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Novel Coatings for Solid-Phase Microextraction of Phosphates and Methylphosphonates

LIU Mingming[1], ZENG Zhaorui[1], WANG Chaoling[1], TAN Youjin[2], LIU Hua[2]

(*1. College of Chemistry & Molecular Science, Wuhan University, Wuhan 430072, China; 2. Chemical Defense Office, General Equipment Headquarters, Guangzhou Military District, Guangzhou 510650, China*)

Abstract: Copoly (hydroxy-terminated silicone oil/divinylbenzene) (OH-TSO/DVB) was synthesized as a stationary phase coating with vinyltriethoxylsilane (VTEOS) as the bridge using the sol-gel coating method and cross-linking technology. This stationary phase was applied for solid-phase microextraction (SPME) of phosphates and methylphosphonates. Compared with commercial SPME fibers, the novel coatings showed better selectivity and sensitivity in analysis of phosphates and methylphosphonates. Some important parameters, such as extraction time, extraction temperature, effect of salt and desorption time, were optimized. The limits of detection for dimethyl methylphosphonate (DMMP), trimethyl phosphate (TMP) and tributyl phosphate (TBP) in water were 0.34, 2.20 and 0.01 mg/L, respectively. Relative standard deviations from 3.67% to 6.44% ($n=6$) can be achieved depending on the compounds. The linear ranges were about 1－2 orders of magnitude. The recoveries of spiked water samples were 89.46% to 90.88%.

Key words: gas chromatography; solid-phase microextraction; sol-gel; phosphate; methylphosphonate

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用于磷酸酯和甲基膦酸酯类化合物测定的固相微萃取新型涂层

刘名茗[1]， 曾昭睿[1]， 王朝领[1]， 谭有金[2]， 刘 华[2]

(1. 武汉大学化学与分子科学学院，湖北 武汉 430072；2. 广州军区装备部队防化技术大队，广东 广州 510650)

摘要：以羟基硅油和二乙烯基苯为涂层材料，采用溶胶-凝胶技术和自由基引发交联的方法制备了一种新型的固相微萃取探头。采用顶空固相微萃取与气相色谱联用的方法模拟检测了水中磷酸酯和甲基磷酸酯类化合物。与商品化固相微萃取探头相比，该新型涂层可获得高的萃取效率。甲基膦酸二甲酯、磷酸三甲酯和磷酸三丁酯的最低检测限分别为 0.34，2.20 和 0.01 mg/L，相对标准偏差为 3.67%～6.44%，线性范围为 1～2 个数量级，方法重现性好，回收率为 89.46%～90.88%。

关键词：气相色谱；固相微萃取；溶胶凝胶；磷酸酯；甲基膦酸酯

The nerve agents are the most toxic compounds known. Sarin, Soman, Tabun, and *O*-ethyl-*S*-[2-(diisopropylamino) ethyl]-methylphosphonothiolate (VX) are the representatives of methylphosphonate nerve agents. They are rather volatile and easy to degrade. Alkylphosphonic acids and their monoesters are the important hydrolysis products of nerve agents and related species. Dimethyl methylphosphonate (DMMP) is structurally similar to methylphosphonate nerve agent, while possesses much less toxicity, generally used as simulant for nerve agents, as in previous studies by many researchers[1－3]. Trimethyl phosphate (TMP) represents internal standard of Sarin. Tributyl phosphate (TBP) represents internal standard of VX. The pretreatment and determination of nerve agents and their hydrolysis products in aqueous or environmental matrixes is challenging because they are highly polar compounds and easy to hydrolyze, and moreover, they have no chromophore for UV or fluorescence detection.

Solid-phase microextraction (SPME) is a new extraction technique. It integrates extraction, concentration and sample introduction into one single step without the use of organic solvents. The commercially available SPME fibers are generally prepared by mere physical deposition of the polymer coating on the surface of the fused-silica fiber. The lack of proper chemical bonding between the stationary phase and fused-silica fiber surface may be responsible for the low thermal and chemical stability and short lifetime[4,5]. Sol-gel coating technology can solve these problems by providing efficient incorporation of or-

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Biography: LIU Mingming, female, born in 1978, master.

Corresponding author: ZENG Zhaorui, professor, Tel: (027)87686155, E-mail: zrzeng@whu.edu.cn.

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ganic components into the inorganic polymeric structures in solution under extraordinarily mild thermal conditions[5,6]. Secondly, the porous structure of sol-gel coating provides higher surface area, enhances sample extraction capacity, and accelerates mass transfer rate[6,7]. Thirdly, selectivity can be improved by changing the composition and surface coverage of coating materials.

In this work, copoly (hydroxyl-terminated silicone oil/divinylbenzene) (OH-TSO/DVB) fibers were first prepared by sol-gel and cross-linking technology and applied for the detection of phosphates and methylphosphonates. DMMP, TMP and TBP were employed as model compounds to assess the extraction procedure and simulate the detection of methylphosphonate nerve agents in water.

1 Experimental

1.1 Apparatus

The experiments were carried out on a SP-6800A capillary gas chromatographic (GC) system (Shandong, China) equipped with a capillary split/splitless injector system and a flame ionization detector. Online data collection and processing was done on Chromatopac model SISC-SPS (Beijing, 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 commercially available polydimethylsiloxane (PDMS, 100 μm), polyacrylate (PA, 85 μm), and copoly (dimethylsiloxane/divinylbenzene) (PDMS/DVB, 65 μm) coated fibers for comparison were purchased from Supelco (Bellefonte, PA, USA).

1.2 Fiber preparation

The sol solution was prepared as follows: 90 μL of divinylbenzene (DVB), 90 mg of hydroxyterminated silicone oil (OH-TSO), 100 μL of tetraethoxysilane (TEOS), 50 μL of vinyltriethoxysilane (VTEOS), 10 mg of poly (methylhydrosiloxane) (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 50 μL volume of trifluoroacetic acid (TFA) containing 5% (v/v) water was sequentially added to the resulting solution with ultrasonic agitation for another 5 min. The mixture was centrifuged at 12 000 r/min for 8 min. The top clear sol solution was collected for fiber coating. The pretreatment and coating of fused-silica fiber and other operation were performed according to reference [8].

1.3 Headspace (HS) solid-phase microextraction procedure

For all analyses, a 50 μL of standard solution with 10 g/L of DMMP, 10 g/L of TMP and 1 g/L of TBP, 5 mL of deionized water and 1 g NaCl were mixed in a 12 mL vial with a magnetic stirring bar. The SPME procedure was performed according to reference [8].

1.4 GC conditions

Separation was carried out on a 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 ℃ for the injection port, 280 ℃ for the detector. The temperature program for the analysis was: 50 ℃, hold for 2 min, then ramp at 10 ℃/min to 120 ℃, finally ramp at 20 ℃/min to 250 ℃, hold for another 2 min.

2 Results and discussion

In sol-gel chemistry, a gel can be formed by the simultaneous hydrolysis and polycondensation of the organometallic precursor and other sol-gel active ingredients followed by aging and drying under ambient atmosphere. 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. A commonly used precursor for a glass matrix, TEOS, was hydrolyzed in conjunction with a second monomeric unit, which contains a vinyl substituent. In this experiment we selected VTEOS as the co-precursor, which reacted with DVB by radical cross-linking reaction under UV to produce chemical bonding of DVB to other coating ingredients. Thus, a surface-bonded polymeric coating (OH-TSO/DVB) was formed by sol-gel and cross-linking technology.

The comparison of sol-gel-derived OH-TSO/DVB and OH-TSO fibers is presented in Fig. 1. The

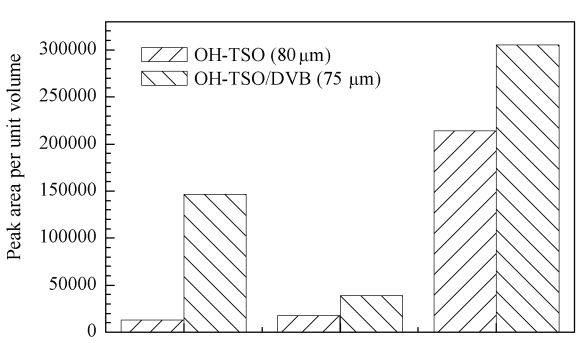

Fig. 1 The comparison of extraction efficiency of sol-gel-derived OH-TSO/DVB and OH-TSO fibers

sol-gel-derived OH-TSO/DVB fiber has higher extraction efficiency due to the introduction of large quantities of phenyl group by cross-linking reaction.

The extraction efficiencies of the novel sol-gel-derived OH-TSO/DVB fiber were compared with the commercially available PDMS, PA and PDMS/DVB fibers, as shown in Fig. 2. According to the principle of "like dissolves like", phosphates and methylphosphonates have higher affinities for OH-TSO/DVB and PDMS/DVB fibers than those for PA and PDMS fibers since the former two fibers are less polar. At the same time, the three-dimensional network in the coating structure provides a higher surface area and sample capacity for the sol-gel-derived OH-TSO/DVB fiber, which exhibits higher extraction efficiencies for phosphates and methylphosphonates than that for PDMS/DVB fiber.

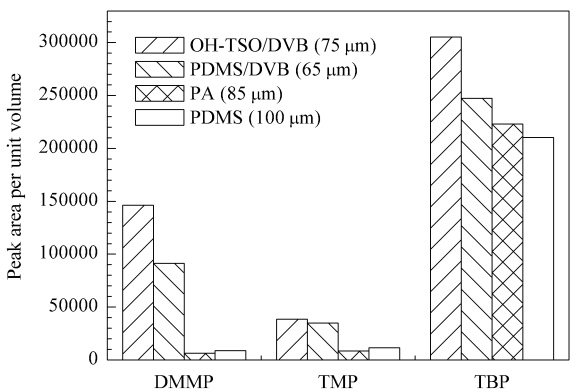

Fig. 2 Coating comparison of the sol-gel-derived OH-TSO/DVB fiber with commercial PDMS, PA, PDMS/DVB fibers

The extraction time profiles for the three analytes in water were shown in Fig. 3.

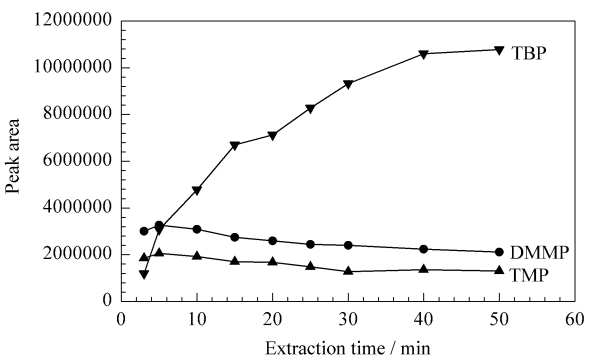

Fig. 3 Effect of extraction time on the extraction efficiency for phosphates and methylphosphonate extracted from water sample
1. TBP; 2. DMMP; 3. TMP.

The extraction temperature profiles for the three compounds in water were shown in Fig. 4.

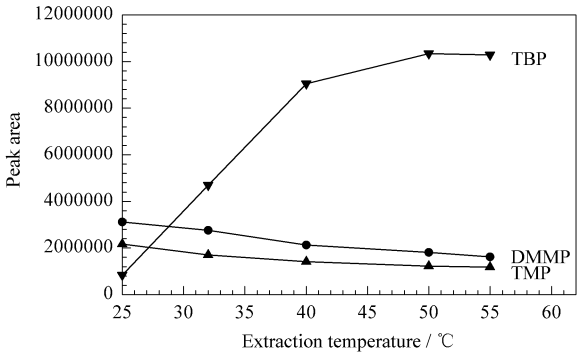

Fig. 4 Influence of extraction temperature on the amounts of phosphates and methylphosphonate extracted from water sample
1. TBP; 2. DMMP; 3. TMP.

In Fig. 5, it is illustrated that the extraction for all analytes increases with the increase of NaCl contents, then approaches a plateau or even decreases.

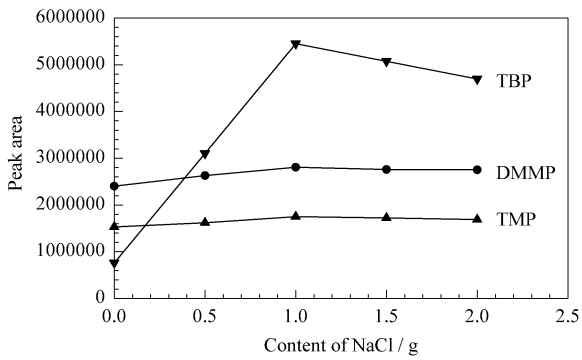

Fig. 5 Effect of NaCl content on the extraction efficiency for water sample
1. TBP; 2. DMMP; 3. TMP.

To avoid carryover effects that may occur among subsequent SPME analyses, the time needed for complete desorption of analytes from the OH-TSO/DVB fiber has to be carefully determined. The carryover was measured with a series of blank analyses following the initial desorption. Total desorption of the three analytes was obtained in 5 min.

Table 1 summarizes the detection limits (LODs), relative standard deviations (RSDs) and linear ranges for the extraction of phosphates and methylphosphonate from aqueous samples using the sol-gel-derived OH-TSO/DVB fiber. The LODs were based on the lowest detectable peak that had a signal three times of the background noise (signal/noise =

Table 1 Limits of detection (LOD), linear ranges and precision for phosphates and methylphosphonate in water samples

Compound	LOD/(mg/L)	RSD/% ($n=6$)	Linear range (mg/L)	Regression equation	r
DMMP	0.34	5.04	4.51 − 450.8	$Y=95\,725.2+22\,018.3X$	0.999 9
TMP	2.20	3.67	7.51 − 375.6	$Y=166\,230.2+21\,220.4X$	0.998 6
TBP	0.01	6.44	0.25 − 19.67	$Y=92\,216.6+1.04\times10^{6}X$	0.999 0

3). Six consecutive extractions of water samples were performed to investigate the precision of SPME.

The established SPME method was successfully applied to analyze tap water sample. None of the analytes was detected in the tap water. Therefore, a 50 μL of standard solution was spiked into 5 mL of the tap water to calculate the recovery of the method. Table 2 represents the recovery of phosphates and methylphosphonate in tap water.

Table 2 Recovery of phosphates and methylphosphonate in tap water ($n=4$)

Sample	Mean peak area	RSD/%	Recovery/%
DMMP	10 425 928	5.88	89.86
TMP	2 309 054	8.45	90.88
TBP	37 641 542	4.90	89.46

Fig. 6 is a chromatogram of the tap water sample spiked with phosphates and methylphosphonate extracted by sol-gel-coated OH-TSO/DVB fiber and then analyzed on an SE-54 column under the same extraction conditions.

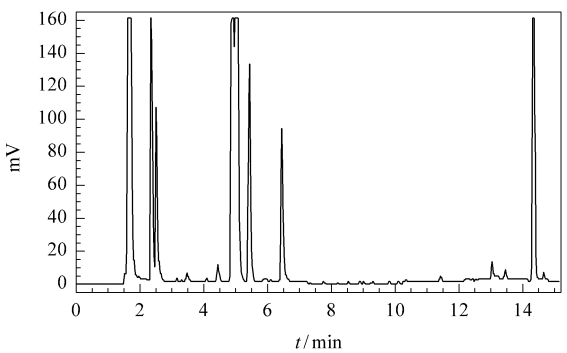

Fig. 6 The chromatogram of a tap water sample spiked with phosphates and methylphosphonate

1. DMMP; 2. TMP; 3. TBP.

3 Conclusion

In this article, a novel SPME fiber OH-TSO/DVB was first prepared by sol-gel and cross-linking technology. Compared with commercial SPME fibers, the sol-gel-coated OH-TSO/DVB fiber showed better selectivity and sensitivity towards phosphates and methylphosphonates, especially for DMMP, which represents the methylphosphonate nerve agents. Therefore, the novel sol-gel-derived OH-TSO/DVB fibers may be a good choice for analyzing warfare agents with SPME technique. Some important parameters with the new fiber were investigated. The optimum conditions are: extraction time, 15 min; extraction temperature, 32 ℃; 1 g NaCl and constant stirring.

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