

Electrochemically polyaniline-coated microextraction needle for phthalates in water

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Abstract: A stainless-steel needle (Hamilton 90022, 22 gauge, 718- μm o.d., 413- μm i.d., 51-mm length, bevel tip) with an electrochemically coated polyaniline layer having a microbore tunnel was newly prepared as a device for headspace in-needle microextraction. For designing the needle, the polyaniline layer length was optimized, and to evaluate the extraction efficiency for polycyclic aromatic hydrocarbons, numerous cyclic voltammetry scans were conducted. In addition, the optimization of the analytical conditions (including the adsorption and desorption parameters) and the validation of the analytical method were conducted. The optimized adsorption and desorption conditions were 40 °C for 30 min and 230 °C for 60 s, respectively. Finally, in this study, a polyaniline layer was electrochemically deposited on the in-needle surface, and it exhibited good thermal stability. The needle with the polyaniline layer was repeatedly used more than 200 times during this study. This method has some advantages in terms of the extraction time, extraction efficiency, and analysis cost.

Key words: polyaniline, cyclic voltammetry, polycyclic aromatic hydrocarbons, microextraction needle

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds with two or more fused rings and they can exist as various combinations. They are generated naturally or artificially and mostly formed under the incomplete burning of organic substances such as coal, crude oil, meat and tobacco. The distribution of PAHs in environment including air, soil, or water is available and they show different behaviors depending on their volatilization, dissolution, and adsorption onto solid. Due to environmental concern of PAHs, US Environmental Protection Agency (US EPA)

designates 16 priority PAHs list including naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, fluoranthene, benz(a)anthracene, chrysene, benzo(a)pyrene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, and benzo(a,h)anthracene. Some of them are considered to have a potential for carcinogen and to affect human health.¹⁻³ For these reasons, a few investigations about PAHs from environmental and edible samples have been conducted. Especially, studies of PAHs analysis in river water, tidelands, and sediment were reported.⁴⁻⁸

According to references, analytical methods for

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PAHs in various matrixes are summarized as liquid-liquid extraction (LLE),⁹⁻¹¹ microwave-assisted extraction⁴, solid-phase extraction (SPE),¹⁰⁻¹² solid-phase microextraction (SPME),^{6,13} and ultrasonication extraction.¹⁰ SPME method is often used for PAHs in aqueous sample and has some advantages such as solventless technique and one process for extraction and concentration. However, there are some limitations of SPME technique that adsorbent is easily damaged because it is exposed to outside during extraction, and SPME tool is expensive. To overcome these limitations, in-needle microextraction (INME) method was recently developed.¹⁴⁻¹⁷

INME is an extraction technique using a needle coated with variable adsorbent inside. A needle used for INME has an adsorbent layer on the inside walls having a micro-bore tunnel. Needles packed with various adsorbents have been developed to use in INME method.¹⁴⁻¹⁷ In this study, polyaniline (PANI) was electrochemically deposited on the in-needle surface. PANI as an adsorbent can be prepared by electrochemical polymerization having advantages including no use of catalyst, direct deposition on the electrode surface in a single step, and easy modification of the film thickness.²⁰ Adsorption on PANI might be occurred due to porous surface, hydrophobicity, π - π interaction, ion exchange property, and electroactivity.^{18,19} Using these characters of PANI, research about extraction using SPME tool applied PANI has been reported.^{18,20,21-23}

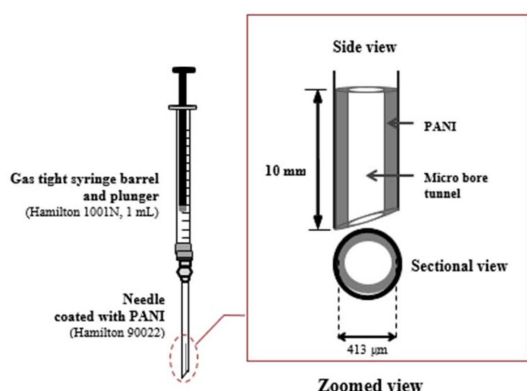


Fig. 1. Illustration of side and sectional views of the needle coated with PANI.

In this study, PANI was synthesized electrochemically to be deposited inside of the needle (Fig. 1). The purpose of this study was to develop a method to qualitatively and quantitatively analyze PAHs in aqueous sample. Optimization of PANI fabrication and extraction conditions was performed by gas chromatography-flame ionization detection (GC-FID) and validation of the proposed analytical method was determined by gas chromatography/mass spectrometry (GC/MS) based on extraction efficiency.

2. Experimental Section

2.1. Chemicals and reagent

In this study, the target compounds were selected among various PAHs. Naphthalene (>98.0%), acenaphthylene (>90.0%), acenaphthene (>99.0%), fluorene (>95.0%), and fluoranthene (>98.0%) were purchased from TCI (Japan). Anthracene (>99%), 1,2,4,5-tetramethylbenzene (>98%) as an internal standard, and aniline (>99.5%) as a monomer were obtained from Sigma-Aldrich (USA). Sulfuric acid (>95.0%) as supporting electrolyte was obtained from Dae-Jung Chem (Korea). Stock solution of PAHs was prepared in methanol:dichloromethane (1:1, v/v). The working solution was weekly prepared by dilution of stock solution. All solvents used in this experiment were of HPLC grade.

A Hamilton 90022 needle (stainless steel, metal hub, 22 gauge, 718 μ m O.D., 413 μ m I.D., bevel tip, 51 mm length) was used and a 1 mL Hamilton 1001N (gas tight syringe, luer lock gas tight syringe barrel, USA) and plunger (polytetrafluoroethylene, Teflon, USA) were used for adsorption and desorption.

2.2. Fabrication of a needle coated PANI layer

The PANI was directly deposited on the in-needle surface using cyclic voltametry (CV) technique. Electrochemical polymerization was performed using a three-electrode CV system (CHI Instrument Inc., USA) by oxidation of 0.1 M aniline solution in 0.5 M sulfuric acid. Prior to the polymerization process, the needle was cleaned in acetone using an

ultrasonic bath for 20 min and was dried at room temperature during overnight. The outside surface of the needle was wrapped using Teflon tape to prevent surface from being coated. CV was carried with a CHI 620A Electrochemical Analyzer. The needle was used as the working electrode, a platinum wire and Ag/AgCl electrode were employed as the counter electrode and the reference electrode, respectively. CV system was operated at a scan rate of 20 mVs⁻¹. The potential range was decided to avoid oxidation of unexpected product. After CV process, the coating layer was washed with distilled water several times in order to remove the unreacted chemicals such as residual aniline and supporting electrolyte. By insertion in the GC injector port, the fiber was dried at 80 °C for 30 min and then purified at 220 °C for 1 hr under continuous nitrogen flow.

2.3. Characterizations of PANI layer

To analyze functional groups of PANI, infrared spectra were recorded by the KBr pellet method on a Perkin Elmer Spectrum 100 (USA) in range of 400 ~ 4000 cm⁻¹.

Thermal stability of PANI was determined by a TG 209 F3 thermogravimetric analyzer (NETZSCH,

Germany). Temperature condition of thermogravimetric analyzer was initially started at 28.0 °C and increased with 20.0 °C/min until 800 °C.

To identify morphology of the needle coated with PANI, the needle tip was observed using field emission-scanning electron microscope (FE-SEM, MIRA, TESCAN, Czech).

2.4. Headspace In-Needle Microextraction using a Coated Polyaniline Layer (HS-INME-PANI)

For headspace extraction, water sample spiked with PAHs working solution was prepared and the INME needle coated with polyaniline was exposed to the headspace of the vial. Dynamic extraction was performed by automatic compression and aspiration, which offers high extraction efficiency of in-needle using a homemade reciprocating pump. Speed of the reciprocating pump was 6 cycle/min (1 cycle/ 10 sec. Thermal desorption of analytes was conducted at 230 °C. Then, the analytes were analyzed by gas chromatography (GC) system.

2.5. Optimization and Validation of HS-INME-PANI for PAHs

In order to evaluate the extraction capability of

Table 1. The operating conditions of gas chromatography-flame ionization detection (GC-FID) and gas chromatography/mass spectrometry (GC/MS)

	GC-FID		GC/MS	
	GC (HP 5890)		GC (7820A , Agilent)	
Column	HP5 [®] (30 m × 0.25 mm × 0.25 μm, (5 %-Phenyl)-methylpolysiloxane, Agilent)		HP5 [®] (30 m × 0.25 mm × 0.25 μm, (5 %-Phenyl)-methylpolysiloxane, Agilent)	
Oven Temp. program	50 °C (for 2 min) → 20 °C/min → 220 °C (for 5 min) → 40 °C/min → 280 °C (for 10 min)		50 °C (for 2 min) → 20 °C/min → 220 °C (for 5 min) → 40 °C/min → 280 °C (for 10 min)	
Injector Temp.	230 °C		230 °C	
Split ratio	splitless		splitless	
Carrier gas	N ₂ (99.99 %)		He (99.999 %)	
Flow rate	1 mL/min		1 mL/min	
	Detector			
	FID		MS (5977E, Agilent)	
Detector Temp.	290 °C		Mass transfer line	280 °C
FID gas	H ₂ (99.99 %), Air (99.99 %)		Ionization voltage	70 eV
			Ion source	230 °C
			Quadruple	150 °C
			Scan mode	Selected ion monitoring

PANI layer for PAHs from aqueous samples, HS-INME-PANI was performed with various parameters affecting extraction efficiency. Parameters were varied for adsorbent length, CV scan number, adsorption temperature, adsorption time, and desorption time. The optimum conditions were selected by comparing peak area of standard compounds in triplicate. Validation of HS-INME-PANI was performed at the optimized conditions. Quantitative analysis was performed by internal standard method.

2.6. Gas Chromatography

Optimization of HS-INME-PANI was determined by GC-FID (Hewlett-Packard, HP 5890, USA). Validation of analysis method, comparison of extraction efficiency, and quantitative analysis of real samples were determined by GC/MS with selected ion monitoring (SIM) of three characteristic ions. Ions used for SIM were m/z 128, 127, 129 for naphthalene, m/z 152, 151, 150 for acenaphthylene, m/z 154, 153, 152 for acenaphthene, m/z 166, 165, 164 for fluorene, m/z 178, 176, 179 for anthracene, and m/z 202 for fluoranthene, respectively.

GC/MS system was equipped with 7820A GC system and MSD 5977E quadrupole mass spectrometer (Agilent Technologies, USA). Separation of PAHs was performed using a capillary column HP-5 ((5 %-phenyl)-methylpolysiloxane, 30 m \times 0.25 mm \times 0.25 μ m, Agilent Technologies, USA). Detailed analysis conditions are summarized in Table 1.

3. Results and Discussion

3.1. Characteristics of PANI layer

In this study, PANI layer served as an adsorbent and was synthesized in our laboratory. Aniline was known to be easily polymerized with electrochemical oxidation reaction. The characteristics of conducting polymer made by electropolymerization were affected by counter ion, reaction medium, and reaction condition.²⁴⁻²⁶ With reference to other works, sulfuric acid was suitable medium for electrochemical polymerization of aniline.²⁷⁻²⁸

Fig. 2 shows cyclic voltammogram obtained from the oxidation of aniline and stainless steel needle in sulfuric acid with a potential range from -0.2 to 1.2 V at scan rate of 20 mVs⁻¹ after 30 cycle. Following the Fig. 2(a), oxidation of blank was shown at high voltage with 1.0~1.2 V. Peak at 0.2 V could be related to the presence of a side product²⁹ as shown in Fig. 2(b). Therefore, a potential range for polymerization of PANI was determined 0.65~0.90 V that oxidation of blank and generation of unwanted product were not occurred.

Principal functional groups in PANI were identified through infrared (IR) spectra. IR bands were appeared at 3429.87 cm⁻¹ (-NH stretching), 1579.21 cm⁻¹ (benzoid ring vibration), 1495.37 cm⁻¹ (quinoid ring vibration), and 1132.52 cm⁻¹ (sulfate ion). It was confirmed that the resulting PANI layer was formed successfully. The thermogravimetric analysis (TGA)

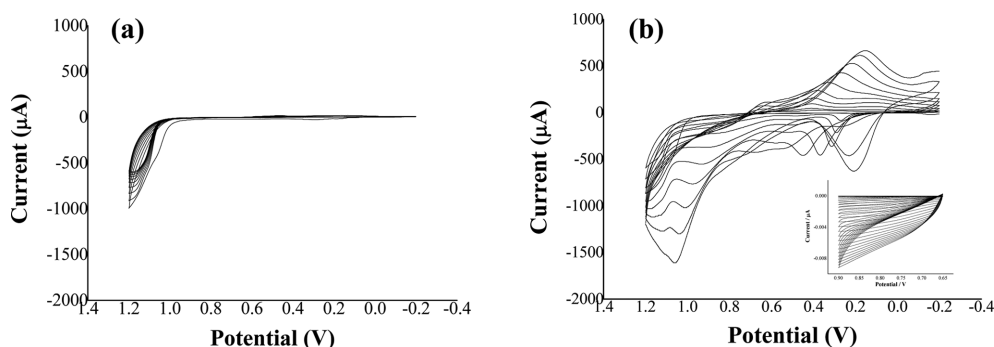


Fig. 2. Cyclic voltammograms of (a) stainless steel needle and (b) aniline in sulfuric acid with a potential range from -0.2 to 1.2 V at scan rate of 20 mVs⁻¹ after 30 cycle.

of the PANI revealed that the PANI was stable up until 250 °C (data not shown).

3.2. Optimization of HS-INME-PANI

The analysis conditions were optimized by varying parameters in order to extract PAHs effectively in aqueous phase. Parameters for design of PANI layer and analysis condition including adsorption conditions and desorption condition were varied including PANI layer length, the number of CV scans, adsorption temperature, adsorption time, and desorption time. Each parameter was changed at while others were

fixed.

3.2.1. Design of PANI layer

The length and CV scan number of PANI layer were investigated to evaluate the extraction efficiency of adsorbent. PANI layer with 1.0 cm and 2.0 cm showed the good extraction efficiency as shown in Fig. 3(a). However, 2.0 cm PANI layer produced relative standard deviation was in range 20.0 ~ 34.5 % while 1.0 cm offered good reproducibility. Therefore, 1.0 cm was determined as optimum adsorbent length.

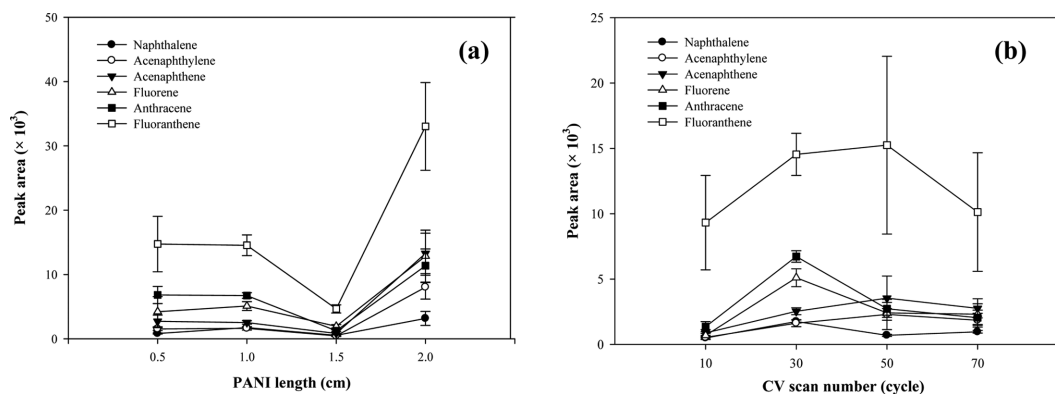


Fig. 3. Cyclic voltammograms of (a) stainless steel needle and (b) aniline in sulfuric acid with a potential range from -0.2 to 1.2 V at scan rate of 20 mVs^{-1} after 30 cycle.

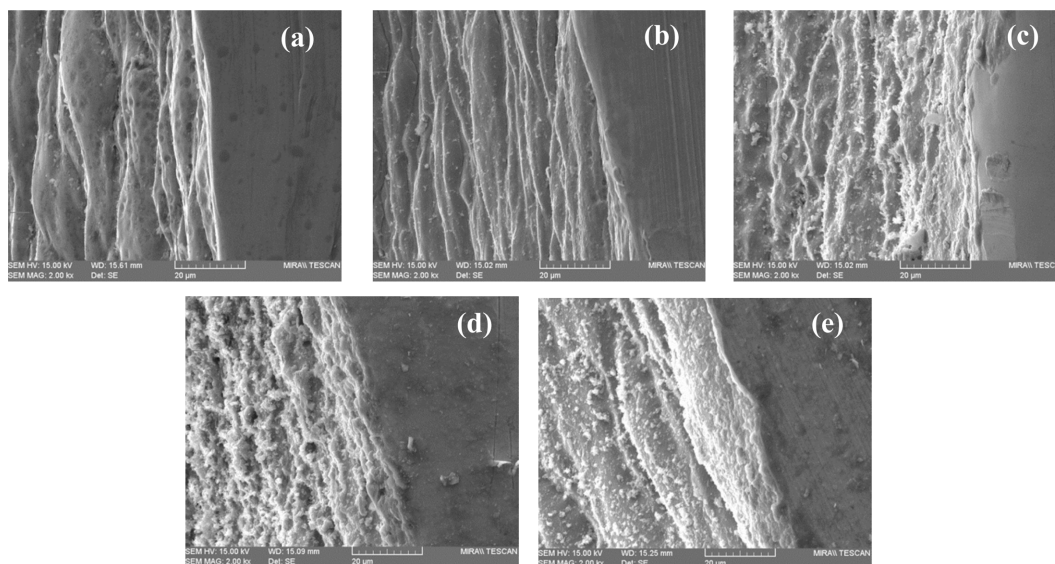


Fig. 4. SEM images of PANI deposited on needle tip for (a) 0 CV cycle, (b) 10 CV cycle, (c) 30 CV cycle, (d) 50 CV cycle, and (e) 70 CV cycle.

The number of CV scans that might modify the roughness or thickness of PANI was varied. Morphology of PANI layer obtained by the various CV cycle was confirmed by SEM and shown in Fig. 4. It was confirmed that the PANI was more deposited as increasing CV scan number. The PANI layers with 30 cycle and 50 cycle were rougher than that with 70 cycle. It seemed that aggregation was progressed while scan number was increased.

In consideration with the morphology of PANI and extraction efficiency, as shown in Fig. 3(b), the PANI layer with 10 cycle extracted in low level because PANI was not properly deposited yet. The PANI layer with 30 cycle and 50 cycle had similar extraction ability but reproducibility of 30 cycle was better than that of 50 cycle. Therefore, the layer generated by 30 cycle was decided to be optimum CV scan number.

3.2.2. Optimization of adsorption conditions

Adsorption temperature is a factor affecting the equilibrium between the adsorbent and sample during the SPME extraction.³⁰ As shown in Fig. 5(a), two compounds, anthracene and fluoranthene, having boiling points above 300 °C showed that extraction efficiency increased in adsorption temperature. The extraction efficiency of other compounds having boiling below 300 °C decreased. When the temperature of the target compounds increases, the diffusion

coefficient is increased and the equilibrium time is shorter.³¹ During headspace microextraction, increasing temperature of sample tends to decrease sensitivity of low boiling point molecules and to increase sensitivity of high boiling point molecules.³² After consideration of this tendency applied to the headspace microextraction for PAHs, the optimum adsorption temperature was set at 40 °C.

Adsorption time might mean the time to reach the equilibrium. The effect of adsorption time was investigated by changing adsorption time from 10 min to 60 min. As shown in Fig. 5(b), extraction efficiency of compounds with high boiling point above 300 °C tended to increase with increasing of adsorption time. However, extraction efficiency of other compounds maintained or decreased with increasing of adsorption time. For this reason, all target PAHs were efficiently extracted during 30 min showing relatively high reproducibility. The optimum adsorption time was evaluated as 30 min.

3.2.3. Optimization of desorption conditions

The TGA study on the PANI revealed that it was stable until 250 °C (data not shown). To avoid the thermal degradation of PANI, desorption temperature was set at 230 °C. As shown in Fig. 6, desorption efficiency was decreased during 90 s, and 120 s. It could be confirmed due to loss of analytes in the GC injector at longer desorption time.¹⁶ Therefore,

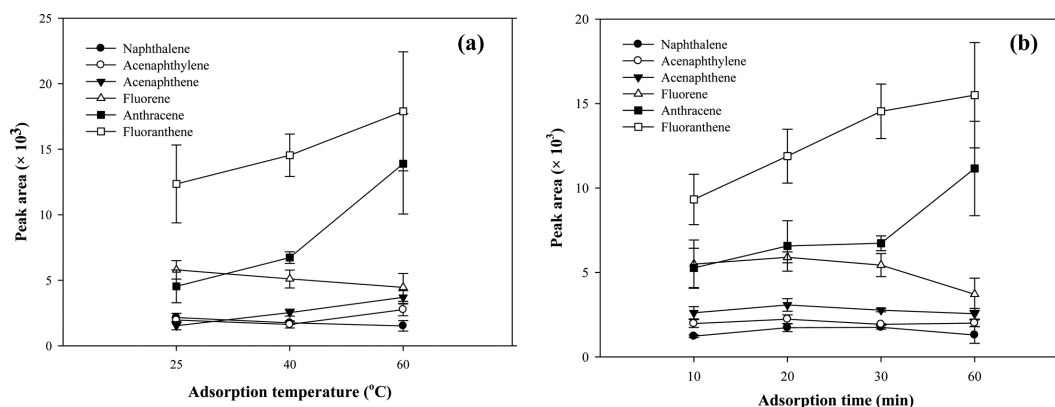


Fig. 5. Optimum adsorption temperature (a) and time (b) were determined by peak area of standard PAHs compounds. HS-INME-PANI conditions: PANI length of 1.0 cm, CV scan number of 30 cycle, adsorption at 40 °C, desorption at 230 °C during 60 s.

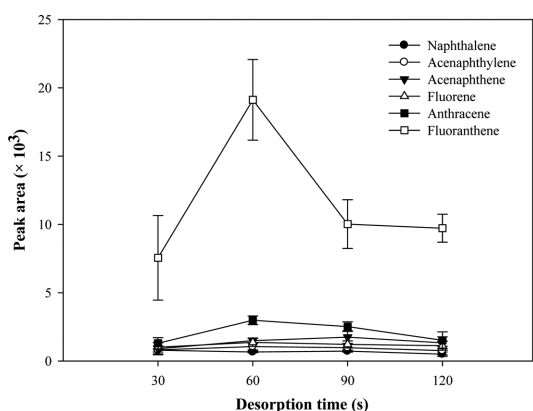


Fig. 6. Optimum desorption time was determined by peak area of standard PAHs compounds. HS-INME-PANI conditions: PANI length of 1.0 cm, CV scan number of 30 cycle, adsorption at 40 °C, desorption at 230°C during 60 s.

desorption time was determined for 60 s due to desorption efficiency.

3.3. Validation of analysis method

To validate HS-INME-PANI method, limit of

detection (LOD), limit of quantification (LOQ), recovery, and reproducibility were performed at optimum analysis condition and summarized in Table 2. LOD and LOQ were defined and calculated following ISO definition (11843-2). Calibration curves of all PAHs had r^2 (coefficient of determination) values greater than 0.990, which means the good linearity. The LOD and LOQ ranges for each PAH were calculated for 8.00 ng ~37.48 ng and 26.69 ~ 124.93 ng, respectively. Based on the dynamic range of each standard, it was confirmed that quantitative analysis for each compound was possible in the range from nanograms to micrograms.

Accuracy of HS-INME-PANI was evaluated through recovery test by adding low concentration at 0.25 μg and high concentration at 2.5 μg of PAHs standard compounds to tap water triplicate. As shown in Table 3, recovery was 94.42 ~ 104.71 % at low level and 84.25 ~ 95.60 % at high level. The reproducibility is presented as the relative standard deviation of intra (run to run, $n = 5$) and inter assays (needle to needle,

Table 2. Validation data of HS-INME using PANI layer

Compound	Regression equation	r^2 *	LOD** (ng)	LOQ*** (ng)	Dynamic range (ng)
Naphthalene	$y = 2941.3x - 32233$	0.9924	8.00	26.69	$26.7 \sim 3.00 \times 10^3$
Acenaphthylene	$y = 2546.1x - 23842$	0.9960	18.15	60.52	$60.5 \sim 3.00 \times 10^3$
Acenaphthene	$y = 2787.3x - 12057$	0.9903	21.37	71.25	$71.2 \sim 3.00 \times 10^3$
Fluorene	$y = 3409.0x - 45283$	0.9962	19.82	66.07	$66.1 \sim 3.00 \times 10^3$
Anthracene	$y = 132.26x + 28629$	0.9916	37.48	124.93	$124.9 \sim 5.00 \times 10^3$
Fluoranthene	$y = 276.75x + 35926$	0.9927	32.33	107.77	$107.8 \sim 5.00 \times 10^3$

* r^2 : linearity

**Limit of detection

***Limit of quantitation

Table 3. Validation data of HS-INME using PANI layer; recovery of standard PAH compounds and reproducibility

Compound	Recovery (mean \pm RSD%, $n=3$)		Reproducibility (\pm RSD%, $n=5$)	
	0.25 μg (low level)	2.5 μg (high level)	Intra assay (run to run)	Inter assay (needle to needle)
Naphthalene	97.97 ± 8.48	84.25 ± 9.96	6.92	10.48
Acenaphthylene	103.64 ± 6.60	94.36 ± 9.70	6.09	8.43
Acenaphthene	104.71 ± 10.30	90.27 ± 5.07	9.56	8.21
Fluorene	97.30 ± 4.83	95.60 ± 6.39	6.41	11.00
Anthracene	94.42 ± 3.58	90.41 ± 7.70	8.30	11.56
Fluoranthene	100.93 ± 4.17	84.66 ± 5.42	9.77	8.76

n = 5). As a result, the relative standard deviation was achieved less than 10 % computed from intra assay and 20 % from inter assay, respectively.

3.4. Comparison of extraction efficiency

Among various extraction methods for PAHs, SPME was chosen to be compared with INME method for extraction efficiency. It was determined by computing concentration factor based on peak area of each PAH standard.

$$CF = \frac{A_1}{A_0}$$

CF means the concentration degree of analytes on adsorbent during pretreatment process and larger CF refers better extraction efficiency than smaller CF values. In equation, A_0 is peak area obtained from static headspace (static HS) method and A_1 is peak area obtained from HS-INME-PANI or HS-SPME-PDMS. Static HS method was carried out by collecting the analytes from headspace without agitation. The calculated CFs are shown in Table 4. The CFs of SPME in naphthalene, acenaphthalene, acenaphthene, and fluorene were greater than INME method. However, the CFs of anthracene, and fluoranthene having boiling point above 300 °C were higher in INME method.

Octanol/water partition coefficients of PAHs defined as $\log K_{ow}$ can be linked with polarity.³³⁻³⁵ The higher value means the less polar. The order of $\log K_{ow}$ is as follows: fluoranthene, anthracene, fluorene, acenaphthylene, acenaphthene and naphthalene.

Table 4. Extraction efficiency values of HS-INME-PANI expressed as concentration factors of PAHs in aqueous sample

Compounds	log K_{ow}	Concentration factor (mean \pm std, n = 3)	
		INME-PANI	SPME-PDMS
Naphthalene	3.37	17.06 (± 0.88)	42.54 (± 2.30)
Acenaphthylene	4.07	60.70 (± 2.74)	136.42 (± 6.34)
Acenaphthene	3.98	36.48 (± 1.06)	177.64 (± 8.92)
Fluorene	4.18	104.49 (± 11.49)	220.02 (± 24.53)
Anthracene	4.50	452.17 (± 34.98)	327.10 (± 34.36)
Fluoranthene	4.90	71.49 (± 7.37)	10.76 (± 0.46)

Extraction efficiency followed the order of $\log K_{ow}$, except for fluoranthene. It may be conducted that HS-INME-PANI has higher extraction efficiency for non-polar compounds than polar compounds.

3.5. Application of HS-INME-PANI

The PAH compounds of aqueous sample were analyzed using HS-INME method at optimized condition. The aqueous sample was taken from low flow stream in Seoul. The sample was collected using large container at three different locations before stirring up the stream. Then, appropriate portion of water was transferred into a small container and stored at 4 °C prior to further analysis. Six different phthalates we have investigated were detected by HS-INME method proposed in this study. However, as a result, target PAHs was not able to be quantified due to peak area smaller than LOQ (Data not shown).

4. Conclusions

In this study, in-needle microextraction (INME) using electrochemically coated with polyaniline (PANI) layer was developed successfully. For electrochemical polymerization of aniline, polymerization was conducted at potential range the between 0.65~0.90 V for avoiding oxidation of needle and generation of side products. Principal functional groups in PANI layer generated by electrochemical polymerization were identified as -NH, benzoid ring, quinoid ring, and sulfate ion. The PANI layers were aggregated as CV scan number was increased. The PANI layer was stable until 250 °C that performed by TGA.

The optimal parameters of HS-INME-PANI were investigated for 6 PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, and fluoranthene using GC-FID. The optimum conditions were determined as 1.0 cm of PANI length, 30 cycle of CV scan number, 40 °C of adsorption temperature, 30 min of adsorption time, 230 °C of desorption temperature, and 60 s of desorption time.

To validate HS-INME-PANI, calibration curves, LOD, LOQ, recovery, reproducibility, and concentration factor were determined at optimum condition by

GC/MS system. The needle of PANI layer was repeatedly used more than 200 times during this study. In conclusion, the proposed method showed reasonable extraction efficiency, extraction time and cost effectiveness.

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