Analysis of Naphthalene Residues in Textile Samples by GC–FID Using Sol-Gel-Derived SPME Fiber

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Abstract

Solid-phase microextraction (SPME) coupled to gas chromatography (GC) has been developed for the analysis of naphthalene residues in five textiles samples using sol-gel-derived 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-diglycidyloxycalix[4]arene/hydroxy-terminated silicone oil fiber. The main parameters affecting extraction and desorption process such as temperature and time were optimized statistically. Compared with four commercial stationary phases and sol-gel-derived OH-TSO SPME fiber, this fiber showed statistically highest enrichment capability for naphthalene in the textile sample. SPME–GC–flame ionization detection method showed good linearity for the tested concentration range with regression coefficient being 0.9996. Detection limits was 1.17 ng/g. Relative standard deviations (n = 6) of method at three concentration levels of 1.0, 0.5, and 0.1 µg/g ranged between 1.1% and 5.4%, which provided good analytical precision. In addition, this fiber had satisfying fiber to fiber and batch to batch reproducibility. Recoveries for the analyte ranged from 78.3% to 102.7%. It indicated that this method developed was an efficient and accurate procedure for determination of naphthalene residues in textiles samples.

Introduction

Due to its moth-proof function, the camphor ball is extensively used in households and businesses for pest control, and camphor does no harm humans if it is used properly. Naphthalene (Nap) is a bicyclic aromatic compound and white solid that readily sublimes at room temperature. As the simplest member of the polycyclic aromatic hydrocarbons (PAHs), naphthalene can be found environmentally as a constituent of coal tar, crude oil, and cigarette smoke. It is also utilized in chemical manufacturing as a chemical intermediate for many commercial products ranging from pesticides to plastics (1). Nap can also protect the textile against insects. Because of their low cost, Nap balls are often used illegally as camphor balls for sale in the market, however, and it is harmful to humans. The toxicology of Nap has been the subject of numerous assessments. Of particular interest was an evaluation for the potential to induce tumors (1). Although the manufacture and sale of Nap balls as a moth-proof agent has been prohibited in China since 1993, some manufacturers and sellers were still engaged in the illegal dealing. Therefore, residual Nap in the textile has become a potential threat towards humans by breath and skin, and could result in accidents. It is necessary to develop a fast, convenient, and efficient analytical method to determine Nap residues in textile samples.

Nap in different sample matrixes was usually determined using chromatographic technique, including gas chromatography, gas chromatography mass spectrometry, and high-performance liquid chromatography, preceded by different sample preparation methods to achieve a proper chromatogram of the level of contamination, such as liquid–liquid extraction or solid-phase extraction (2–4). However, these conventional pretreatment methods either were time-consuming or used large quantities of organic solvents. The substances involved were toxic and not reusable. Solid-phase microextraction (SPME), because of its simple, fast, low-cost, solvent-free, and easy-to-automate properties, has experienced a sharp growth for analyte matrix separation and preconcentration over the last decade (5–10). It was generally regarded as one of the optimal alternatives to conventional extraction method. At present, SPME technique has been widely proposed for determination Nap residue in all kinds of matrix samples like honey (11), urine (12), river (13), soil (14), and textile products (15). Researchers usually selected, as specified by the manufacturer for PAHs, a SPME fiber coated with polydimethylsiloxane (PDMS) layer for the analysis of these organic compounds. However, most commercial stationary phases were normally prepared by physical deposition or partial cross-linking on the surface of the fused-silica rods, which may be responsible for the lower thermal and chemical stability of these fibers. Although for apolar organic compounds like Nap reports continued to indicate that the efficiency obtained by SPME was still poor, owing to a limited number of commercially

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available coatings. Heretofore, novel advanced coating materials had been prepared by different production approaches, such as electrochemical procedures (16), high-temperature epoxy immobilization (17), in-situ polymerication (18), carbonaceous adsorbent (19), and sol-gel technique (20–21). Sol-gel technology was a convenient path to the synthesis of advanced material for being used to prepare SPME fibers coating with excellent properties (e.g., high thermal stability, good solvent stability, long lifetime, and high enrichment capability) (22–29). The sol-gel-derived 5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-diglycidyloxycalix[4]arene/hydroxy-terminated silicone oil (diglycidyloxy-C[4]/OH-TSO) SPME fiber had been prepared to accommodate to the harsh extraction conditions. And it had been successfully utilized for extracting propranolol in the human urine samples (23). Compared with the commercial stationary fiber (PDMS fiber), this sol-gel-derived SPME fiber had showed higher enrichment ability for analysis of chlorobenzenes in soil samples (24).

The purpose of the present work was to develop a facile analytical method for the determination of Nap residues in the textiles samples using sol-gel-derived diglycidyloxy-C[4]/OH-TSO coating fiber by HS–SPME–GC–FID. And it promoted the wide application of diglycidyloxy-C[4]/OH-TSO fiber in the analysis of Nap residues in textiles samples. The important variables, including extraction temperature, extraction time, equilibration time, and the effect of carry over, were optimized in detail. In addition, analytical characteristics such as linearity, detection limits, precision, and accuracy have been examined for Nap residues in textiles, and the evaluated SPME procedure was developed.

Experimental

Instrumentation

A GC 7890 II system (Techcomp, Shanghai, China) equipped with a split/splitless injector system and flame-ionization detector (FID) was used. On-line data collection and processing was performed by a Sepu3000 workstation (Puhucomp, Hangzhou, China). Stirrer DF-101B (Leqing, China) was used to control temperature of the sample during the SPME process. The home-made SPME fiber coated with sol-gel-derived diglycidyloxy-C[4]/OH-TSO (65 µm) (23) was used to extract Nap in the textile samples. For purposes of comparison, the hydroxy-terminated silicone oil (OH-TSO) SPME fiber (65 µm) was also coated by sol-gel technique with an identical preparation procedure except that diglycidyloxy-C[4] was not added to the sol solution (23). A laboratory-made SPME device was used to transfer the extracted Nap to GC injector. The commercial SPME holder for manual use and four commercial available SPME fibers, including polydimethylsiloxane (PDMS, 100 µm), polyacrylate (PA, 85 µm), polydimethylsiloxane–divinylbenzene (PDMS–DVB, 65 µm) and carbowax–divinylbenzene (CW–DVB, 65 µm), were purchased from Supelco (Bellefonte, PA). According to the instructions provided by the manufacturer, all commercial fibers were conditioned under nitrogen in the hot injector of GC. The home-made SPME fibers were conditioned in the injector of GC at 300°C for 2 h before experiment.

Materials

Nap and methanol were analytical-reagent grade. The inferior camphor ball (Nap ball) was purchased from the local market (Wuhan, China). Pure wool textile, pure cotton textile, 80% flax/20% cotton textile, 55% flax/45% cotton textile and 20% flax/80% cotton textile were purchased from the local supermarket (Wuhan, China).

GC–FID condition

The capillary column (30 m × 0.32 mm i.d., 0.33 µm thickness) coated with SE-54 (Lanzhou Institute of Chemical-Physics Chinese Academy of Sciences, Lanzhou, China) was used in all chromatographic analysis in this work. Nitrogen was used as carrier gas at a linear velocity of 15 cm/s. The detector gases were air and hydrogen; their flow-rates were regulated at 335 and 32 mL/min, respectively. Nitrogen was used as make-up gas at 30 mL/min. The split ratio was 1:20 and splitless time was selected for 2 min. The injector was held isothermally at 260°C for Nap desorption. The column temperature program was as follows: initial temperature 120°C held for 1 min, then increased at 10°C/min up to 200°C held for 2 min. The FID system was maintained at 260°C. All results were performed in triplicate to ensure reproducibility except for special explanation.

Method

Preparation of Nap standard solution

Nap was dissolved in methanol to make standard solutions. Their concentrations were 0.005, 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, and 2.5 mg/mL, respectively. Standard solutions were stored at 4°C in refrigeration before use.

Preparation of spiked textile samples and SPME procedure

The blank textile samples (without Nap) were divided into small slices (~ 5 mm × 5 mm) and were stored in the sealed vials for the following experiments. In order to find out the optimal SPME conditions for being suitable to all the textile samples, 5 g blank textile samples contained 1 g of each textile sample in the condition experiment.

To prevent Nap from being absorbed on the glass wall, the vials were acid washed and silanized prior to the experiments. For SPME procedure, 5 g blank textile sample and 10 µL aliquot of the standard solution of Nap at the concentration level of 0.1 mg/mL were placed in the vial with 20 mL volume. Then, the vial was closed with butyl-rubber stopper wrapped with PTFE sealing tape, sealed with aluminium cap. Nap in textile samples was extracted into the calixarene fiber or desorbed off under optimization SPME conditions. The optimal conditions for extraction and desorption were as follow: extraction temperature, 35°C; extraction time, 5 min; no equilibration time; desorption temperature, 260°C; and desorption time, 1 min.

In linearity experimental, the concentrations of Nap in spiked textile samples were 0.01, 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 µg/g, respectively.

Preparation of real textiles samples and procedure of SPME

These inferior camphor balls have been wrapped all the textile samples in the sealed vessels for three months. After that, these textile samples were divided into small slices (~ 5 mm × 5 mm) and were stored in the sealed vials for the following experiments.

For the analysis of the real samples, the 5 g of textile sample and 10 µL aliquot of methanol were placed into the vial. The SPME procedure of real textiles samples were similarly performed under SPME conditions.

Statistical analysis

Regarding the optimal conditions for extraction and desorption of Nap in textile samples, as well as coating evaluation for the extraction efficiencies of Nap with PDMS-, PA-, CW–DVB-, PDMS–DVB-, sol-gel-derived OH-TSO- and sol-gel-derived diglycidyloxy-C[4]/OH-TSO coating fibers, statistical significance was performed using an analysis of variance (ANOVA) followed by least significant difference tests for multiple comparison. $P < 0.05$ was considered to indicate statistical significance.

Results and Discussion

Optimization of SPME procedure

Optimization of parameters that affect the SPME procedure is of great importance. In order to achieve higher extraction efficiency for the target analytes, the extraction conditions were optimized by changing the following variables: extraction temperature, extraction time, equilibration time, desorption temperature, and time.

Effect of extraction temperature

The extraction temperature and time required for the analyte to reach equilibrium between the headspace and the stationary phase was interactional. Extraction temperature was firstly optimized because it has double influence on the SPME process. One is that the diffusion coefficient of analyte in samples into the coating are high in the condition of high extraction temperature, which can shorten the extraction time. The other is that the high temperature leads to the decrease of partition coefficient of the analyte between coating and headspace because the absorption step is generally seen as an exothermic process (27). The effect of extraction temperature on the extraction efficiency was studied by varying the temperature from 25°C to 75°C for 5 min. The extraction temperature profile for Nap in the textile samples shown in Figure 1. Statistical analysis explained that there were significant differences for extraction efficiencies of Nap in temperature condition experiments ($P < 0.05$). The extracted Nap reached the highest extraction amount at 35°C ($P < 0.05$). When the extraction temperature was higher than 35°C, signal intensity of Nap decreased obviously. Therefore, 35°C was selected for the optimum temperature in further experiments.

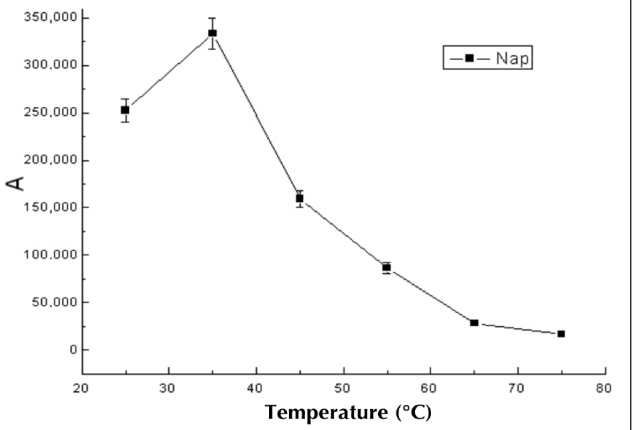

Figure 1. Extraction temperature profile of naphthalene in the textile samples. Extraction time, 5 min; no equilibration time, desorption temperature, 260°C; and desorption time, 1 min. The concentrations of naphthalene in textile samples was 0.2 µg/g.

Effect of extraction time

All the extractions were performed in the range from 0.5 to 30 min. Figure 2 illustrates the extraction time profile for Nap in textile samples. Equilibrium was reached for Nap after 5 min. Extraction amount of Nap changed obviously when extraction time ranged between 0.5 min and 5 min ($P < 0.05$). However, no significant difference was observed when extraction was longer than 5 min ($P > 0.05$). Therefore, 5 min was set as optimal extraction time in the analysis.

Effect of equilibration time

For the equilibration time, it meant the time between the vial with the textile samples being placed into the stirrer and introduction of SPME fiber into the headspace of the vial. If the appropriate equilibration time for SPME process was selected, the analyte in samples would volatilize fully and diffuse evenly in the vial. It is advantageous to the precision of the analytical method. Figure 3 showed the equilibration time profile for Nap in samples. No difference in the signal intensity of Nap was observed when the equilibration time ranged from 0 min to 15 min ($P > 0.05$). Either the vapor pressure change of Nap was not so great from 25°C to 35°C or the vial temperature equilibrated very rapidly relative to the extraction time. So the equilibration time was not needed in the following experiments.

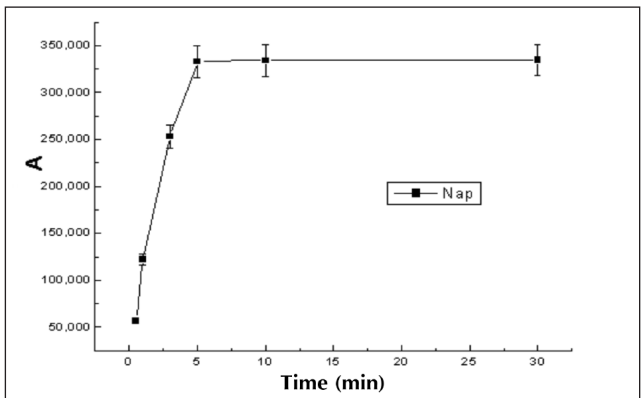

Figure 2. Extraction time profile of naphthalene in the textile samples. Extraction temperature, 35°C, and other conditions as Figure 1 except for extraction time.

Effect of desorption temperature and time

The effect of carry over was investigated by desorption temperature and time in GC injector after the SPME process. If the analytes still remain absorbed on the fiber after the hot desorption, which decrease the sensitivity of SPME–GC method or lead to false information in following experiments (27). Although the analytes can be desorbed fully under a higher temperature in a shorter time, lifetime of the fiber (especially for available commercial fibers) will be affected. The fibers will even be physically damaged or the analytes be decomposed if the desorption temperature is clearly excessive. Effect of desorption temperature on the signal intensity of Nap was shown in Figure 4. Desorption temperature did not play an important role on the effect of carry over when the temperature of the injector was more than 250°C ($P > 0.05$). However, significant difference was observed when desorption temperature was set as 260°C versus 250°C ($P < 0.05$). Hence, 260°C was chosen as optimal desorption temperature. There were many factors affecting desorption behavior, such as the boiling point as well as the partition constant of the analytes, the thickness of the stationary phase, and the desorption temperature. Desorption time was studied by introduction in the injector length of time ranging from 0.5 to 10 min after the SPME process. In Figure 5, Nap extracted could be desorbed off after desorption of 1 min. And there was significant difference when desorption time was selected as 1 min versus 0.5 min ($P < 0.05$). One min was selected as optimal desorption time.

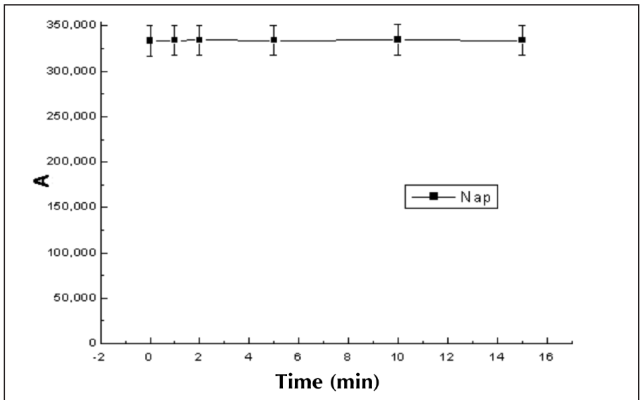

Figure 3. Equilibration time profile of naphthalene in the textile samples. Extraction temperature, 35°C, and other conditions as Figure 1 except for equilibration time.

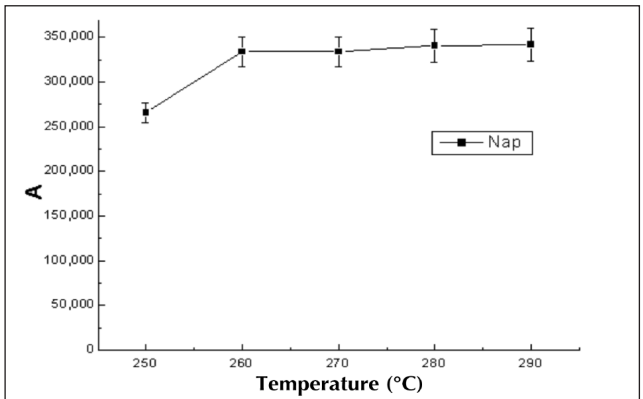

Figure 4. Desorption temperature profile of naphthalene in the textile samples. Extraction temperature, 35°C, and other conditions as Figure 1 except for desorption temperature.

Comparison of extraction efficiencies with commercial available fibers and OH-TSO SPME fiber

Figure 6 compares the extraction efficiencies of sol-gel-derived diglycidyloxy-C[4]–OH-TSO coating fiber with those of four commercial available fibers and OH-TSO SPME fiber for Nap in textile samples. These fibers were run at their respective optimum conditions. The diglycidyloxy-C[4]–OH-TSO fiber showed statistically the highest extraction efficiencies among

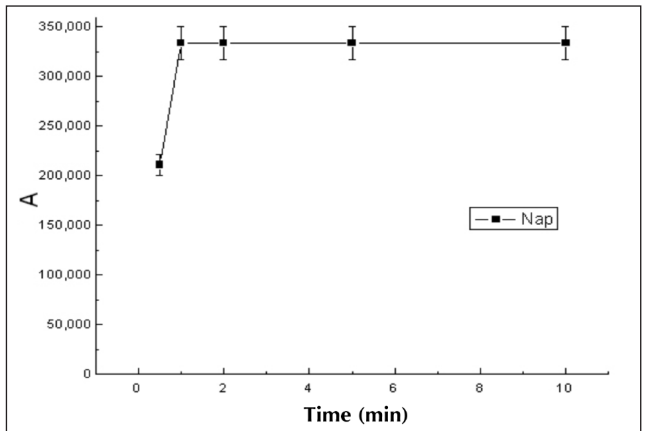

Figure 5. Desorption time profile of naphthalene in the textile samples. Extraction temperature: 35°C, and other conditions as Figure 1 except for desorption time.

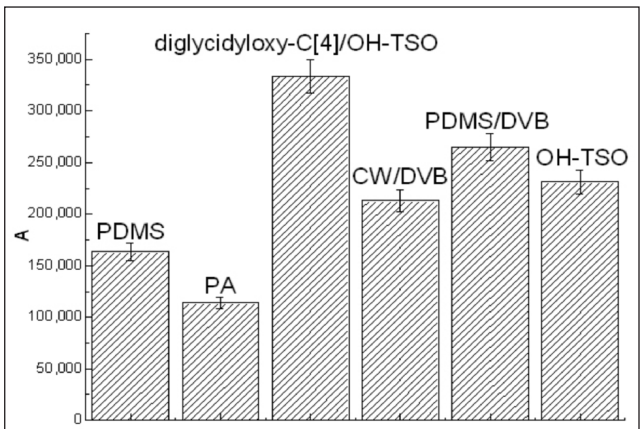

Figure 6. Comparison the extraction efficiencies of sol-gel-derived diglycidyloxy-C[4]–OH-TSO coating fiber with those of four commercial available fibers (PDMS, PA, CW–DVB, PDMS–DVB) and the OH-TSO SPME fiber for naphthalene in textile samples. Extraction temp., 35°C, and other conditions as Figure 1. For the optimal conditions of four commercial available fibers and the OH-TSO SPME fiber, extraction temp., 40°C; extraction time, 10 min; no equilibration time; desorption temp., 260°C and desorption time, 2 min (PDMS); extraction temp., 30°C; extraction time, 10 min; no equilibration time; desorption temp., 260°C and desorption time, 2 min (PA); extraction temp., 30°C; extraction time, 8 min; no equilibration time; desorption temp., 250°C and desorption time, 2 min (CW/DVB); extraction temp., 30°C; extraction time, 8 min; no equilibration time; desorption temp., 260°C and desorption time, 2 min (PDMS/DVB); extraction temp., 35°C; extraction time, 5 min; no equilibration time; desorption temp., 260°C, and desorption time, 1 min (OH-TSO).

these fibers ($P < 0.01$). The best extraction capability of this calixarene coating is based on two factors. Firstly, it is attributed to the π–π interaction, hydrophobic interaction, hydrogen bonding, dipole–dipole interactions, and some specific interactions, such as inclusion complexes with the cavities formed by the supramolecules (23). Secondly, the three-dimensional porous network in the coating that was addressed by sol-gel technology provided a higher surface area and extraction capacity for analytes in the samples (20).

Linearity, detection limits, and precision

Analytical characteristics, including linearity, detection limits and precision, have been examined for Nap residues in textile under the optimal condition. As shown in Figure 7, linearity for Nap was more than two orders of magnitude with correlation coefficients being 0.999 6. Limit of detection was estimated by the concentration of Nap in textile samples that gives rise to a peak with a signal-to-noise (S/N) ratio of three. Detection limits was 1.17 ng/g. The RSD values for Nap in textile samples were 1.1, 3.2, and 5.4 % (n = 6) at three concentration levels of 1.0, 0.5, and 0.1 µg/g, respectively.

Reproducibility of the different fibers with the sol-gel-derived diglycidyloxy-C[4]–OH-TSO coating

In order to investigate the fiber-to-fiber and batch-to-batch reproducibility of the fibers with the diglycidyloxy-C[4]–OH-TSO coating, six diglycidyloxy-C[4]/OH-TSO fibers (the thickness with 65 µm for each) prepared within same batch and other six fibers for different batches (the thickness with 65 µm for each) were extracted Nap at the concentration levels of 1.0 µg/g in the textile samples, respectively. Relative standard deviations (n = 6) of fiber-to-fiber was 7.7%, 9.3% for batch-to-batch reproducibility. This indicated that diglycidyloxy-C[4]–OH-TSO fiber had a satisfying reproducibility not only between the same batch but also between different batches.

Samples analysis

The developed SPME–GC–FID was applied to determine the Nap residues in five real textile samples, including pure wool textile, pure cotton textile, 55% flax/45% cotton textile, 80% flax/20% cotton textile and 20% flax/80% cotton textile samples.

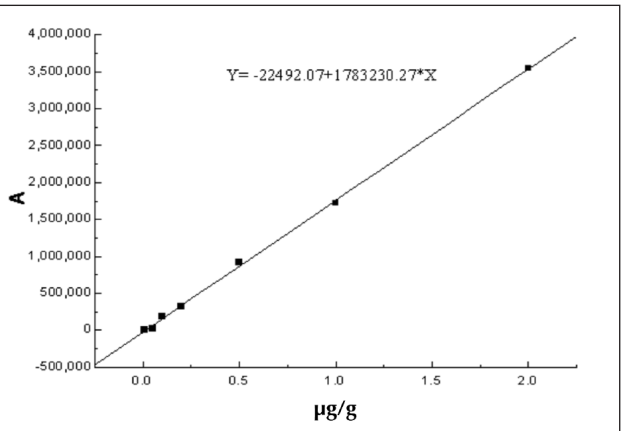

Figure 7. Linearity of the developed HS-SPME–GC–FID method using diglycidyloxy-C[4]–OH-TSO coating fiber.

The results for five real samples were 194, 202, 214, 198, and 197 ng/g, respectively. The found concentration of Nap residues in each textile sample was calculated from the linear regression equation of the calibration curve for standards going through the HS-SPME–GC-FID method. The typical HS-SPME–GC-FID chromatogram of Nap residues in pure wool textile sample matrix was shown in Figure 8. Recovery tests were performed in order to investigate the accuracy of this method. Recovery tests were based on the addition of known amounts of Nap to each real textile sample. Nap was added to every textile samples as follows: the high spiked level was that a 10 µL aliquot of the standard solution of Nap at the concentration level of 0.5 mg/mL was added to 5 g textile sample; the medium spiked level was that standard solution of Nap (0.05 mg/mL) with the same volume was added to textile sample; the similar process was performed for the low spiked level and standard solution of Nap is 0.005 mg/mL. Recoveries of the developed method were shown in Table I. The results were satisfying, with recoveries above 78.3% and below 102.7% for Nap in all textile samples at investigated concentrations.

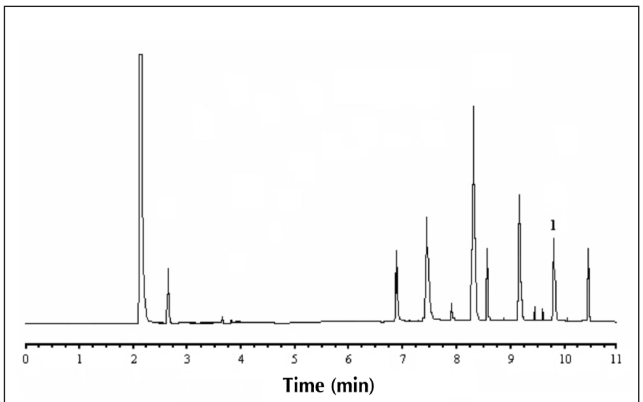

Figure 8. The typical HS–SPME–GC–FID chromatogram of naphthalene residues in pure wool textile sample matrix; extraction temperature, 35°C; other conditions as Figure 1. Peaks: 1 = naphthalene.

Table I. Recoveries of the HS–SPME–GC–FID Method using the Sol-Gel-Derived Diglycidyloxy-C[4]/OH-TSO Coating Fiber

Textile samples	Added ng/g	Result ng/g	Recoveries (%)
	1000	945	94.5
Pure wool textile	100	91.9	91.9
	10	7.83	78.3
	1000	957	95.7
Pure cotton textile	100	91.1	91.1
	10	8.02	80.2
	1000	981	98.1
55% flax/45% cotton textile	100	93.9	93.9
	10	8.58	85.8
	1000	1027	102.7
80% flax/20% cotton textile	100	94.7	94. 7
	10	8.61	86.1
	1000	975	97.5
20% flax/80% cotton textile	100	92.3	92.3
	10	8.13	81.3

Conclusion

The sol-gel-derived diglycidyloxy-C[4]–OH-TSO SPME fiber was firstly applied for HS-SPME–GC-FID to determine Nap residues in textiles samples. The optimal conditions for extraction and desorption were as follow: extraction temperature, 35°C; extraction time, 5 min; no equilibration time; desorption temperature, 260°C; and desorption time, 1 min. Linearity of this method was more than two orders of magnitude, limit of detection was 1.17 ng/g, and relative standard deviations (n = 6) for Nap were found to be from 1.1 to 5.4% at investigated concentrations. Compared with four commercial SPME fibers and OH-TSO SPME fiber, this fiber showed statistically best enrichment capability towards Nap. In addition, this fiber had satisfying fiber-to-fiber and batch to batch reproducibility. Recoveries of Nap ranged from 78.3 to 102.7% for all textiles samples. It indicated that HS-SPME–GC–FID based on diglycidyloxy-C[4]/OH-TSO fiber was a feasible approach to determine Nap residues in textiles samples.

Acknowledgements

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