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Determination of Aniline in Soils and Sediments by Headspace Solid-Phase Microextraction Coupled with Gas Chromatography-Mass Spectrometry

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Abstract. Aniline is an important chemical raw material that is highly toxic and can cause serious pollution to the environment if discharged without effective treatment. In this study, headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry was found to be effective in extracting aniline from soil and sediment samples. An HP-INNOWAX polar column, 85 μm CAR-PDMS fiber head, pure water solution with pH of 12, an extraction temperature of 75 °C, an extraction time of 55 min, an extraction speed of 20 mm/s, and a resolution time of 3 min was selected. The method exhibited good linear in the range of 0-250 ng, with a relative standard deviation of the relative response factor of 3.9%. The blank spiked recoveries of aniline ranged from 110% to 116% with a relative standard deviation of 2.09%. The spiked recoveries of soil and sediment ranged from 81.4% to 92.0% and 92.2% to 109% respectively, with detection limits of 1.5 μg/kg. The method is simple, practical, accurate and reliable, and can be used for the determination of aniline in soil and sediment.

Keywords. Headspace solid-phase microextraction, gas chromatography-mass spectrometry, soil, sediment, aniline

1. Introduction

Aniline is an important chemical raw material that is widely used in dyeing, rubber, pharmaceutical, tanning and plastics processes [1], resulting in the production of over 300 different chemical products and intermediates [2]. Aniline is a highly toxic substance and can cause serious environmental pollution if discharged without proper treatment. Due to its high solubility in water, aniline can easily permeate through soil and contaminates groundwater, leading to its presence in the environment at certain concentrations [2-4]. Aniline is known to be carcinogenic, teratogenic and mutagenic. It can enter the human body through inhalation, ingestion, or skin contact, causing tissue hypoxia and damage to the central nervous system, cardiovascular system and other organs [5, 6]. Given its harmful effects, the US Environmental Protection Agency (EPA) has listed aniline as one of the 129 priority pollutants for control, and China has also

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designated it as a priority pollutant for regulation. Therefore, it is crucial to enhance the detection of aniline.

Currently, common pretreatment methods for aniline in soil and sediment include Soxhlet extraction, pressurized fluid extraction and ultrasonic extraction [7-8]. However, these methods have disadvantages such as complex operation, high reagent consumption, and low aniline recovery. Solid-phase microextraction (SPME) is a novel sample pretreatment technique that utilizes fused silica fibers coated with sorbents to adsorb organic compounds from the sample for extraction purposes. It is an effective analytical method as long as the appropriate extraction head is selected and the corresponding experimental conditions are controlled [9-14]. Commonly used methods for the detection of aniline include gas chromatography (GC) [15, 16], gas-mass spectrometry (GC-MS) [17, 18] and liquid chromatography (LC) [19-21]. Due to the complex matrix of soil and sediment, the GC-MS method is preferred for analysis as it can effectively avoid false positives. In this study, headspace solid-phase microextraction coupled with GC-MS was used for the determination of aniline in soil and sediment. The conditions of the type of solid-phase microextraction fiber head, salt addition, extraction temperature, extraction time and extraction speed were optimized and combined with GC-MS was employed for the determination of aniline in soil and sediment. The developed method showed low detection limits, good reproducibility and high accuracy, achieving satisfactory results, and providing an effective analytical method for the determination of aniline in soils and sediments.

2. Results and Discussion

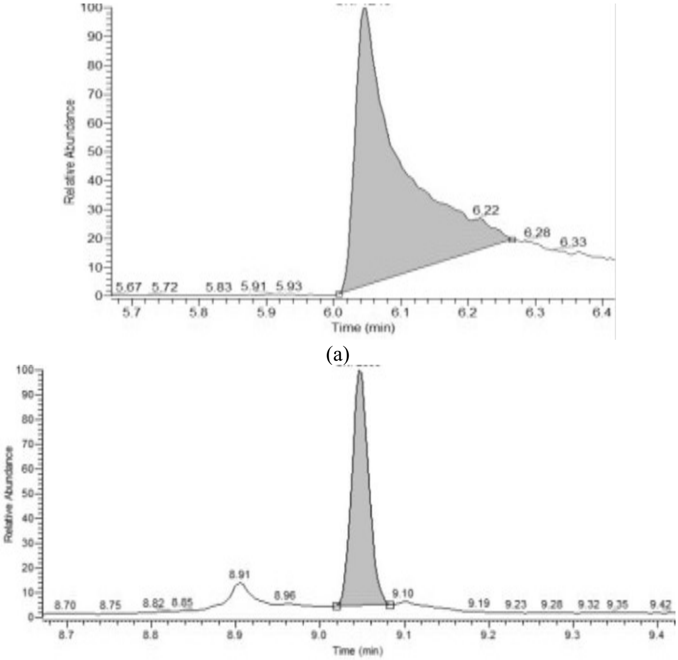
2.1. Optimization of GC Column

Two columns of opposite polarity, TG-5MS (30 m×0.25 mm×0.25 μm) and HP-INNOWAX (30 m×0.25 mm×0.5 μm) were selected for the determination. After the solid phase microextraction pretreatment, the spectra obtained from the gas chromatography-mass spectrometer were compared. It was found that the aniline peak on the TG-5MS column exhibited significant trailing, and could not be accurately integrated, while the aniline peaks on the HP-INNOWAX column had better shaped without trailing (Figure 1). Therefore, the HP-INNOWAX column (30 m×0.25 mm×0.5 μm) was chosen for the determination of aniline.

2.2. Selection of Inlet Liner

Three types of inlet liners were compared: non-split liners, split liners and SPME-specific liners. It was found that there was no significant difference in the determination of aniline using a TG-5MS column (30 m × 0.25 mm × 0.25 μm) with any of the three types of liners. In all cases, the peaks of aniline exhibited heavy trailing, and the degree of trailing was not significant. When aniline was measured on the HP-INNOWAX column (30 m × 0.25 mm × 0.5 μm), there was no significant difference in the determination of aniline using these three types of liner tubes, and the peaks of aniline were all well-shaped without trailing.

In the present method, the split mode was selected for the inlet, allowing for the use of both a regular split liner and an exclusive liner for SPME. However, the SPME liner was not filled with glass wool and could not trap the debris caused by the penetration of the spacer into the sample. Therefore, a regular split liner filled with glass wool was chosen for the determination.



(a)

(b)

Figure 1. Total ion current diagrams of aniline: (a) TG-5MS ,30m×0.25mm×0.25μm; (b) HP-INNOWAX,30m×0.25mm×0.5μm).

2.3. Optimization of SPME Fiber Coating Material

The 50/30 μm DVB-CAR-PDMS fiber coating, 85 μm CAR-PDMS fiber coating, 85 μm polyacrylate fiber coating, and 65 μm PDMS-DVB fiber coating were selected to treat the spiked quartz sand according to the corresponding procedures. The results are provided in Figure 2, where it can be observed that the response of aniline was highest when the 85 μm CAR-PDMS fiber coating was used for extraction, far greater than when the other three fiber coatings were used. Therefore, the 85 μm CAR-PDMS fiber coating was determined to be optimal. The results are showed in Figure 2.

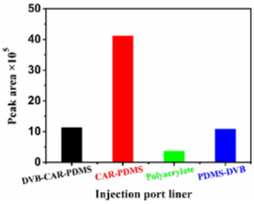


Figure 2. Average response values of three determinations of aniline by different solid phase microextraction fiber coatings.

2.4. Optimization of pH Value

The pH of the quartz sand was adjusted with hydrochloric acid and sodium hydroxide to pH values of 2, 7, 9, 11 and 12. The quartz sand was treated according to the corresponding experimental procedures, and the results were determined as shown in Figure 3. The increase in the peak area of aniline from pH 11 to 12 was minimal, therefore, pH 12 was chosen as the best.

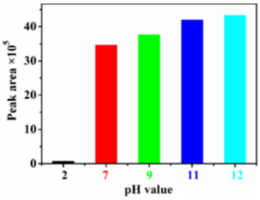


Figure 3. Average response values of three determinations of aniline obtained at different pH values.

2.5. Optimization of Sodium Chloride Addition

As shown in Figure 4, with the increase in sodium chloride addition, the peak area of aniline gradually increased and reached the maximum when 5.0 g of sodium chloride was added. At this point, the response of aniline met the relevant requirements for determination. To save sodium chloride, no more sodium chloride was added. Therefore, 5.0 g of sodium chloride was determined to be optimal.

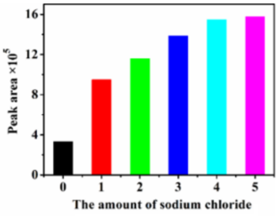


Figure 4. Average response values of three determinations of aniline obtained with different amounts of sodium chloride.

2.6. Optimization of Extraction Temperature

For the SPME temperatures, 40 °C, 45 °C, 50 °C, 55 °C, 60 °C, 65 °C, 70 °C, 75 °C and 80 °C were selected. The treatment was performed according to the corresponding procedures, and the results were provided in Figure 5. It can be observed that the peak area reached the maximum at an extraction temperature of 75 °C, and then began to decline. Therefore, 75 °C was determined to be the optimal extraction temperature.

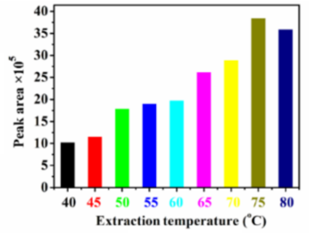


Figure 5. Average response values of three determinations of aniline obtained at different extraction temperatures.

2.7. Optimization of Extraction Time

The extraction times of 5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 35 min, 40 min, 45 min, 50 min, 55 min and 60 min were selected, and the results were determined according to the corresponding experimental procedures shown in Figure 6. When the extraction time reached 55 min, the peak area of aniline reached the maximum. After that, with the increase of extraction time, the peak area of aniline no longer increased. Therefore, 55 min was determined to be the optimal extraction time.

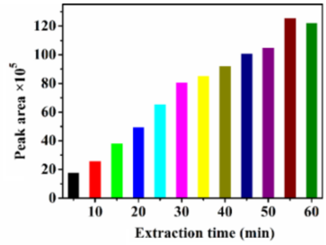


Figure 6. Average response values of three determinations of aniline vs extraction time.

2.8. Optimization of Extraction Rate

For the extraction rates, 5 mm/s, 10 mm/s, 15 mm/s, 20 mm/s, 25 mm/s, 30 mm/s, 35 mm/s, 40 mm/s and 45 mm/s were selected. The treatment was performed according to the corresponding procedures and the results are provided in Figure 7. It can be observed that the peak area of aniline at 20 mm/s was slightly higher than at other speeds. Hence, 20 mm/s was determined to be the optimal extraction rate.

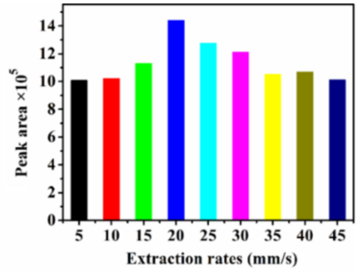


Figure 7. Average response values of three determinations of aniline at different extraction rates.

2.9. Optimization of Resolution Time

For the resolution times, 1 min, 2 min, 3 min, 4 min, 5 min, 6 min and 7 min were selected. The treatment was performed according to the corresponding procedures, and the results are provided in Figure 8. It can be observed that that the peak area of aniline reached the maximum when the resolution time was 3 min. Therefore, 3 min was determined as the optimal resolution time.

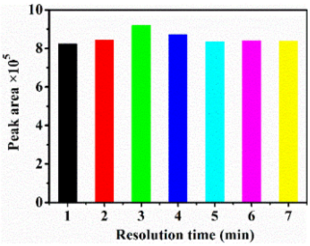


Figure 8. Average response values of three determinations of aniline with different resolution time.

3. Method Evaluation

The linearity equation was determined by weighing seven portions of 2 g quartz sand into 20 mL headspace bottles, adding 5 g of sodium chloride and 5 mL of pure water solution at pH>12. Then 25 ng, 50 ng, 80 ng, 100 ng, 150 ng, 200 ng, 250 ng of standard solution of aniline, and 100 ng of standard solution of internal standard 1.2-dichlorobenzene-d_4 were added, and the caps were tightened. The standard solutions were placed in the injection tray for determination according to the optimum instrumental conditions. The standard curve was calculated using the relative response factor method. The mean relative response factor RRFi was 0.1617 with an RSD% of 3.9%, which was less than 20% (Table 1).

Table 1. Relative response factors of the standard curve.

	Aniline peak area	Aniline mass (ng)	Peak area of internal standard	Internal standard mass (ng)	RRF_i
Marking 01	938847	25	23709923	100	0.1584
Marking 02	2023263	50	26557877	100	0.1524
Marking 03	3218581	80	24918139	100	0.1615
Marking 04	4126815	100	23984843	100	0.1721
Marking 05	5958059	150	23822878	100	0.1667
Marking 06	7642916	200	23730770	100	0.1610
Marking 07	9891626	250	24730966	100	0.1600

The limit of detection was determined by weighing seven portions of 2 g quartz sand into 20 mL headspace vials, each with 5 g NaCl and 5 mL of pure water solution with pH=12. Then, 10 ng of the standard solution and 100 ng of the internal standard 1.2-dichlorobenzene-d_4 were added, and the determination was carried out according to the optimum instrumental conditions. The detection limit was calculated using the method specified in EPA SW-846, MDL = 3.143δ (where δ is the standard deviation repeated 7 times) For aniline, the detection mass was determined to be 3 ng and the detection limit was 1.5 μg/kg in soil or sediment.

To evaluate the recovery and precision: six parallel samples of quartz sand blanks spiked with 50 ng of aniline were prepared and spiked with different concentrations of soil and sediment samples. After determination, the recoveries of the blanks spiked with aniline found to be 110%-116% with a relative standard deviation of 2.09%. The recoveries for soil spiked at 20 ng, 50 ng, 100 ng and 200 ng were 85.0%-92.0%, 84.9%-86%, 81.4%-82.8% and 81.7%-82.1% for soil spiked, respectively. The spiked recoveries for sediment spiked at 20 ng, 100 ng and 200 ng were 101%-102%, 105%-109% and 92.2%-93.2% respectively. These results indicate that the spiked recoveries and precision of aniline are good and the method is accurate and reliable.

4. Conclusion

In conclusion, a method for the determination of aniline in soil and sediment using solid-phase microextraction coupled with GC-MS was developed. The optimum solid-phase microextraction conditions for aniline were determined to be an 85 μm CAR-PDMS fiber head, 5 g of sodium chloride, 5 mL of pre-prepared pure water solution adjusted to pH>12 with sodium hydroxide, an extraction temperature of 75 ºC, an extraction time of 55 min, an extraction speed of 20 mm/s, and a resolution time of 3 min. Under these conditions, satisfactory response values and recoveries of aniline could be obtained. The recoveries of aniline were 110%-116% for blank spiked with a relative standard deviation of 2.09%, 81.4%-92.0% for soil spiked samples and 92.2%-109% for sediment spiked samples. The method has a limit of detection of 1.5 μg/kg and a relative standard deviation of 3.9% for the relative response factor of the standard curve. The method is simple, has low detection limits, good reproducibility and high recoveries, making it suitable for the determination of aniline in soil and sediment.

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