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Determination of aniline in silica gel sorbent by one-step in situ microwave-assisted desorption coupled to headspace solid-phase microextraction and GC–FID

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Abstract

Microwave-assisted desorption (MAD) coupled to in situ headspace solid-phase microextraction (HS–SPME) was first proposed as a possible alternative pretreatment of samples in absorbent collected from workplace monitoring. Aniline collected on silica gel was investigated. Under microwave irradiation, the aniline was desorbed from silica gel and directly absorbed onto the SPME fiber in the headspace. Having been sampled on the SPME fiber, and desorbed in the GC injection port, aniline was analyzed using a GC–FID system. Parameters that affect the proposed extraction efficiency, including the extraction media and its pH, the microwave irradiation power and the irradiation time as well as desorption parameters of the GC injector, were investigated. Experimental results revealed that the extraction of a 150-mg silica gel sample using a 0.8-ml aqueous solution (pH 12) and a PDMS/DVB fiber under medium-high-powered irradiation (345 W) for 3 min maximized the efficiency of extraction. Desorption of aniline from the SPME fiber was optimal at 230 °C held for 3 min. The detection limit was 0.09 ng. The proposed method provided a simple, fast, and organic solvent-free procedure to analyze aniline from a silica gel matrix.

Keywords: Aniline; Microwave-assisted desorption; Headspace SPME; GC–FID; Silica gel

1. Introduction

Aniline is an important industrial material widely used in the manufacture of pharmaceuticals, photographic developers, shoe polish, and other products [1–3]. It is a suspected carcinogen. In addition to measuring blood methemoglobin levels in workers as an exposure index, aniline is monitored in workplace by collecting samples for chemical analysis to evaluate the exposure of laborers to toxic chemicals.

In the monitoring of a workplace, silica gel is commonly used as a sampling mediator for polar pollutants, such as aniline in air. Before chemical analysis, pretreatment must typically be performed, involving desorption using organic solvent, concentration, and then gas chromatographic analysis [4–7]. Although the procedure efficiently yields precise results, it is relatively time-consuming, hazardous to health because it involves organic solvents, and very expensive because the solvents used must be disposed of. Therefore, pretreatments that take a short time and used little or no organic solvents have led to the recent development of new techniques of extraction. Solid-phase microextraction (SPME) coupled with GC analysis has been used successfully to analyze pollutants in environmental matrices [8–15]. With SPME, the sampling, extraction, and enrichment are accomplished in a single-step that involves no organic solvent. Later, the headspace solid-phase microextraction (HS–SPME) was developed and applied to prevent matrix effects and eliminate interference from matrix species for volatile analytes [9,16,17]. Over the last decade, microwave energy has been studied and extensively applied in accelerating the sample digestion, extraction, and chemical reactions of samples [18–20]. The authors' recent studies developed microwave-assisted HS–SPME to achieve the one-step in situ headspace sampling of semi-volatile organic

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compounds in aqueous samples, vegetables, and soil before GC analysis [21–24]. Therefore, microwave-assisted desorption (MAD) coupled with HS–SPME has the potential to improve the pretreatment steps associated with the monitoring of toxicant in workplace.

In this work, MAD in situ on-line HS–SPME coupled with GC/FID was systematically investigated to develop a simple, fast and solvent-free analytical process for analyzing aniline in silica gel mediator.

2. Experimental

2.1. Chemicals and reagents

Deionized water was produced using a Barnstead Nanopure water system (Barnstead, NY, USA) for all aqueous solutions. All chemicals and solvents were of ACS reagent grade. Aniline and ethylene glycol were purchased from Riedel-deHäen (Hanover, Germany). Ethanol (95%), iso-propanol, acetic acid, and *n*-butyl alcohol were purchased from J.T. Baker (USA). Acetone was obtained from Mallinckrodt (KY, USA). Sodium hydroxide was obtained from Tedia. Hydrochloric acid (36.5%) was from Fisher (USA). A standard stock solution of aniline (1.0 mg ml^{-1}) was prepared by dissolving 0.1 g aniline in 100 ml ethanol; the solution was stored at 4 °C in silanized brown glass bottles with Teflon-lined caps. Fresh working solutions were prepared by appropriately diluting the stock solutions with ethanol (Mallinckrodt). Silica gel (grade 12, 20/40 mesh) and silica gel tubes (ORBO-52) were obtained from Supelco. Highly pure nitrogen (99.9995%) and hydrogen (99.9995%) were obtained from Lien-Hwa (Taichung, Taiwan). A real sample was collected from a rubber-additive manufacture factory at Da-Chia Youth industrial park. Sampling was conducted at a flow-rate of 50 ml min^{-1} for 365 min.

2.2. GC/FID system

The GC employed herein was a Hewlett-Packard 6890 system (PA, USA) equipped with a flame ionization detector (FID), and a split/split-less injector. Separations were performed using a fused silica CP-WAX 52 CB capillary column (30 m × 0.53 mm i.d., 1.0 μm film thickness) (Agilent Technologies, Palo Alto, CA). Separation was conducted isothermally at 120 °C with the carrier gas (N_2) at a flow-rate of 16.4 ml min^{-1}. The injector was held at 230 °C to desorb the aniline (3 min). The FID was maintained at 280 °C. A Chem-Lab Data system (Chem-Lab Co., Taipei, Taiwan) was used to obtain the chromatogram and perform data calculations.

2.3. MAD–HS–SPME system

The microwave oven was a modified SM-1912 system (2450 MHz, MIDEA, Thailand), for used in the home, with a maximum power of 700 W. After modification, the microwave operated at powers of 95, 172, 255, 345, and 477 W for weak, medium-low, medium, medium-high and high irradiation, respectively. The headspace sampling apparatus included a cooling condenser (inner-tube: 3 mm i.d., 5 mm o.d., 180 mm length) connected to a water circulator (9D-610, DENG YNG, Taiwan) to control the sampling temperature of SPME. The amount of sampling medium (such as silica gel) used in monitoring a working place was only 150 mg, so the sample vial in the proposed system was minimized to reduce the headspace volume. The proposed MAD–HS–SPME system was set up as shown in Fig. 1. Aluminum foil was tacked onto the inner wall and the outer wall of the microwave in the interface between the microwave body and the headspace sampling apparatus to prevent microwaves from leaking. A microwave leak detector (MD-2000, Less EMF Inc., NY, USA) was employed to determine the safety of the set-up before the experiment was performed.

The SPME device, consisting of the holder and the fiber assembly for manual sampling, was purchased from Supelco (Bellefonte, PA, USA) and used without modification. The fibers used herein were 1 cm long and coated with PDMS/DVB (65 μm film thickness). They were conditioned under nitrogen in the hot injection port of the GC at 250 °C for 0.5 h before they were used. The needle on the SPME manual holder was set to its maximum length of 4 cm in the GC injector port. A desorption temperature of 230 °C, held for 3 min, was set to generate the highest sensitivity to aniline. All analyses were conducted using a 20-ml vial that contained a collected 150 mg silica gel sample and 0.8 ml of 0.10 M NaOH.

2.4. Preparation of the silica gel spiked sample

Three portions of 3 g of silica gel were individually spiked with 3.2 ml of 500 μg ml^{-1}, 4.0 ml of 1000 μg ml^{-1}, and 6.0 ml of 1000 μg ml^{-1} aniline standard solutions (in ethanol). After they had been thoroughly mixed, the ethanol was removed to dryness through an evaporator. Silica gel spiked with 0.08, 0.2, and 0.3 mg of aniline per 150 mg was obtained, respectively.

2.5. Procedure

Silica gel or silica gel spiked samples (150 mg) was added with 0.8 ml of 0.10 M NaOH to a 20-ml sample vial. After swirling, the vial was place in the microwave oven and connected to the HS–SPME system. A SPME device with a fiber was inserted into the hollow part of the condenser connected to a cooler (water circulator) to control the sampling temperature. The aniline was absorbed onto the SPME fiber in the headspace directly under 340 W of microwave irradiation for 3 min. After aniline was collected on fiber, the SPME fiber was desorbed in the GC injector and analyzed using the GC system.

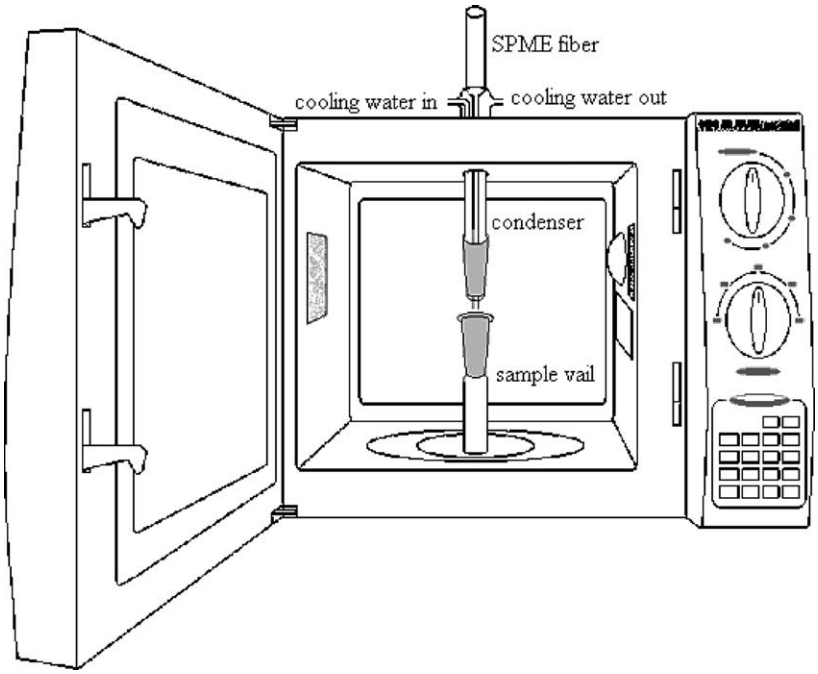

Fig. 1. The assembly of MAD–HS–SPME apparatus.

3. Results and discussion

In order to optimize the MAD–HS–SPME sampling technique for aniline in silica gel, factors that influenced the efficiency of sampling, such as the power of the microwaves and the irradiation time (fiber absorption time), the extraction solution and its pH, the fiber used, the sampling temperature in the condenser and the desorption conditions, were studied thoroughly.

3.1. Selection of SPME fiber coating

The chemical properties of the target analyte (polarity, volatility, solubility in water, and molecular weight) determine the type of a fiber coating used. Seven commercial SPME fiber coatings (100 μm PDMS, 65 μm PDMS/DVB, 85 μm PA, 75 μm CAR/PDMS, 85 μm CAR/PDMS, 65 μm CW/DVB, and 50/30 μm DVB/CAR/PDMS) were evaluated to select an appropriate coating for the MAD–HS–SPME sampling. A fortified aqueous sample (5 μl of 1022 μg ml^{-1} aniline spiked in 0.8 ml of 0.1 M NaOH solution) was analyzed in triplicate using each fiber. After 3 min of MAD–HS–SPME sampling at 350 W of microwave irradiation and GC–FID determination, the results were shown in Fig. 2. It can be seen the mixed PDMS/DVB fiber absorbed aniline most efficiently, and was, therefore, used herein.

3.2. Microwave irradiation conditions

Microwave-assisted desorption combined with HS–SPME was employed herein to collect the aniline from the silica gel sample. The influence of the irradiation power and the duration of irradiation using the microwaves on the extraction was investigated. The results of a series of tests revealed that microwave irradiation at medium-high power (345 W) for 3 min achieved the best extraction efficiency by HS–SPME of aniline from silica gel.

3.3. Effect of pH and solution/silica gel ratio on extraction

In this study, 150 mg silica gel spiked with 20 μg of aniline was used as the spiked sample. Because the partition ratio of aniline between the headspace and the silica gel was typically very low, so the headspace sampling for aniline was very limited. Microwave irradiation tended to increase the partition ratio in the proposed method. However,

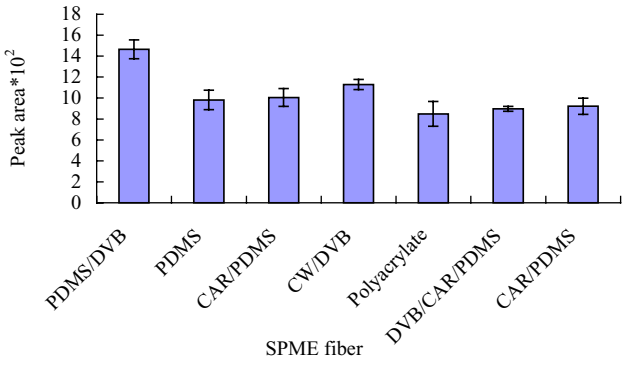

Fig. 2. The extraction efficiency on various SPME fibers.

a very low recovery of aniline was obtained in the direct microwave-assisted desorption from silica gel and the in situ headspace SPME extraction, implying that the energy absorbed by the silica gel was not enough to desorb the aniline into the headspace. Therefore, polar water was added into the silica gel to enhance the absorption of energy from the microwave irradiation. The silica gel was acidic, so the aniline in the acidic aqueous extraction medium was in the form of anilinium ions, which did not favor evaporation into the headspace. Therefore, 0.1 M NaOH was used to neutralize the acidity of the extraction medium to enhance the evaporation of aniline into the headspace. The pK_b of aniline is 9.3, so the pH of the extraction was adjusted to above 12 to ensure that the aniline was in its neutral molecular form (aniline) and so able to evaporate. The effect of the extraction solution/silica gel ratio on extraction was investigated. A series of studies revealed that for 150 mg silica gel, the peak area did not increase if less than 0.4 ml of 0.1 M NaOH was added, beyond which volume the area increased to a maximum at 0.8 ml addition, then decreased slowly. The first 0.4 ml of NaOH added neutralized the acidic silica gel. After neutralization, the NaOH increased the pH of the extraction medium. The effect of dilution was appeared after 0.8 ml had been added. Therefore, in subsequent studies, 0.8 ml of aqueous 0.1 M NaOH solution was added to extract aniline from 150 mg of silica gel in the MAD–HS–SPME process.

3.4. Temperature of sampling system

A 150-mg of silica gel, spiked with 5 μg of aniline, was added to a 20-ml vial that contained 0.8 ml of 0.1 M NaOH, to elucidate the effect of sampling temperature on the recovery of aniline. The results indicated that the peak area increased with the sampling temperature, reaching a maximum at 50 °C, and then declining. Thus, the sampling temperature was controlled at 50 °C to enable aniline to be absorbed on the SPME fiber.

3.5. Thermal desorption of aniline from SPME fiber

Thermal desorption must proceed for at least a minimum duration to ensure sufficient separation efficiency and resolution. The optimal temperature and duration of desorption of aniline in the hot GC injector were sought in the ranges 190–270 °C and 1–5 min, respectively. A series of tests revealed that the peak area (referred to desorption efficiency) increased with the injector temperature, reaching a maximum at 230 °C, and then decreased, implying that aniline may be unstable at temperature above 230 °C. A desorption time of 1 min is enough to desorb aniline from the SPME fiber. The fiber was desorbed at 230 °C for 3 min to ensure that the desorption was complete and that the fiber regenerated. Then, no significant blank values were observed for the re-injection. Thus, no further regeneration mode for the fiber was necessary.

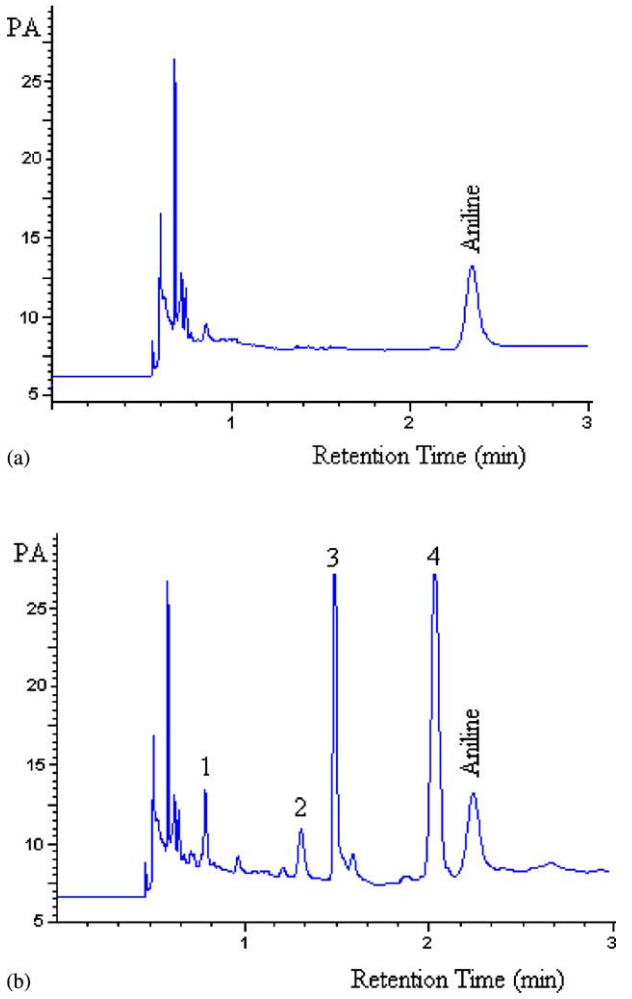

Fig. 3. Chromatogram of aniline in silica with the proposed methods: (a) for spiked silica gel sample; (b) for real sample collected from rubber-additive manufacture factory. Peaks: (1) hexane; (2) ethanol; (3) toluene; (4) methyl ethyl ketone.

3.6. Validation of the methods

To evaluate the applicability of the proposed MAD–HS–SPME–GC–FID method to the quantitative determination of the aniline in silica gel, silica gel that had been spiked with aniline was used for calibration, following complete treatment that involved MAD–HS–SPME and thermal desorption from the fiber into the chromatographic system. Fig. 3(a) shows a FID chromatogram of the aniline standard that spiked in silica gel, obtained under the chromatographic conditions described previously. A calibration plot was built-up over a concentration range of 4.0–400 μg/150 mg silica gel. The plot was specified with equation of $Y = 9.53 \times 104X - 3.77$. The linear relationship between the peak area and the spiked quantity was in good agreement with a correlation coefficient of 0.9994. The slope of a calibration plot represents the detection sensitivity of an analyte, so the extraction recovery by the proposed MAD–HS–SPME was obtained from the ratio of the slope of the linear regression equations

Table 1
Comparison analytical results by the proposed method and the conventional method

Methods	Spiked quantity (mg)	Peak area	Test number	R.S.D. (%)
Proposed method	0.08	8242	6	3.23
	0.20	20130	6	3.56
	0.30	29785	6	3.26
Conventional method	0.08	940	6	3.20
	0.20	2597	6	2.50
	0.30	3787	6	1.62

(for MAD–HS–SPME and the direct injection of standards). Approximately 1.08% aniline in silica gel was collected on the SPME fiber during the MAD–HS–SPME process. The detection limit was calculated by dividing three times the average background noise by the detection sensitivity (slope of calibration plot), which was 0.09 ng. The precision of this method was estimated by performing six extractions of three sets of aniline spiked in silica gel at concentrations of 0.08, 0.2, and 0.3 mg per 150 mg of silica gel, as described in the experimental section. The precisions ranged between 3.26 and 4.23% R.S.D., which are satisfactory for determining the aniline in silica gel. Fig. 3(b) is the chromatogram of a real workplace monitoring sample collected from a rubber-additive plant. It can be seen that the aniline was well resolved from other organic solvents in the sample matrix. Apart from the aniline peak in the chromatogram, peaks 1–4 referred to hexane, ethanol, toluene, and methyl ethyl ketone, respectively. They were identified by retention behaviors and also mass spectra. The concentration of aniline in silica gel was 0.19 mg/150 mg silica gel and that in air was 2.74 ppm.

3.7. Comparison of the proposed method with the conventional extraction method

In the conventional method for extracting aniline from silica gel, 1 ml of 95% alcohol and 150 mg of silica gel sample were added to the vial; after being shaken in a 1-h extraction process, 1 μl of the solution was injected into GC to analyze the aniline. Table 1 lists the analytical results for three samples spiked with silica gel, obtained by the proposed MAD–HS–SPME method and the conventional extraction method. The peak areas obtained by the proposed method are about eight to nine times those obtained by the conventional method, with comparable precision. Therefore, the proposed method potentially has a lower detection limit for one-order than the conventional method. Although the precision of the proposed method is poorer than that of the conventional extraction method, it is acceptable in environmental analysis. However, it depicts that total solvent extraction is slightly precise to the SPME method, which is based on the equilibrium between the solid-phase (fiber) and the gas phase (headspace vapor). Besides, the pretreatment of the sample takes only 6 min (including MAD–HS–SPME and thermal desorption in the injector), compared to over 1 h required by conventional solvent extraction.

4. Conclusion

This study proposes the determination of aniline collected in silica gel by the proposed MAD–HS–SPME with GC/FID system, and the optimal conditions were established. Results of this study demonstrate the applicability of the proposed method as a simple, fast, and convenient procedure that does not involve organic solvent, for collecting aniline from silica gel. The technique has potential as an alternative to the conventional sample pretreatment protocol of collected samples in the workplace monitoring.

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