, high temperature epoxy immobilization or partial crosslink of the polymer coating on the surface of the fused-silica fibers. The lack of proper chemical bonding between the polymer coating and fiber surface may be responsible for the low thermal and chemical stability and short lifetime [30–32]. These limiting factors have hindered the development of SPME to a certain extent. It is evident that future advancements in SPME technology would greatly depend on new developments in the areas of sorbent chemistry and coating technology that will allow preparation of chemically immobilized coatings from advanced material systems providing desired selectivity and performance in SPME.

Sol–gel coating technology, established by Malik and coworkers [32–35], has solved these problems. It provides a versatile tool for the synthesis of organic-inorganic hybrid materials with advanced properties that are often difficult to achieve either from totally inorganic or from totally organic materials. Sol–gel process usually involves catalytic hydrolysis of the alkoxide precursors and polycondensation of the hydrolyzed products and other sol–gel-active components present in the sol solution to form a macromolecular network structure of sol–gel materials [36,37]. Selective coating materials can be incorporated with the inorganic polymeric structure by the polycondensation of hydroxyl groups [32], and be chemically bonded with other organic components by ring opening polymerization [38–40] or radical cross-linking reaction [41,42]. The sol–gel approach provides direct chemical bonding of the stationary phase to the fiber substrate, which results in higher thermal and solvent stability of the stationary phase compared with the conventional technique. It allows for the creation of thick coatings that are porous. Such coatings inherently possess enhanced surface area and sample capacity. It also provides flexibility in fine-tuning the selectivity of the stationary phase through adjusting the composition of the sol solution used to create these stationary phases. Because of these inherent advantages over conventional approaches, the sol–gel approach is gaining popularity in all major areas of separation science. Malik and co-workers have applied sol–gel coating technology to open tubular column GC [33], capillary electrophoresis (CE) [35]. They have also used the sol–gel coating technique for a SPME fiber (10 μm PDMS) [32]. In our group, polyphenylmethylsiloxane [41], crown ether [38,39], divinylbenzene [42], and calixarene [40] coating materials have been prepared with sol–gel coating technology. Compared with conventional SPME coatings, they showed better selectivity and sensitivity toward polar analytes (phenols [38], aromatic amines [39,40], phosphate and phosphonate [42]), non-polar analytes (benzene derivatives [40,41], PAHs [40,41]), and high boiling point compounds (phthalate esters [40]).

Acrylate, including methyl acrylate (MA), methyl methacrylate (MMA) and butyl methacrylate (BMA), which contain a vinyl substituent, are one of the standard hydrophobic monomers for organic/inorganic coating materials [43], polymeric membranes [44] and monolithic columns with templated porosity [45,46]. Cross-links can be formed between acrylate and the alkoxysilane precursor that contains a vinyl substituent; at the same time, the self cross-linking reaction can also be occurred under ultraviolet light.

In this work, co-poly(methyl acrylate/hydroxy-terminated silicone oil) (MA/OH-TSO), co-poly(methyl methacrylate/OH-TSO) (MMA/OH-TSO) and co-poly(butyl methacrylate/OH-TSO) (BMA/OH-TSO) fiber coating materials were prepared for the first time by sol–gel method and cross-linking technology. The selectivity of the three kinds of acrylate/silicone fibers was compared. The concentra-

tion of BMA and OH-TSO in sol solution was optimized. The characteristics of these fibers were also evaluated. The novel sol–gel-derived BMA/OH-TSO (3:1) fiber was then applied to headspace solid-phase microextraction (HS-SPME) of CEES in soil matrix.

2. Experimental

2.1. Apparatus

A SP-6800A capillary GC system (Shandong, China) equipped with a capillary split/splitless injector and flame ionization detection system was used. Online data collection and processing was done on Chromatopac model SISC-SPS (Beijing, China). To mix various solution ingredients thoroughly, an Ultrasonator model SY-1200 (shengyuan, China) was used. A Centrifuge model TGL-16C (Shanghai Anting Instrument Factory, Shanghai, China) was used to separate the sol solution from the precipitate. The fused-silica fiber (120 μm, o.d.) with protective polyimide coating was provided by the Academy of Post and Telecommunication, Wuhan, China. A magnetic stirrer DF-101B (Leqing, China) was employed for stirring the sample during extraction. A homemade SPME syringe was used to transfer the extracted sample to the GC injector for analysis. The laboratory-made SPME fibers used in this work include 80 μm sol–gel-derived OH-TSO, 75 μm MA/OH-TSO (3:1), 72 μm MMA/OH-TSO (3:1) and 75, 85 μm BMA/OH-TSO (3:1)-coated fibers. They were all conditioned at 250–350 °C for 2 h before used. The commercially available PA coated fiber and holder were purchased from Supelco (Bellefonte, PA, USA). Prior to use, the PA fiber was conditioned following the manufacturer's recommendations. Blank runs were completed at least once daily before use of any fibers for sampling to ensure no carryover of analytes from previous extractions. IR spectra were done on IR instrument model FTIR-8201PC (Shimadzu).

2.2. Reagents and materials

OH-TSO was purchased from Chengdu Center for Applied Research of Silicone (Chengdu, China). Tetraethoxysilane (TEOS), poly (methylhydrosiloxane) (PMHS), and vinyltriethoxylsilane (VTEOS) were obtained from the chemical plant of Wuhan Univercity, China. Trifluoroacetic acid (TFA) was purchased from Merck, Germany. MA, MMA and BMA were purchased from Shanghai Chemical Factory, China. CEES was purchased from Aldrich (Milwakee, WI, USA). All solvents used in this work were analytical-reagent grade.

2.3. GC condition

Separation was carried out on a laboratory-made capillary column (25 m × 0.32 mm i.d.) coated with SE-54. Nitrogen was used as the carrier gas at a linear velocity of 30 cm/s. Splitless injections were performed. Temperature was maintained at 250 °C for the injector, 280 °C for the detector. The column was held at 50 °C for 2 min, and then ramped at 10 °C/min to 250 °C, held for another 2 min.

2.4. Fiber preparation

Prior to sol–gel coating, the 6-cm-long fused-silica fiber was dipped in acetone for 3 h to remove the protective polyimide layer, in a 1 M NaOH solution for 1 h to expose the maximum number of silanol groups on the surface, cleaned with water, and dipped in 0.1 M HCl solution for 30 min to neutralize the excess NaOH, cleaned again with water and air-dried at room temperature.

MA, MMA and BMA were purified by washing with 5% sodium hydroxide aqueous solution, followed by washing with water. The organic portion was then dried for 24 h under anhydrous sodium sulfate, filtered, and finally distilled under reduced pressure.

The sol solution was prepared as follows: 270 μl of BMA, 90 mg of OH-TSO, 100 μl of TEOS, 50 μl of VTEOS, 10 mg of PMHS and 8 mg of benzophenone (BP) were dissolved in 120 μl of methylene chloride and mixed thoroughly by ultrasonic agitation in a plastic tube. A 100-μl volume of TFA containing 5% water was sequentially added to the resulting solution with ultrasonic agitation for another 5 min. The mixture was centrifuged at 12,000 rpm for 8 min. The top clear sol solution was collected for fiber coating. A sol–gel coating was formed on the outer surface of the fiber end (about 1 cm), after the fiber was dipped vertically into the sol–gel solution for 30 min. For each fiber, this coating process was repeated several times until the desired thickness of the coating was obtained. After that the fibers were irradiated under ultraviolet light for 30 min, then placed in a desiccator for 12 h at room temperature and conditioned at 250–350 °C under nitrogen protection for 2 h in the GC injection port. The final thickness of the sol–gel-derived BMA/OH-TSO (3:1)-coated fiber was measured by microscope. It was the semidiameter of the coated fiber minus the semidiameter of the bare fiber.

The coating preparation of the sol–gel-derived MA/OH-TSO (3:1) and MMA/OH-TSO (3:1)-coated fibers was identical with that of the sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. Moreover, other sol–gel-derived BMA/OH-TSO fibers were coated with an identical procedure except that the proportion of BMA to OH-TSO was changed from 1:1, 2:1, and 3:1 to 4:1. A sol–gel-derived OH-TSO fiber was also coated for comparison with the same procedures except that BMA was not added into the sol solution.

2.5. IR experiment

The sol–gel-derived OH-TSO and BMA/OH-TSO fibers were conditioned at 350 °C under nitrogen protection for 2 h, and then dipped in methylene chloride for 2 h before the IR experiment. A section of the coating was harvested with a razor blade from the pretreated fiber, then ground and blended

with potassium bromide (KBr). The KBr pellet spectra of the coatings were acquired with air as background at a resolution of 4 cm^{-1} over the full mid-IR range (4000–400 cm^{-1}). In addition, IR spectrum of pure BMA was also recorded by liquid film method over the same frequency region and at the same resolution for comparison. The film of BMA was prepared on a sodium chloride plate. The IR spectrum was acquired with the sodium chloride window as a background.

2.6. Thermal and chemical stability

The thermal stability was evaluated by conditioning the fiber for 2 h at 250, 280, 300, 320 and 350 °C, respectively. The chemical stability was estimated by dipping the fiber in methylene chloride, acetonitrile, acetone for 2 h, and distilled water for periods of up to 12 h, respectively.

2.7. Preparation of standard solution

Stock solution was prepared by dissolving 10 mg of CEES in a 10-ml volumetric flask diluted with acetonitrile to give a standard solution of 1 mg/ml at room temperature.

2.8. Soil sample preparation

Red clay, used as a standard soil, was obtained from Wuhan province, China. It was air-dried to constant weight at room temperature, pulverized and sieved to a grain size of 2 mm. After homogenization, the soil sample was stored at 4 °C. Blank analysis of the standard soil was carried out before spiking. Red clay, sandy soil and agriculture soil samples applied to evaluate the recovery of the method were obtained from the suburb of Wuhan city, China.

2.9. Soil headspace solid-phase microextraction procedure

Freshly spiked soil sample was prepared by adding a 10-μl of CEES standard solution to 1 g of the standard soil, then shaking carefully to homogenize it. The final concentration of the spiked soil sample was 10 μg/g. A 2-ml of deionized water saturated out with NaCl was added to the soil. The volume of water added to the soil was large enough to form slurry. To avoid sample evaporation, the vials were enclosed with butyl rubber stoppers wrapped with PTFE sealing tape, and then sealed with aluminum caps. The slurry was stirred by magnetic stirring. The needle of the home-made SPME syringe was first passed through the septum, and then the fiber was pushed out of the needle into the headspace above the soil for 30 min at 40 °C. After the extraction, the fiber was immediately inserted into the heated injector of the gas chromatograph with 5 min desorption time. Each analysis was undertaken in duplicate using different vials.

Five consecutive extractions of the spiked soil samples with 10 μg/g of CEES were performed under the optimized HS-SPME conditions and analyzed by GC-FID for the investigation of the precision of this method. A series of standard solutions at 0.01, 0.05, 0.1, 0.5 and 1 mg/ml were prepared in acetonitrile by dilution of the 1 mg/ml stock solution. These standards were used for spiking standard soil samples to yield concentrations ranging from 0.1 to 10 μg/g. Each concentration level was extracted in triplicate. The sampled fibers were analyzed by GC-FID to obtain the calibration curve and linear range of this method. The LOD was based on the lowest detectable peak that had signal three times of the background noise (signal/noise = 3).

Blank analysis of the red clay, sandy soil and agriculture soil samples was carried out before the recovery experiments. A 10-μl of 0.1 mg/ml of CEES standard solution was spiked into 1 g of soil to obtain a concentration of 1 μg/g. The spiked soil samples were kept at 4 °C but allowed to warm to room temperature prior to SPME analysis. SPME experiments were performed as described under the standard soil procedures. Each analysis was undertaken in triplicate. The recovery of the method was obtained by comparing the peak areas of the spiked soil samples with the corresponding peak areas of the standard soil.

3. Results and discussion

3.1. Underlying mechanism of the coating process

Table 1 lists the compounds and chemical structures of the principal ingredients of the sol–gel coating solution. The sol–gel solution contains appropriate amounts of stationary phase (OH-TSO and acrylate), two different alkoxysilane precursors (TEOS and VTEOS), a surface deactivation reagent (PMHS), and an acid catalyst (95% TFA, containing 5% water). OH-TSO is added into this system not only to lengthen the silica network leading to the increased surface area of the fiber but also to help to spread the stationary phase on the fiber uniformly. MA, MMA and BMA molecules in the sol–gel network are selective coating materials. Unlike the commonly used sol–gel process, in which only one metal alkoxide is used as the precursor to produce silica fiber, our process involves two different silica monomers as co-precursors [41,42]. A commonly used precursor for glass matrix, TEOS, was hydrolyzed in conjunction with a second monomeric unit precursor that contains a vinyl substituent. In this study, we selected VTEOS as co-precursor, which reacted with acrylate (MA, MMA or BMA) by radical cross-linking reaction to produce chemical bonding of acrylate to another coating ingredient (OH-TSO). The self cross-linking reaction of acrylate also occurred during the sol–gel process under UV with benzophenone (BP) as an immobility catalyst. Thus, surface-bonded polymeric coatings MA/OH-TSO, MMA/OH-TSO and BMA/OH-TSO were formed with the aid of VTEOS as bridge using sol–gel-coating method and cross-linking technology, and the chemical structure is shown in Fig. 1.

Table 1
Compounds, functions and chemical structures of the coating solution ingredients for sol–gel-derived acrylate/silicone co-polymer coatings

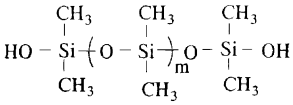
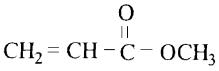
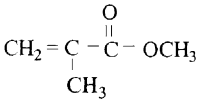
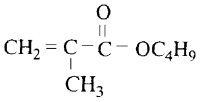
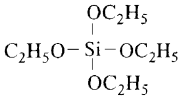
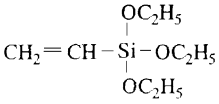
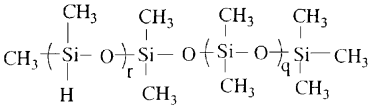
Ingredient	Function	Chemical structure
Hydroxy-terminated silicone oil (OH-TSO)	Coating stationary phase	
Methyl acrylate (MA)	Coating stationary phase	
Methyl methacrylate (MMA)	Coating stationary phase	
Butyl methacrylate (BMA)	Coating stationary phase	
Tetraethoxysilane (TEOS)	Sol–gel precursor	
Vinyltriethoxylsilane (VTEOS)	Sol–gel precursor	
Poly(methylhydrosiloxane) (PMHS)	Deactivation reagent	
Trifluoroacetic acid (95% TFA)	Acid catalyst	CF_3COOH

Fig. 2 shows the IR spectra of sol–gel-derived OH-TSO stationary phase, sol–gel-derived BMA/OH-TSO stationary phase and pure BMA. The feature identified for BMA (1720.55 cm^{-1} ($\nu_{C=O}$)) also appeared in sol–gel-derived BMA/OH-TSO coating. It demonstrated the successful binding of BMA to the stationary phase.

3.2. Characteristics of the sol–gel-derived acrylate/silicone co-polymer coatings

3.2.1. Selectivity of the coating

The selectivity of sol–gel stationary phases can be easily fine-tuned by adjusting the composition of the coating sol solution and the concentration of the sol solution ingredients.

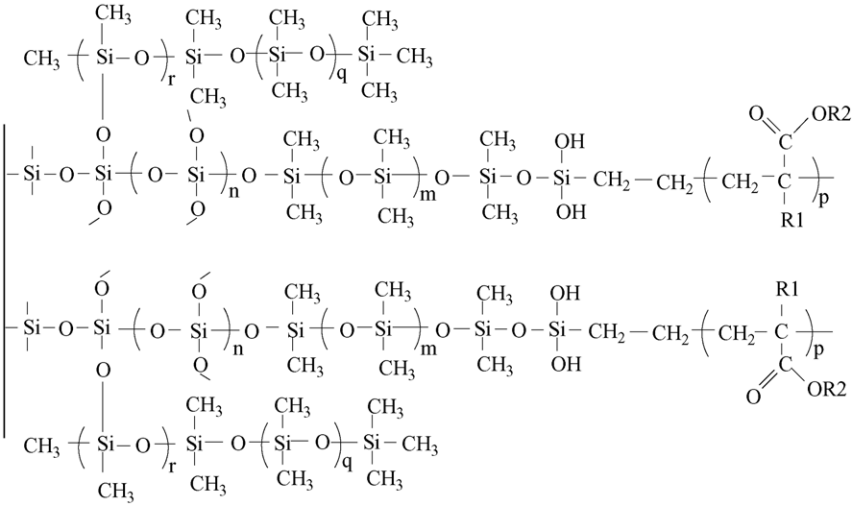


Fig. 1. The possible structure of the sol–gel-derived acrylate/silicone co-polymer coatings. R1 = H, CH_3; R2 = CH_3, C_4H_9; MA (R1 = H; R2 = CH_3); MMA (R1 = CH_3; R2 = CH_3); BMA (R1 = CH_3; R2 = C_4H_9).

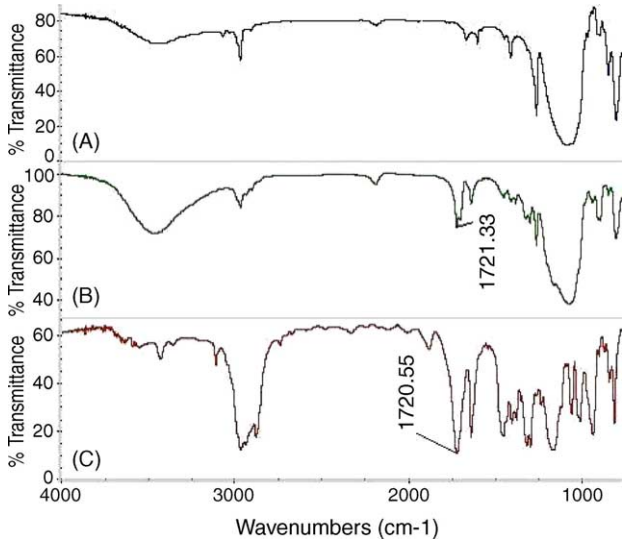


Fig. 2. IR spectra of sol–gel-derived OH-TSO stationary phase (A), sol–gel-derived BMA/OH-TSO stationary phase (B) and pure BMA (C).

Table 2 lists the octanol–water partition coefficient ($\log K_{ow}$), water solubility (W_{sol}) and boiling point (B_p) of target analytes diethyl sulfide (DES), CEES, mustard and three kinds of acrylate coating materials. The sequence of $\log K_{ow}$ is BMA > MMA > MA, and that of W_{sol} is BMA < MMA < MA. The polarity of the coating increases with the decline of $\log K_{ow}$ and the increase of W_{sol}. Therefore, the sequence of the polarity is BMA < MMA < MA. Furthermore, $\log K_{ow}$ and W_{sol} of BMA are close to those of DES, CEES and mustard. According to the principle of "like dissolves like", DES, CEES and mustard would be expected to partition more readily into the medium polar BMA coating rather than the more polar MMA and MA coatings. Fig. 3 compares the extraction efficiency of the three kinds of sol–gel-derived acrylate/silicone-coated fibers. The experiment results are consistent with the hypothesis. Maximal extraction quantities per unit volume for CEES are obtained by the sol–gel-derived BMA/OH-TSO (3:1)-coated fiber.

Fig. 4 shows the extraction capability of sol–gel coated OH-TSO fiber and BMA/OH-TSO (3:1) fiber with the identical preparation procedure. The sol–gel-derived BMA/OH-TSO (3:1) coating gave much higher response to CEES than the OH-TSO fiber. Undoubtedly, BMA plays an important role in the extraction.

Table 2
The octanol–water partition coefficient ($\log K_{ow}$), water solubility (W_{sol}) and boiling point (B_p) of diethyl sulfide (DES), 2-chloroethyl ethyl sulfide (CEES), bis(2-chloroethyl) sulfide (mustard) and three kinds of selective coating materials, including methyl acrylate (MA), methyl methacrylate (MMA) and butyl methacrylate (BMA)

Compounds	$\log K_{ow}$[a]	W_{sol} (mg/l)[a]	B_p[a] (°C)
DES	1.95	8.02E+002	92.1
CEES	2.18	7.43E+002	156–157
Mustard	2.41	6.84E+002	215–217
MA	0.80	4.94E+004	80.2
MMA	1.38	1.50E+004	100.5
BMA	2.66	4.39E+002	155

[a] Data obtained from [47].

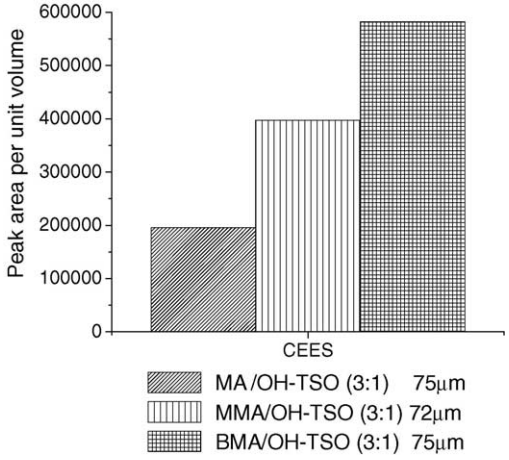


Fig. 3. Coating evaluation for the extraction of 10 μg/g CEES in soil with sol–gel-derived MA/OH-TSO (3:1), MMA/OH-TSO (3:1) and BMA/OH-TSO (3:1)-coated fibers. SPME conditions: 1 g standard soil; 2 ml distilled water saturated out with NaCl; extraction time, 20 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min.

The concentration of BMA and OH-TSO in the sol–gel solution was optimized by changing the proportion of BMA to OH-TSO from 1:1, 2:1, and 3:1 to 4:1. Fig. 5 compares the extraction efficiency of the four BMA/OH-TSO fibers with different concentration of BMA and OH-TSO. From the figure, we can see that the concentration of BMA is very important in improving the selectivity and sensitivity of the BMA/OH-TSO fibers toward CEES. The BMA/OH-TSO (3:1)-coated fiber possesses the highest extraction efficiency. A proportion of BMA to OH-TSO higher than 3:1 in sol–gel solution may lead to precipitation due to the sol–gel solution lacking enough dissolubility for BMA. Therefore, the extraction efficiency of BMA/OH-TSO (4:1)-coated fiber exhibits a little decrease in contrast to

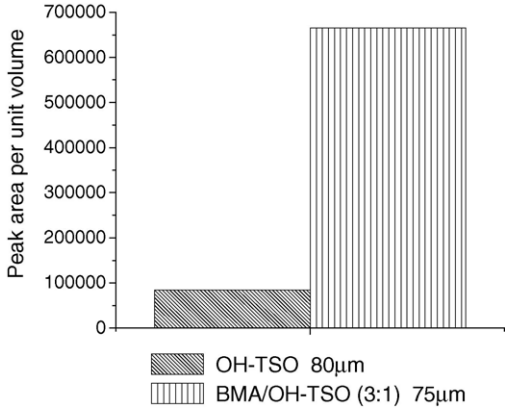


Fig. 4. Comparison of the extraction capability of the sol–gel-derived OH-TSO fiber and BMA/OH-TSO (3:1) fiber with the identical preparation procedure for the extraction of 10 μg/g CEES in soil. SPME conditions are the same as in Fig. 3. Duplicate extractions were made using different vials.

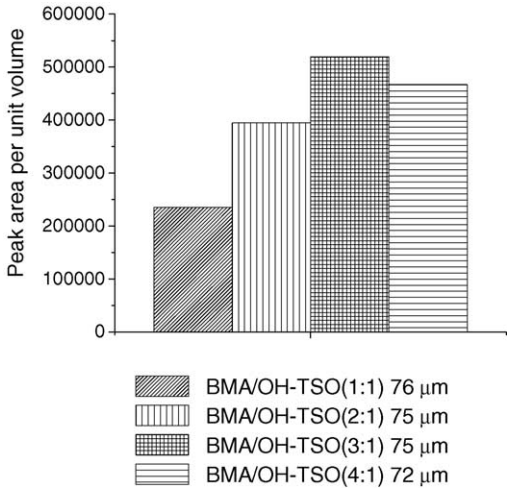


Fig. 5. Effect of the concentration of BMA and OH-TSO in sol solution on the extraction ability of the sol–gel-derived BMA/OH-TSO fiber for the extraction of 10 μg/g CEES in soil. SPME conditions are the same as in Fig. 3. Duplicate extractions were made using different vials.

that of BMA/OH-TSO (3:1)-coated fiber. The BMA/OH-TSO (3:1)-coated fibers were chosen for subsequent experiments.

Fig. 6 shows the comparison of extraction ability of the sol–gel-derived BMA/OH-TSO (3:1) fiber with commercially available PA fiber. As can be observed from the figure, the sol–gel-derived BMA/OH-TSO (3:1) fiber has higher extraction efficiency than PA fiber since the polarity of sol–gel-derived BMA/OH-TSO fiber is similar to that of CEES. At the same time, based on the results of recent studies [32,48], the sol–gel coating possesses a porous structure, which should significantly increase the available surface area on the fiber, and thus, provides enhanced stationary-phase loadings and higher sample capacity for sol–gel-derived BMA/OH-TSO fiber.

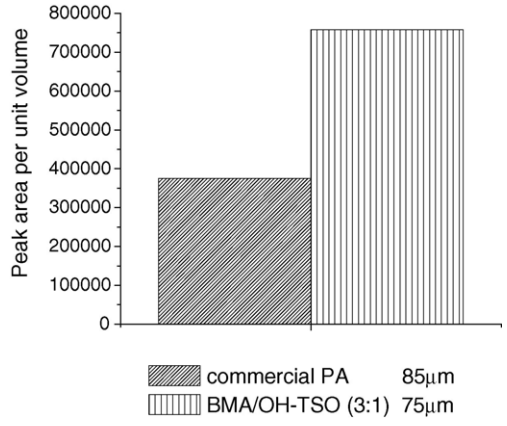


Fig. 6. Comparison of extraction efficiency of the sol–gel-derived BMA/OH-TSO (3:1)-coated fiber with commercially available PA coating for the extraction of 10 μg/g CEES in soil. SPME conditions are the same as in Fig. 3. Duplicate extractions were made using different vials.

Table 3
The reproducibility of coating preparation for sol–gel-derived BMA/OH-TSO (3:1)-coated fibers

Within batch		Between batches	
Fiber (n = 3) (μm)	Peak area[a]	Fiber (n = 3) (μm)	Peak area[a]
85	23720089	75	20455807
85	24572195	75	20216846
85	23486802	75	21585642
RSD (%)	2.39	RSD (%)	3.52

SPME–GC conditions: carrier gas, nitrogen; splitless injections; injector temperature, 250 °C; FID temperature, 280 °C; column temperature, 50 °C held for 2 min, then ramped at 10 °C/min to 250 °C, held for another 2 min; 1 g standard soil; 2 ml distilled water saturated out with NaCl; extraction time, 10 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min.

[a] Each peak area value was shown as mean with n = 3, representing three individual samples.

3.2.2. Reproducibility of the coating

The repeatability of coating preparation was also studied. Table 3 represents the fiber-to-fiber and batch-to-batch reproducibility of the sol–gel-derived acrylate/silicone-coated fibers. Three sol–gel-coated BMA/OH-TSO (3:1) fibers (each thickness was 85 μm) prepared within batch and three identically prepared BMA/OH-TSO (3:1) fibers between batches (each thickness was 75 μm) were used for the analysis of CEES in soil. It showed that BMA/OH-TSO fibers have an acceptable reproducibility not only within batch (RSD, 2.39%) but also between batches (RSD, 3.52%).

3.2.3. Thermal and chemical stability and lifetime of the coating

A coating's lifetime is important for practical application (decline of efficiency with the number of analysis). The coating is damaged mainly by high temperature of the injector of gas chromatograph and solvent in the matrix.

Fig. 7 illustrates the thermal stability of sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. It is obvious that the ex-

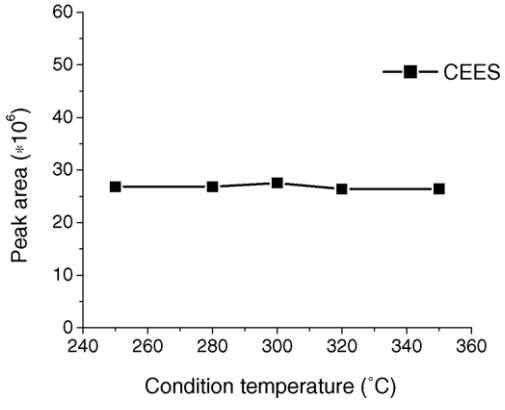


Fig. 7. Effect of condition temperature on the stability of the sol–gel-derived BMA/OH-TSO (3:1) fiber on the amounts of CEES extracted. SPME conditions: 1 g standard soil; 2 ml distilled water saturated out with NaCl; extraction time, 10 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min. Duplicate extractions were made using different vials.

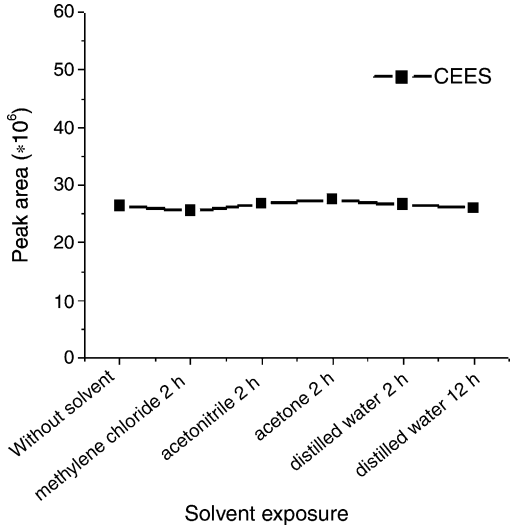


Fig. 8. Effect of solvents exposure on the stability of the sol–gel-derived BMA/OH-TSO (3:1) fiber on the amounts of CEES extracted. SPME conditions are the same as in Fig. 7. Duplicate extractions were made using different vials.

traction peak areas of CEES did not significantly decrease after the fiber was conditioned at 250–350 °C. Such high thermal stability can expand the SPME application range toward higher boiling compounds. Fig. 8 represents the solvent stability of sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. It shows that the extraction ability had no obvious decline after the fiber was dipped in different solvents. The high thermal and chemical stability is due to the strong chemical binding formed between the coating and the surface-bonded silica substrate by sol–gel technology.

Table 4 shows the change of extraction efficiencies of BMA/OH-TSO (3:1) fiber in extracting CEES from soil after being used for 20, 50, 80, 100, 120 and 150 times. To allow standardized comparisons, the ratios used in the table are the comparison of the peak areas in the chromatogram measured by HS-SPME with the corresponding areas obtained by direct injection of 0.2 μl of a solution with the same concentration. The ratios of peak areas obtained after the fibers were used for different times are convenient in order to account for the change of the factors of the SPME–GC conditions. As can be seen from the table, the ratios did not evidently decrease after being used for 150 times. The results indicate that its extraction efficiency had no obvious decline. It was still stable and reusable.

Table 4
The lifetime of sol–gel-derived BMA/OH-TSO (3:1) fibers

Times	Peak area[a] by SPME	Peak area[a] by direct injection	Ratios[b]
0	22086107	12525370	1.7633
20	22811997	13071707	1.7451
50	24509248	13982461	1.7529
80	25362876	14433177	1.7573
100	23669318	13715508	1.7257
120	22232948	12701673	1.7504
150	22716925	13150754	1.7274

SPME–GC conditions are the same as in Table 3.

[a] Each peak area value was shown as mean with $n = 3$, representing three individual samples.

[b] Ratios are obtained by comparison of the peak areas in the chromatogram measured by HS-SPME with the corresponding areas measured by direct injection of 0.2 μl of a solution with the same concentration.

3.3. Extraction and analysis of CEES in soil

3.3.1. Optimization of the HS-SPME process

Development of a particular procedure for determination of CEES in soil using the HS-SPME technique requires the optimization of the variables related to both extraction and desorption steps, including the volume of water added to the soil, extraction time, extraction temperature, salt effect, desorption time, and desorption temperature, etc.

The degree of partitioning of semivolatile organic compounds between the soil and the headspace is generally low, and the addition of small amounts of water can facilitate the desorption and vaporization of analytes, as indicated by Zhang and Pawliszyn [49,50], due to the release of volatile organic compounds from their absorption sites in the soil by the polar water molecules. Responses obtained when different amounts of saturated salt solution ranging from 0.5 to 4 ml were added into the 1 g spiked soil system using headspace SPME–GC procedure are given in Fig. 9. As can be seen from the figure, the response obtained in the dry soil system is rather low in contrast to that obtained in the wet soil system. An important increase in the response for CEES can be observed with the addition of 0.5–2 ml of water. The response reached the maximum when 2 ml of water was added into the soil, which is large enough to form slurry. A slight decrease in the response was observed for volumes higher than 2 ml, although an improvement in sensitivity against the dry sample occurred, because the addition of higher amounts of water would dilute the concentration of the analytes and increase

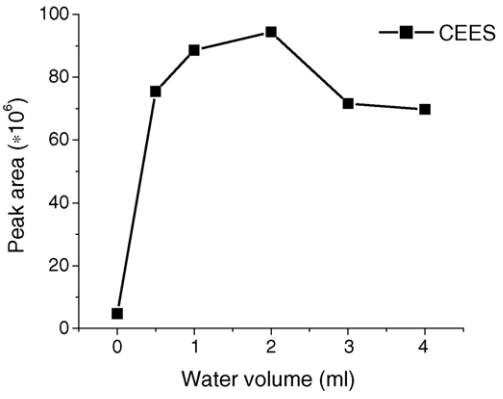


Fig. 9. Effect of water added on the extraction amounts of CEES in soil using sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. SPME conditions: 1 g standard soil; distilled water saturated out with NaCl; extraction time, 30 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min. Duplicate extractions were made using different vials.

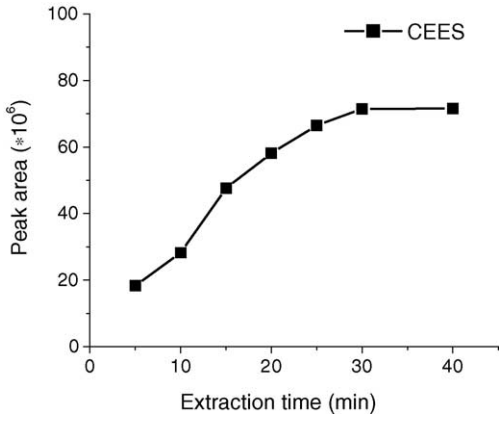


Fig. 10. Effect of the extraction time on the signal intensity of CEES in soil using sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. SPME conditions: 1 g standard soil; 2 ml distilled water saturated out with NaCl; extraction temperature, 27 °C; constant stirring; desorption time, 5 min. Duplicate extractions were made using different vials.

the diffusion barrier of CEES from aqueous phase to gaseous phase.

Equilibrium time depends on the mass transfer of the analytes through the three-phase system: coating, headspace and the soil matrix. It is generally accepted that the reduction of the diffusion layer is essential in order to reach equilibrium faster, which is easily achieved by sample agitation. Therefore, magnetic stirring was applied during the extraction step. Fig. 10 shows a typical time profile for SPME analysis. The time to reach equilibration is about 30 min.

Fig. 11 represents the extraction temperature profile for SPME analysis. The amount of CEES extracted increased with the increase in temperature, and decreased above 40 °C. This is mainly because the extraction temperature has two opposing effects on the SPME technique. Increasing temperature enhances the diffusion coefficient of analytes, which

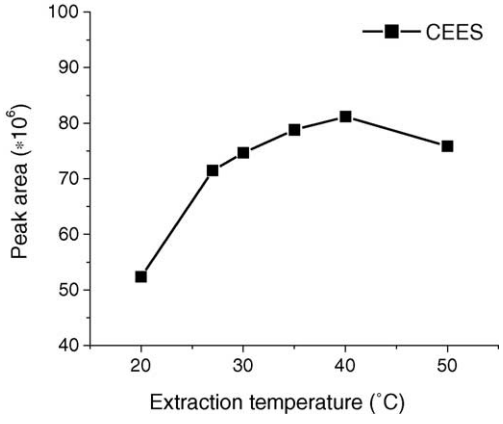


Fig. 11. Effect of the extraction temperature on the signal intensity of CEES in soil using sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. SPME conditions: 1 g standard soil; 2 ml distilled water saturated out with NaCl; extraction time, 30 min; constant stirring; desorption time, 5 min. Duplicate extractions were made using different vials.

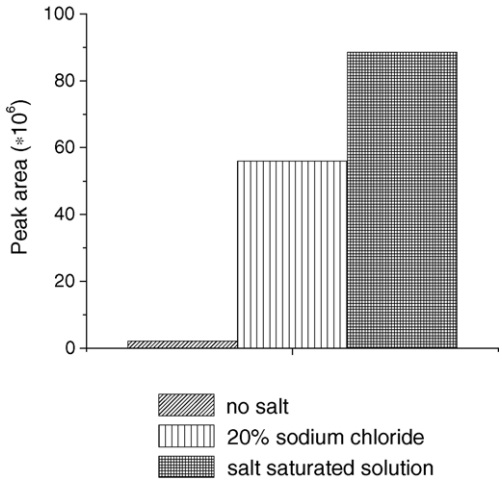


Fig. 12. Effect of ionic strength on the extraction amounts of CEES in soil using sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. SPME conditions: 1 g standard soil; 2 ml distilled water; extraction time, 30 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min. Duplicate extractions were made using different vials.

effectively transfer from the matrix to the fiber coatings; on the other hand, as the adsorption is an exothermic process, increasing temperature reduces the distribution constant of the analytes, resulting in a diminution in the equilibrium amount of analytes extracted. A reasonable compromise in this study was thought to be 40 °C.

Fig. 12 illustrates the effect of salt on the extraction of CEES in soil. It is obvious that the amount of CEES extracted greatly enhanced with the increase of salt concentration. The largest amount of CEES, which was nearly 40 times of that acquired in a no-salt solution, was obtained in a saturated salt environment. The addition of salt increases the ionic strength of the slurry. This makes CEES less soluble and forces it to distribute from the slurry into the stationary phase. Therefore, a higher equilibrium concentration of CEES can be achieved in the fiber coating.

To avoid carryover effects that may occur among subsequent SPME analysis, the time and temperature needed for complete desorption of analytes from the fiber were also studied in this work. However, no carryover was observed when desorption was carried out at 250 °C for 5 min, for the boiling point of CEES is rather low (156–157 °C).

3.3.2. Linearity, precision and detection limits

The optimized headspace SPME procedures were evaluated with respect to precision, linear range and limit of detection (LOD). The reproducibility expressed as relative standard deviation (RSD) was found to be satisfactory for SPME, with a RSD of 2.19%. The HS-SPME procedure with sol–gel-derived BMA/OH-TSO (3:1) fiber showed excellent linearity in concentrations ranging from 0.1 to 10 μg/g, with correlation coefficient of 0.9999. Owing to the high sensitivity of the sol–gel-derived BMA/OH-TSO coating, low detection limit (about 2.7 ng/g) was achieved for CEES in soil.

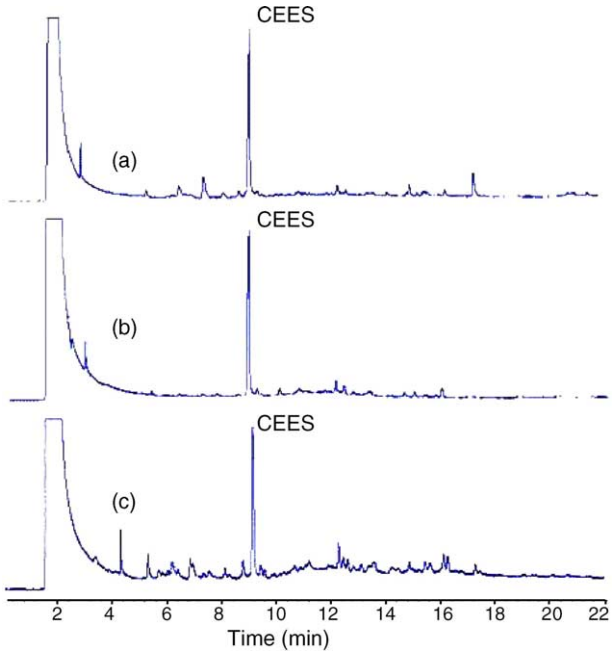


Fig. 13. SPME–GC-FID chromatograms of a red clay (a), a sandy soil (b) and an agriculture soil (c) spiked with CEES standard solution using sol–gel-derived BMA/OH-TSO (3:1)-coated fiber. SPME conditions: 1 g soil; 2 ml distilled water saturated out with NaCl; extraction time, 30 min; extraction temperature, 40 °C; constant stirring; desorption time, 5 min.

3.3.3. Environmental soil sample analysis

The established HS-SPME method using the sol–gel-derived BMA/OH-TSO (3:1) fiber was then applied to analyze a red clay, a sandy soil and an agriculture soil sample. There were no detectable levels of the target analytes in the soils before spiking. To evaluate the accuracy of the proposed method, the recovery of CEES in the three kinds of soils was evaluated. It was 88.06% in agriculture soil, 92.61% in red clay and 101.95% in sandy soil, respectively. A recovery approaching 100% indicates that matrix effect in these soils is very small when the treated red clay is used as standard. In addition, the recovery obtained in soils is different from each other owing to the distinct adsorption characteristics of different soil matrices. The results show that the matrix effect in agriculture soil is more serious than in red clay and in sandy soil.

Fig. 13 represents typical HS-SPME–GC chromatograms of a red clay, a sandy soil and an agriculture soil sample spiked with CEES standard solution, extracted by the sol–gel-derived BMA/OH-TSO (3:1)-coated fiber.

4. Conclusion

In this work, the sol–gel coated acrylate/silicone copolymer coatings, including MA/OH-TSO, MMA/OH-TSO and BMA/OH-TSO, were prepared and investigated for the first time. Among the three kinds of acrylate/silicone fibers, the sol–gel-derived BMA/OH-TSO fiber has the best affinity for CEES. Moreover, the content of BMA and OH-TSO in sol solution was also optimized, and the BMA/OH-TSO (3:1)-coated fibers possessed the highest extraction efficiency. It exhibits high sensitivity, good thermal and chemical stability and long lifetime, and satisfying repeatability. A simple and rapid HS-SPME–GC method was developed to sample and analyze of the mustard stimulant compound CEES in soil. For the HS-SPME sampling the spiked soil, the addition of water saturated out with NaCl to the spiked soil samples greatly increased partitioning of CEES to the headspace. The method proposed in this study showed satisfactory linearity, detection limit, precision and accuracy. Since CEES is structurally and characteristically similar to mustard, the novel sol–gel-derived BMA/OH-TSO coating should have high extraction ability for mustard as well. Therefore, the established HS-SPME–GC methods and the sol–gel-derived BMA/OH-TSO materials may be useful for the analysis of mustard as a contaminant of soil or other complex samples.

Acknowledgement

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