เส้นใยระดับนาโนเมตรอิเล็กโทรสปันพอลิอะคริโลไนไตรล์เพื่อเป็นตัวเคลือบเส้นใยในการสกัดระดับ
จุลภาคด้วยวัฏภาคของแข็ง

นางสาวทิชากร สังอรดี

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ELECTROSPUN POLYACRYLONITRILE NANOFIBERS AS FIBER COATING IN SOLID PHASE
MICROEXTRACTION

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ทิชากร สังอรดี : เส้นใยระดับนาโนเมตรอิเล็กโทรสปันพอลิอะคริโลไนไตรล์เพื่อเป็นตัวเคลือบเส้นใยในการสกัดระดับจุลภาคด้วยวัฏภาคของแข็ง (ELECTROSPUN POLYACRYLONITRILE NANOFIBERS AS FIBER COATING IN SOLID PHASE MICROEXTRACTION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร.พุทธรักษา วรานุศุภากุล, 55 หน้า.

โซลิดเฟสไมโครเอกซ์แทรกชันเป็นเทคนิคที่นิยมใช้ในการสกัดสารเพื่อเพิ่มความเข้มข้นสาร ในงานวิจัยนี้ได้เตรียมเส้นใยพอลิอะคริโลไนไตรล์บนลวดโลหะโดยวิธีอิเล็กโทรสปินนิงและใช้เป็นตัวเคลือบเส้นใยในชุดโซลิดเฟสไมโครเอกซ์แทรกชันที่ทำเอง เมื่อตรวจสอบสัณฐานของเส้นใย พบว่า เส้นใยที่ได้มีลักษณะเป็นรูพรุนและสม่ำเสมอ ขนาดของเส้นใยอิเล็กโทรสปันเฉลี่ย 165 ถึง 464 นาโนเมตร จากความเข้มข้นของสารละลายพอลิอะคริโลไนไตรล์ร้อยละ 3 ถึง 10 โดยน้ำหนัก ตัวเคลือบเส้นใยพอลิอะคริโลไนไตรล์ในชุดโซลิดเฟสไมโครเอกซ์แทรกชันที่ทำเองถูกนำไปประยุกต์ใช้ในการสกัดพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน 6 ชนิด ด้วยเทคนิคเฮดสเปซ โดยพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนจะถูกไล่ออกจากตัวดูดซับโดยตรงในส่วนฉีดสารของเครื่องแก๊สโครมาโทกราฟีด้วยความร้อนและวิเคราะห์ด้วย แก๊สโครมาโทกราฟีที่มีเครื่องตรวจวัดแบบเฟลมไอออนไนเซชัน (GC-FID) ภาวะที่เหมาะสมในการสกัดคือ สกัดที่อุณหภูมิ 40 องศาเซลเซียส เป็นเวลา 30 นาที โดยเติมเกลือโซเดียมคลอไรด์ร้อยละ 10 โดยน้ำหนักในสารละลายตัวอย่าง ไล่สารออกจากตัวดูดซับที่อุณหภูมิ 200 องศาเซลเซียส เป็นเวลา 5 นาที ได้ค่าร้อยละการคืนกลับ (%Recovery) ของการสกัดน้ำที่มีการเติมพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนที่ความเข้มข้น 40 ไมโครกรัมต่อลิตร เท่ากับ ร้อยละ 95.8 ถึง 115.1 และส่วนเบี่ยงเบนมาตรฐานสัมพัทธ์ (RSD) น้อยกว่าร้อยละ 12.7 สำหรับตัวเคลือบเส้นใย 5-PAN และเท่ากับร้อยละ 80.3 ถึง 108.6 และส่วนเบี่ยงเบนมาตรฐานสัมพัทธ์น้อยกว่าร้อยละ 7.4 สำหรับตัวเคลือบเส้นใย 7-PAN นอกจากนี้ กราฟมาตรฐานของการวิเคราะห์พอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน 6 ชนิด มีความเป็นเส้นตรงที่ดี ในช่วงความเข้มข้น 5 ถึง 75 ไมโครกรัมต่อลิตร สำหรับ 5-PAN และ 7-PAN โดยมีค่าสัมประสิทธิ์การตัดสินใจ (R^2) ระหว่าง 0.9697 ถึง 0.9954 สำหรับ 5-PAN และอยู่ระหว่าง 0.9797 ถึง 0.9956 สำหรับ 7-PAN ค่า LOD มีค่าเท่ากับ 0.08 ถึง 0.5 ไมโครกรัมต่อลิตร สำหรับ 5-PAN และ 0.1 ถึง 0.9 ไมโครกรัมต่อลิตร สำหรับ 7-PAN ซึ่งตัวเคลือบเส้นใยพอลิอะคริโลไนไตรล์ในชุดโซลิดเฟสไมโครเอกซ์แทรกชันที่ทำเองสามารถใช้งานได้มากกว่า 20 ครั้ง สุดท้ายนำตัวเคลือบเส้นใยอิเล็กโทรสปันพอลิอะคริโลไนไตรล์ในโซลิดเฟสไมโครเอกซ์แทรกชันไปใช้ในการวิเคราะห์พอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนในน้ำตัวอย่างจริงที่มีการเติมพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอนที่ความเข้มข้น 60 ไมโครกรัมต่อลิตร พบว่า ค่าร้อยละการคืนกลับของการสกัดพอลิไซคลิกแอโรแมติกไฮโดรคาร์บอน เท่ากับร้อยละ 53.6 ถึง 155.4

ภาควิชา เคมี	ลายมือชื่อนิสิต	....
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THICHAKORN SUNGORADEE: ELECTROSPUN POLYACRYLONITRILE NANOFIBERS AS FIBER COATING IN SOLID PHASE MICROEXTRACTION. ADVISOR: ASST. PROF. PUTTARUKSA VARANUSUPAKUL, Ph.D., 55 pp.

Solid-phase microextraction (SPME) is widely used to preconcentrate analytes from sample. In this research, the polyacrylonitrile (PAN) nanofibers were fabricated on a metal wire via electrospinning method and used as a fiber coating for a homemade SPME unit. The SEM images show that the fiber coating's surface was porous, and homogeneous. The average nanofibers diameter were 165 nm to 464 nm with PAN concentration from 3 to 10 %w/v. The homemade SPME unit was then applied for the extraction of 6 polycyclic aromatic hydrocarbons (PAHs) in water by headspace technique. Then it can directly transfer and desorb in the GC injection port by thermal desorption and analyzed by GC-FID. The optimum extraction condition was extraction time of 30 minutes, extraction temperature of 40 °C, and NaCl addition of 10% w/v. Desorption time and desorption temperature were optimized at 5 min and 200 °C, respectively. The percentage of recoveries of spiked water at 40 µg/L were 95.8 - 115.1 % with %RSD less than 12.7% for 5-PAN SPME fiber and 80.3 - 108.6% with %RSD less than 7.4% for 7-PAN SPME fiber. In addition, the good linearity for the analysis of 6 PAHs by 5-PAN and 7-PAN SPME fibers were in the range of 5 - 75 µg/L with R^2 between 0.9697 and 0.9954 for 5-PAN and 5 - 75 µg/L with R^2 between 0.9797 and 0.9956 for 7-PAN. The LODs were 0.08 - 0.5 µg/L for 5-PAN SPME fiber and 0.1 - 0.9 µg/L for 7-PAN SPME fiber. For durability, a homemade SPME fibers can reuse up to 20 times. Finally, the electrospun PAN SPME fibers were applied to extract PAHs in trace level (60 µg/L) from real water samples. The %recovery of extraction of PAHs ranged from 53.6 – 155.4 %.

Department: Chemistry   Student's Signature ....

Field of Study: Chemistry   Advisor's Signature ....

Academic Year: 2016

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CHAPTER I

INTRODUCTION

1.1 Statement of purpose

Polycyclic aromatic hydrocarbons (PAHs) are semi volatile organic compounds that consist of two or multiple aromatic rings. PAHs are formed during the incomplete combustion of organic compound. They dispersed in the environment and released into the air. Some of them released through surface water via rainfall. The low molecular weight of PAHs (2-3 aromatic rings) have a significant toxicity and high molecular weight of PAHs are carcinogen and mutagen. Therefore, the contaminated PAHs should be measured. Figure 1.1 are structures of 16 PAHs on the EPA priority pollutant list that regulated by Environment Protection Agency (EPA) [1].
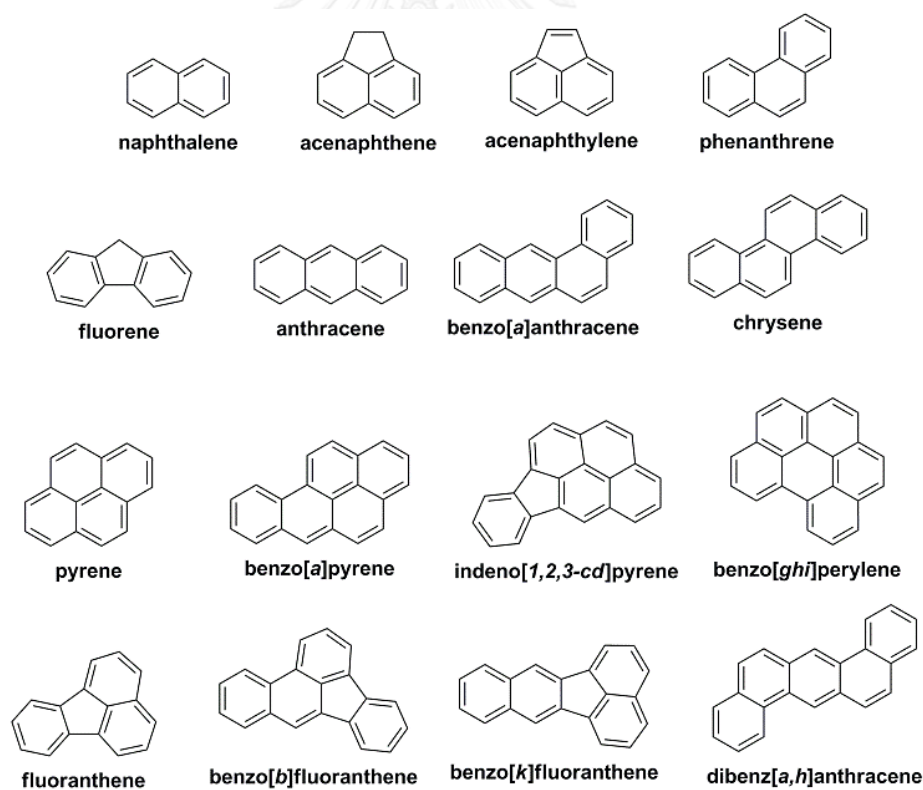
Figure 1.1 Structures and nomenclatures of the 16 PAHs on the EPA priority pollutant list

The common method for determination of PAHs is the extraction by liquid-liquid extraction (LLE) [2], solid-phase extraction (SPE) [3] or solid-phase microextraction (SPME) [4] prior to chromatographic analysis. LLE and SPE are widely used for extraction. However, they require a large volume of solvent and tedious steps. Recently, SPME has been widely used due to a combination of sampling, extraction, preconcentration, and elimination of interferences steps. Moreover, the analytes on SPME unit can directly desorb in the injection port of a gas chromatograph (GC) or a liquid chromatograph (LC) after extraction by thermal desorption in GC or solvent desorption in LC.

In the present, fiber coating in SPME was made from fused-silica. Thus, the fiber could be easily broken. Therefore, the development of new SPME fiber coating has been focused on the improvement of mechanical, chemical and thermal stabilities. Polymer is a good alternative material owing to flexibility, toughness and chemical stabilities. However, commercially available fiber coating is still a coated-polymer on fused silica fiber. The drawback of commercial fiber coatings are still the poor mechanical and thermal resistance. Some of these problems have been solved by applying the sol–gel [5] technique for binding polymer coating to the silica fiber surface. Later, the molecularly imprinted polymers (MIP) [6, 7] that stable and highly selective have been published as a new material and applied as SPME fiber coatings. Furthermore, the electrochemical methods was used for depositing the coating materials on SPME fiber [8]. This method coats the metal fiber used in the SPME with a conducting polymer. In addition, electrospinning method which fabricating the nanofibers on the metal fiber [9] is also applied for assembling the SPME fiber and considered one of the quickest and simplest process of coating an SPME fiber.

Electrospinning is a convenient method that used an electrostatic repulsive force to produce nanofibers from a polymer solution. The obtained electrospun nanofibers have a high surface to volume ratio that leads to good extraction efficiency. Recently, the electrospun nanofibers have been used as an extraction material for SPE [10, 11], μ-SPE [12] and SPME [13, 14].

In 2012, Bagheri and co-worker [13] fabricated a fiber coating in SPME by using electrospinning method. This fiber coating was made from Nylon 6. In this work, the SPME was applied for extraction of phenol and chlorophenols from water sample by headspace technique and analyzed by GC-MS. The presence of amide group in Nylon 6 provided a good efficiency for extraction of polar compounds. Moreover, the electrospun Nylon 6 fiber coating can be used more than 200 runs at 200°C of desorption temperature which is appropriate for thermal desorption of many analytes.

Another research from Minet et al. [15] reported the preparation of a polyacrylonitrile (PAN) /multi-walled carbon nanotubes coated stainless steel fibers for SPME by atom transfer radical polymerization method. The developed fiber coating showed a good selectivity for aromatic compounds such as benzene, toluene, ethyl-benzene, xylene, benzaldehyde, acetophenone, 2-octanone and 2, 6-dimethylphenol because the cyano group from PAN can form **π–π** interactions with aromatic compounds and dipole–dipole interactions with polar species. In addition, the PAN/MWCNTs fiber coating can be operated more than 200 extractions up to 280°C without damage.

Fang and Olesik [16] fabricated the carbon nanotube/polyacrylonitrile composite electrospun nanofibrous as a stationary phase for ultrathin layer chromatography (UTLC). PAN UTLC plates have a good organic solvent stability. 5 PAHs (phenanthrene, fluoranthene, pyrene, chrysene and benzo[a]pyrene). 5 PAHs were retained and separated on PAN plates by **π–π** interactions.

Jadhav et al. [17] used oxidized carbon nanotubes composite polyacrylonitrile electrospun nanofibers as an adsorbent for the removal of pyrene from aqueous solution. The developed nanofibers achieved 96% adsorption of pyrene in 30 minutes contact time at room temperature.

From previous research, an electrospun nanofibers showed a great suitability as a sorbent. Furthermore, polyacrylonitrile (PAN) was an interested alternative material for extraction of PAHs because it comprises of cyano group that can form $\pi-\pi$ interactions with aromatic compounds [18]. Therefore, the fabrication of PAN fiber coating in homemade SPME unit via electrospinning method was interested. Then, the obtained PAN fibers were applied for the extraction of PAHs in water. Important extraction factors were optimized and studied in this work.

1.2 Objective of this research

To fabricate electrospun polyacrylonitrile nanofibers in fiber coating format and use as a sorbent in homemade solid-phase microextraction unit for determination of PAHs in water.

1.3 Scopes of this research

1.3.1 Electrospun polyacrylonitrile nanofibers were fabricated as a fiber coating on a metal wire for a homemade SPME unit via electrospinning technique.

1.3.2 The homemade SPME unit was applied for the extraction of 6 PAHs which are acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, and pyrene in water samples by headspace technique.

1.3.3 The extraction parameters, including extraction time, extraction temperature, desorption time, desorption temperature, and amount of salt, were examined and optimized.

1.4 Benefits of this research

The electrospun polyacrylonitrile fiber coating in SPME can be an alternative sorbent for extraction of PAHs in water samples.

CHAPTER II

THEORY

2.1 Solid-phase microextraction

Solid phase microextraction is a fast, free-solvent sample extraction techniques. The sorbent in SPME is a polymer-coated fused silica fiber. In SPME, analytes establish equilibrium between the sample matrix and fiber coating. Principally, SPME consists of two steps: first analytes in sample were adsorbed onto an adsorptive material. Then, the analytes were transferred from adsorbent into a chromatograph inlet system by thermal or liquid desorption. SPME has been applied to gas chromatography (GC) and liquid chromatography (LC) separations. SPME has significant potential to eliminate or reduce solvent consumption as part of sample preparation.

SPME applications cover a broad range that includes environmental, food, and other fields, for example, aroma compounds in food [19], caffeine and flavors in beverages [20], volatiles in biological fluid [21], residual solvents pharmaceutical sample [22], PAHs in air [23], explosive in wastewater [24] and pesticide in water [25].

2.1.1 Configurations of SPME

Recently, there have been reports many configurations of SPME coating which are the interior of vessels, the magnetic stirring bars or pieces of polydimethylsiloxane tubes and thin membranes as shown in Figure 2.1 [26].

The development of these configuration is to enhance a sensitivity and improve the kinetics of the mass transfer between sample and coating material by increasing the surface to volume ratio of the extraction phase. The main drawback of some configurations of SPME is inconvenience for the introduction of the sample into the analytical instrument.
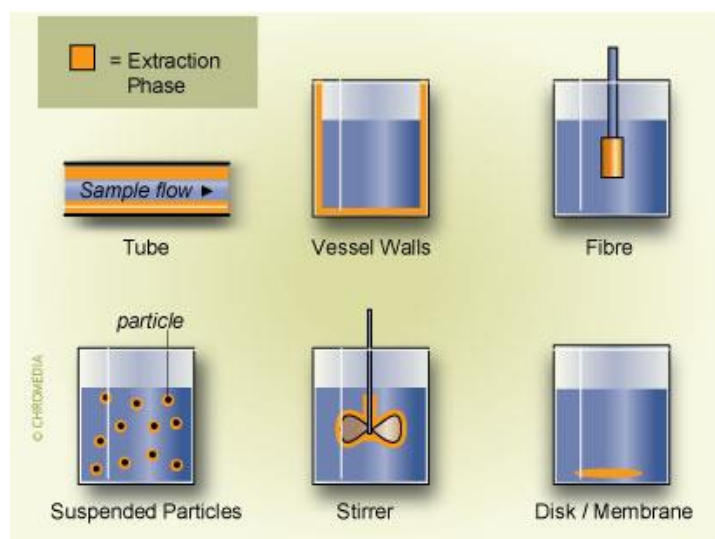
Figure 2.1 SPME configuration

2.1.2 Extraction modes

SPME can be performed in two basic modes: a direct extraction and a headspace extraction (Figure 2.2) [27]. In direct extraction, the fiber coating is dipped into the aqueous sample and allows analytes to transfer from sample to the fiber. The direct method is suitable for samples with high molecular weight and nonvolatile compounds. In headspace mode, the fiber coating is exposed in the headspace (the space above the aqueous sample). Volatile analytes in headspace are extracted onto the fiber coating.
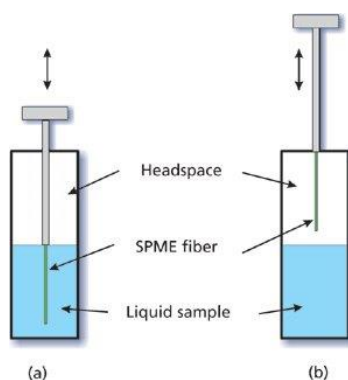
Figure 2.2 SPME extraction mode (a) a direct extraction and
(b) a headspace extraction

2.1.3 Experimental parameters

In order to achieve equilibrium conditions in SPME, the important parameters such as extraction time and temperature, desorption time and temperature, salt addition must be optimized to improve the extraction performance [4, 29].

2.1.3.1 Extraction temperature

Temperature is a major effect on extraction efficiency of SPME process. When increasing the temperature in the case of direct extraction, the distribution coefficient of the analytes between the sample and the fiber coating was increased. For headspace technique, the analytes can vaporize from the aqueous phase into the headspace and adsorb onto the fiber coatings. However, temperature is a limiting factor because increasing the temperature more than a suitable value would decrease a distribution coefficient of the analytes between the aqueous phase or headspace and the fiber coating. Hence, amount of extracted analytes decrease causing a poor extraction efficiency.

2.1.3.2 Extraction time

The extraction time is required to reach equilibrium between the analytes and the fiber coating in SPME. When performed the direct extraction mode, the process of sorption is limited by the rate at which solute molecules can move near the SPME interface. Therefore, agitation (stirring or sonicate) of the sample can reduce the sorption times. However, stirring the aqueous sample does not increase the diffusion rate of absorbed analytes inside the fiber coating layer.

For headspace mode, analytes must first transfer from liquid phase to headspace before encountering the SPME coating. It is hard to ultimate the equilibrium solute amounts in the SPME fiber coating whether the sample is obtained from the liquid or the gas. Therefore, the time to equilibrium include sample phase equilibrium (sample – headspace) and extraction equilibrium (headspace – fiber coating). Nonpolar and volatile analytes that favor the headspace phase will come to equilibrium more rapidly if the SPME coating is exposed to the headspace.

The sampling time should be used the equilibrium times. However, if the equilibrium time is too long, it is possible to perform SPME without reaching the equilibrium. Nonetheless, the operator must ensure that the same sampling time is used for each sample.

2.1.3.3 Headspace volume

This parameter is mainly affect the extraction in headspace mode. The presence of a headspace above a liquid sample causes a competition between volatile process and adsorption process of analytes into the SPME fiber coating. This effect results in a reduction of analytes mass in the SPME layer that depends on both the headspace volume and the partition ratios between the headspace and the liquid sample as well as between the headspace and the SPME layer. Hence, sample and headspace volumes are affected the extraction efficiency.

2.1.3.4 Desorption parameters

The SPME fiber coating must be desorbed the analytes as close to 100% as possible and within the shortest.

In the case of LC analysis, stopping the mobile phase flow in the SPME tube allows time for solute desorption to come to equilibrium between the SPME layer and the liquid mobile phase. Then, the analytes are passed into the LC injection loop and the desorbed materials are introduced into the column.

In the case of GC analysis, SPME fiber coating can conveniently applied into a GC injection system in the same way as a syringe. A desorption temperature must be high enough to thermally desorb the analytes from the SPME fiber coating rapidly. Slow desorption process may lead to peak broadening and tailing. Trapping the analytes at the beginning of the GC column by solvent trapping before temperature programmed can reduce this brodening. However, too high inlet temperature may induce thermal decomposition. During sample desorption, the splitless injection mode is recommended for all of the analytes enter the column in order to transfer all desorb.

2.1.3.5   Salt addition and sample pH

Salt addition increases the ionic strength of the sample solution and drives the volatile or nonpolar molecules to be more readily transferred from sample phase to the fiber coating or from sample phase to the headspace. Hence, the sensitivity of the extraction of volatile compounds from headspace is improved.

The pH adjustment or buffering are the matrix modifications for changing analytes or interference form. Adjusting the analytes into neutral forms by pH adjustment can significantly improve the exraction efficiency. In case of vigorous condition, headspace sampling is the preferred extraction mode, because the direct contact of the fiber coating with sample at very low or high pH levels can damage the fiber coating.

2.2 Polyacrylonitrile

Polyacrylonitrile (PAN) has a polar nitrile group as shown in Figure 2.3. PAN was synthesized for the first time in 1930 by Dr. Hans Fikentscher und Dr. Claus Heuck. However, PAN was not popular because it cannot soluble in common solvents. In 1942, Rein discovered a solvent for PAN that is dimethylformamide (DMF) and developed a technical method to process PAN to fibers and films. In fiber application, PAN is mostly used as polymeric carbon precursor to form carbon fibers [28, 29]. PAN have been used as fibers in gas filtration systems [30], hydrogen storage [31], electrochemistry, separation processes [32]. There are many advantages of PAN involving thermal stability, high strength and chemical resistance. These unique properties have made PAN an essential polymer in technology.
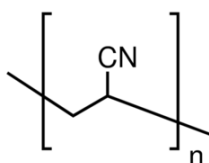
Figure 2.3 Structure of polyacrylonitrile.

2.3 Electrospinning

2.3.1 Electrospinning process

Electrospinning is a widely used method for the electrostatic production of fibers which a scale of diameters from nanometers to micrometers from polymer solutions. The main principle of the electrospinning process is the application of high voltage on a polymer solution to produce a fiber.

The electrospinning set up consists of three parts which are a source of high voltage (a DC voltage tens of kV), a spinneret (small holes through which a fiber-forming solution is forced such as metal needle) and a grounded collector. The electrospinning set up was shown in Figure 2.4 [33]. There are two typical set up of electrospinning, horizontal set up and typical vertical set up.
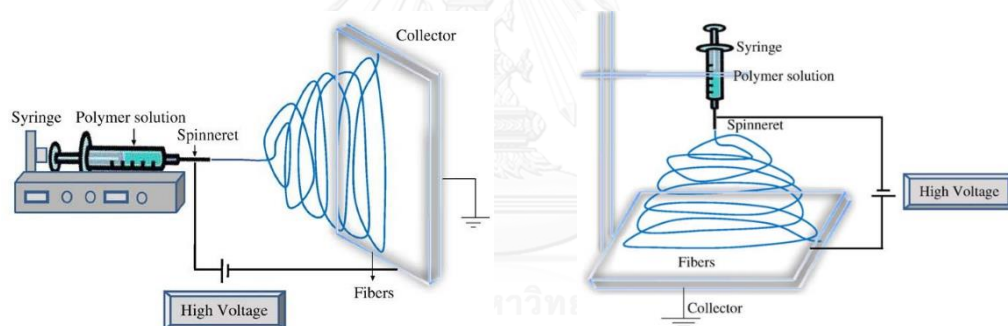
Figure 2.4 Schematic diagram of electrospinning apparatus (a) vertical set up and (b) horizontal set up.

In the electrospinning process, high voltage power supply is connected between the end of a flat needle containing liquid solution and a grounded collector. Before high voltage is applied, the solution is extruded and form the hemispherical droplet at the tip of the spinneret by surface tension. When the electric field intensity increases and overcomes the critical value of surface tension, the hemispherical droplet extends and creates a conical shape known as a Taylor's cone (Figure 2.5) [34]. Eventually, a charged jet solution flies toward to a grounded collector which solvent evaporates during the process. The fibers are then deposited on the collector. The resulting product is a non-woven fibrous layer.
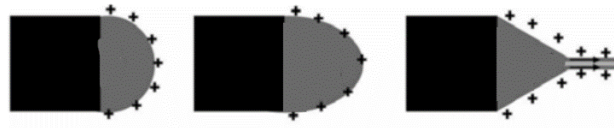
Figure 2.5 Forces acting on a droplet when electric fields are applied.

2.3.2 Parameters of electrospinning

Electrospinning is a simple way of creating nanofiber materials. However, there are several parameters that can significantly influence the formation and structure of produced nanofibers [35].

2.3.2.1   Solution parameters

2.3.2.1.1 Solution concentration

In the electrospinning process, at low solution concentration, it has been found that a mixture of beads and fibers were occurred. When the solution concentration increases, the spherical beads gradually changes to spindle like and finally uniform fibers with increased diameters are formed. At very high concentration, the formation of continuous fibers are forbidden because the formation of large fibers are not able to maintain the flow of the solution at the end of needle. The optimum electrospinning concentration depends on the molecular weight and nature of polymer [36]. Figure 2.6 shows the effect of polymer concentrations on the produced fibers.
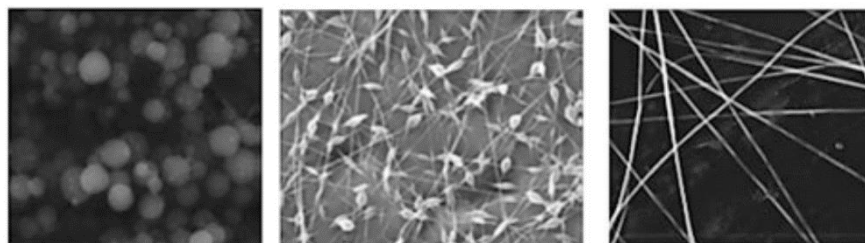
Figure 2.6 SEM images of the evolution of the products with different concentrations from low to high during the electrospinning.

2.3.2.1.2 Viscosity of solution

Solution viscosity has an important role in formation of nanofibers. At very low viscosity, there is no continuous fiber formation and beaded fibers are formed. At very high viscosity, there is difficulty in the ejection of jets from polymer solution. Thus, the optimal viscosity for electrospinning is required. Generally, the solution viscosity can be tuned by adjusting the polymer concentration, molecular weight of the polymer and solvent.

2.3.2.1.3 Surface tension of solution

Surface tension is quite important factor in electrospinning. By reducing the surface tension of the solution, beaded fibers can be change to smooth fibers. The high surface tension of a solution prohibits the electrospinning process due to instability of the jets and the formation of sprayed droplets. Different solvents may contribute different surface tensions. Nonetheless, it is not necessarily that a lower surface tension of a solvent will always be more suitable for electrospinning. The surface tension and solution viscosity can be adjusted by changing the mass ratio of solvents mixture.

2.3.2.1.4 Conductivity of solution

Usually, natural polymers are generally conductive. If the solution has not conductive property, it cannot perform electrospinning process. However, the electrical conductivity of the solution can be adjusted by adding the ionic salts like KH_2PO_4, NaCl. Sometimes high solution conductivity can be also achieved by using organic acid as the solvent. The increase of electrical conductivity of the solution is the cause of a significant decrease in the diameter of the electrospun nanofibers. Whereas, low conductivity of the solution results in sufficient extension of a jet by electrical force to produce uniform fiber, and beads may also be observed. Normally, electrospun nanofibers with the smallest fiber diameter can be obtained with the highest electrical conductivity.

2.3.2.2 Process parameters

2.3.2.2.1 Applied voltage

In the electrospinning process, applied voltage is the precious factor. Only the applied voltage higher than the threshold voltage can eject the charged solution jets from Taylor's Cone. However, the effect of the applied voltages on the diameter of electrospun fibers is a little influential, but the level of significances varies with the polymer solution concentration and on the distance between the spinneret and the collector.

2.3.2.2.2 Feed rate of solution

The flow rate of the polymer solution is another important process parameter. The flow rate of polymer solution was controlled by syringe pump. A lower feed rate will allow the solvent to have enough time for evaporation. The fiber diameter and the pore diameter increases with an increase in the polymer flow rate. Nonetheless, if the flow rate is too high, bead fibers with thick diameter will form owing to the short drying time prior to reaching the collector and low stretching forces. The morphological structure can be slightly changed by adjusting the flow rate.

2.3.2.2.3 Collector distance

The distance between the collector and the tip of the spinneret can also affect the fiber diameter and morphologies. One important parameter of the electrospinning nanofibers is their dryness from the solvent used to dissolve the polymer. Whereas the distance is too short, the charged solution jets will not have enough time to evaporate the solvent before reaching the collector. Longer distance favors the thinner fiber diameter. However, if the distance is too long, fibers cannot fly to the collector and bead fibers might occur. Hence, the optimum distance between the collector and the tip of the spinneret that suitable for evaporation of solvent should be investigated.

2.3.2.2.4 Ambient parameters

Ambient parameters such as humidity, temperature can also affect the fiber diameters and morphologies. Increasing temperature favors the thinner fiber diameter [36]. On the other hand, the viscosity of polymer solution decreases when increasing the temperature. In addition, at low humidity may dry the solvent rapidly. Sometimes the evaporation rate is so fast than compared to the removal of the solvent from the tip of the needle and this would create a problem with electrospinning. Whereas, high humidity will lead to the thick fiber diameter because of the charges on the jet can be neutralized and the stretching forces become small.

2.4 Analysis of PAHs

Analysis of PAHs in environment is challenging because PAHs have to be determined at trace levels. Sample preparation is used to extract PAHs, clean up the sample and preconcentrate before analysis. The widely techniques that used for sample preparation of PAHs are liquid–liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME). Then, PAHs are mostly analyzed by gas chromatography [37] with flame ionization detection (GC-FID) and mass spectrometry (MS), and high-performance liquid chromatography (HPLC) with UV and fluorescence detectors (FLD) [38].

CHAPTER III

EXPERIMENTAL

3.1 Chemicals

1) Polyacrylonitrile (average molecular weight 150,000) (Sigma-Aldrich, USA)

2) N, N-Dimethylformamide, ACS grade (Riedel-de Haën, Germany)

3) Acenaphthene; AC, 99.5% (Dr.Ehrenstorfer GmbH, Germany)

4) Fluorene; FL, 98.0% (Dr.Ehrenstorfer, Germany)

5) Phenanthrene; PHE, 99.5% (Dr.Ehrenstorfer, Germany)

6) Anthracene; AN, 99.0% (Dr.Ehrenstorfer, Germany)

7) Fluoranthene; FA, 98.5% (Dr.Ehrenstorfer, Germany)

8) Pyrene; PY, 99.0% (Dr.Ehrenstorfer, Germany)

9) Cyclohexane, ACS grade (Carlo Erba, France)

10) Sodium chloride, ACS grade (Carlo Erba, France)

11) Ultrapure water (Milli-Q, Millipore, Germany)

3.2 Methodology

3.2.1 Preparation of electrospun PAN fiber coating

The PAN solutions of different concentrations (3, 5, 7, and 10% w/v) were prepared by dissolved in 3 mL of dimelthylformamide (DMF) and stirred for 30 min at 50°C. Then, PAN solution was loaded into 3 mL plastic syringe with a blunt needle (20G). The setup for electrospinning was shown in Figure 3.1. The flow rate of PAN solution was controlled by syringe pump (Prosense B.V., NE-1000, USA) at 8 μL/min and distance between the needle tip and collector is 12 cm. The coating fibers were collected on a metal wire which rotated at 95 cycles per minute and located in front of the copper plate collector as shown in Figure 3.1. Then 23 kV of high voltage was applied by a high voltage power supply (BERTAN series 230, USA). The abbreviations of prepared electrospun PAN fiber coating were summarized in Table 3.1.

Table 3.1 Abbreviations of electrospun PAN fiber coating

Material	Abbreviations
3% w/v of electrospun PAN fiber coating in SPME	3-PAN
5% w/v of electrospun PAN fiber coating in SPME	5-PAN
7% w/v of electrospun PAN fiber coating in SPME	7-PAN
10% w/v of electrospun PAN fiber coating in SPME	10-PAN
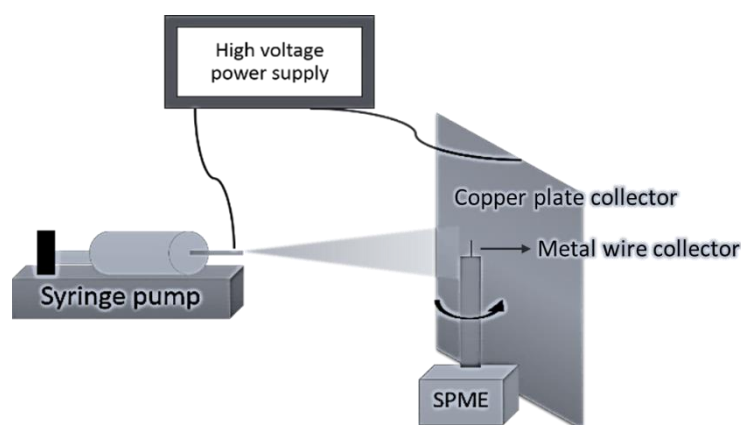
Figure 3.1 Schematic of electrospinning setup

3.2.2 Characterization of electrospun PAN fiber coating

The fiber coating's surface was characterized by scanning electron microscope (JEOL, JSM 6610 LV). The average nanofibers diameter was then determined from SEM image by ImageJ software.

3.2.3 Homemade SPME unit

The homemade SPME unit is composed of 3 parts SPME holder, syringe plunger and SPME fiber as shown in Figure 3.2. GC syringe (Hamilton 1725RN) with 22G needle size was used as SPME holder. The syringe plunger was modified by placing a septum at the end to easily connect the electrospun PAN fiber coating to the plunger. Third, 7 cm of the metal wire that collected the electrospun PAN fiber coating at the end of wire (1 cm length) was connected to the syringe plunger.
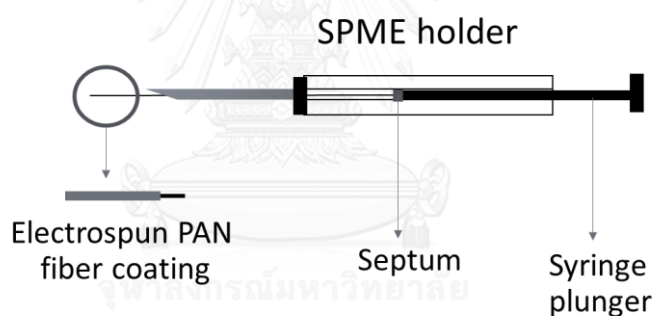
Figure 3.2 Schematic of homemade SPME unit

3.2.4 Preparation of PAHs standard solutions

Each PAH (acenaphthene; fluorene; phenanthrene; anthracene; fluoranthene; and pyrene) was dissolved in cyclohexane with concentration of 1,000 mg/L and used as stock solution. The stock solutions of each PAH were kept in amber vial at 4^OC. Then, mixed PAHs solution were prepared with concentration of 100 mg/L of PAHs by mixing 1,000 mg/L of stock solutions of 6 PAHs. 100 mg/L of mixed PAHs was kept at 4^OC in amber vial and used to prepare spiked samples for SPME study.

3.2.5 Solid-phase microextraction by electrospun PAN fiber coating

Parameters affecting the extraction recovery of PAHs using the PAN fiber coating including extraction time, extraction temperature, desorption time, desorption temperature and amount of salt were investigated. 10 mL of ultrapure water samples spiked with PAHs at 100 µg/L and 7-PAN fiber coating were used for all studies.

3.2.5.1 Extraction procedure

The electrospun PAN fiber coating was assembled in a homemade SPME unit as shown in Figure 3.2. In all experiments, 1 g of sodium chloride was added to 10 mL of aqueous sample in 30 mL amber vial containing a magnetic stirring bar. The aqueous sample was spiked with a mixed PAHs standard solution. The sample vial was heated and stirred (500 rpm) in a heating block on hot plate stirrer (IKA, RCT basic). The homemade SPME unit penetrated the septum on vial cap. Then the PAN fiber coating was exposed to the headspace (the space above the aqueous sample). After the extraction process, the PAN fiber coating was directly inserted into the GC injection port where PAHs on fiber coating can be desorbed by thermal desorption and analyzed immediately by GC-FID.

3.2.5.2 Optimization of extraction time

The extraction time was studied by varying the exposed time of the PAN fiber coating to the headspace of aqueous sample in the range of 10 to 60 minutes. Peak area from GC-FID of extracted PAHs was identified to determine the optimum extraction time.

3.2.5.3 Optimization of extraction temperature

The effect of extraction temperature was evaluated by varying the temperature of sample solution from 30°C to 70°C. Peak area from GC-FID of extracted PAHs was identified to determine the optimum extraction temperature.

3.2.5.4   Optimization of desorption time

PAHs were desorbed from SPME fiber directly in the GC injection port by thermal desorption. Therefore, desorption time was also investigated at the time range of 1 to 5 minutes. The maximum signal of extracted PAHs from GC-FID was identified to determine the optimum desorption time.

3.2.5.5   Optimization of desorption temperature

Desorption temperature was adjusted by changing a temperature of GC injection port between $150^{o}C$ to $220^{o}C$. The temperature that provided the highest signal of extracted PAHs from GC-FID without damaging the PAN fiber coating was identified as the optimum desorption temperature.

3.2.5.6   Optimization of salt addition

The effect of adding salt (NaCl) was studied by varying amount of salt in sample solution from 0% to 10% w/v. Peak area from GC-FID of extracted PAHs was identified to determine the suitable amount of salt.

3.2.6 Performance of electrospun PAN fibers in SPME fiber coating

Electrospun PAN nanofibers in SPME fiber coating fabricating from 5%, 7%, and 10% w/v of PAN were compared for the extraction efficiency of PAHs from water sample. Quantitative analysis of spiked water sample was performed using the optimum condition of SPME extraction. Six PAHs which are acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene and pyrene were selected and determined.

3.2.6.1   Linearity of calibration curve

The linearity of calibration curve for determination of PAHs in water by electrospun PAN SPME fiber, which fabricated from 5%, 7%, and 10% w/v of PAN, was performed using an external standard method. The concentration of PAHs for linearity studied were in range of 5 - 100 µg/L. The linear ranges, correlation coefficients (R^2) and linear equations of each SPME fiber coating were calculated.

3.2.6.2 Method of detection and method of quantitation

The limit of detection (LOD) was defined as the minimum concentration of PAHs that extracted from this work method giving 3 times of signal to noise ratio. The limit of quantitation (LOQ) was the concentration of PAHs giving 10 times of signal to noise ratio.

3.2.6.3 Accuracy of method

The accuracy of electrospun PAN fiber coating in homemade SPME unit was evaluated from the recovery of spiked ultrapure water at 40 μg/L PAHs. The number of PAHs that recovered after extraction was calculated from calibration curve. The extraction recovery was then calculated as follow

%Recovery = (Concentration of recovered / Concentration of spiked) x 100%

3.2.6.4 Reproducibility and repeatability

The reproducibility was estimated by comparing the peak areas after extraction of spiked ultrapure water with 100 μg/L of PAHs by using three coating fibers which fabricated under the same condition. Repeatability was investigated from 3 replicates of the extraction of PAHs in spiked water under optimum condition.

3.2.6.5 Durability of PAN SPME fiber

The durability of electrospun PAN fiber coating was studied by consecutive analysis of PAHs in spiked water at 50 μg/L under optimum condition on a single PAN fiber coating. Then, The GC-FID responses of all PAHs from every run were collected and compared. The consecutive analysis was performed until the GC-FID responses significantly change.

3.2.7 Extraction of PAHs in water sample

Surface water was sampling from pond and drinking water was bought from market. The water samples were spiked at concentration of 60 µg/L of mixed PAHs and extracted by using electrospun PAN fiber coating in homemade SPME unit under optimum condition. The extraction efficiency of PAN SPME fiber was compared with commercial 100 µm PDMS SPME fiber. The extraction condition of the commercial PDMS SPME fiber was shown in Table 3.2. The amount of PAHs that founded after extraction was calculated from calibration curve. The extraction recovery was then calculated.

Table 3.2 The extraction condition of PAHs in water by using commercial PDMS SPME

Parameter	Condition
extraction time	30 min
extraction temperature	$60^{o}C$
desorption temperature	$280^{o}C$
desorption time	2 min
salt concentration	10 %w/v

3.2.8 Analysis of PAHs by GC-FID

GC equipped (Hewlett-Packard 7890) with a flame ionization detector (FID) was used for quantitative determination of PAHs. A GC condition was summarized in Table 3.3.

Table 3.3 GC condition

Column	HP-5 capillary column (0.250 mm i.d. x 30 m, 0.25 μm film thickness)
Carrier gas	Helium, 40 cm/s
Injection	200°C, splitless
Oven	60°C (5 min) to 250°C at 20°C/min and held for 5 min
Detector	FID, 250°C

CHAPTER IV
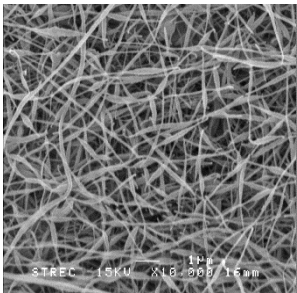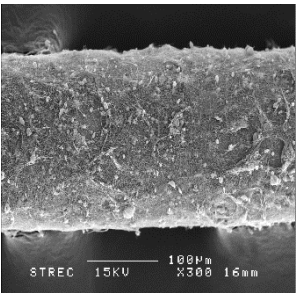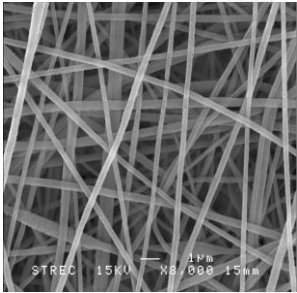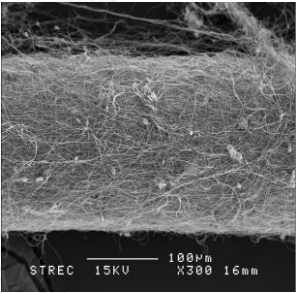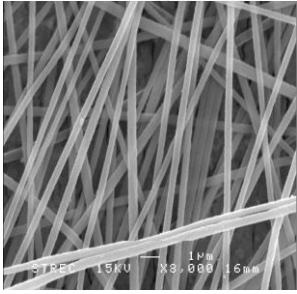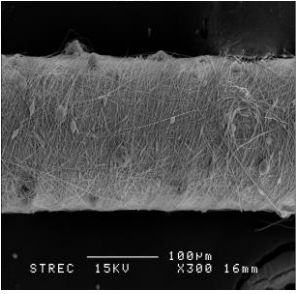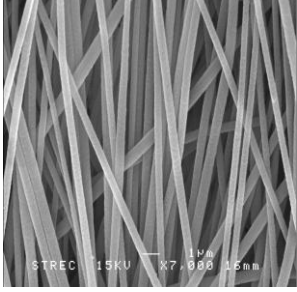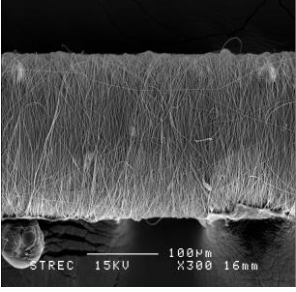
RESULTS AND DISCUSSION

In chapter IV, there are three major sections. First, the characterization of the electrospun PAN fibers on SPME fiber coating were investigated. Then, the condition of PAHs extraction was optimized. Finally, the PAN fiber coating was applied for determination of PAHs in water samples.

4.1 Characterization of the electrospun PAN fiber coating

Morphology of electrospun PAN fibers on SPME fiber coating was examined by scanning electron microscope (SEM). SEM images of the electrospun PAN fibers at difference concentration of PAN were shown in Table 4.1, the average diameter of PAN fibers was increased from 165 nm to 464 nm when increasing the PAN concentration from 3 to 10 %w/v due to the increase in viscosity of PAN solution. In addition, the fibers were fine and smooth except 3% w/v of PAN that formed bead-liked fibers. The alignment of electrospun PAN fibers on SPME fiber was improved when increased the PAN concentration. The best fabrication of SPME fiber was observed when coating with electrospun PAN fibers prepared from 10% w/v of PAN. The alignment in electrospun PAN fibers might cause the decrease of porous and surface to volume ratio that affect to extraction efficiency. However, fibers fabricated from 5, 7 and 10 %w/v of PAN were further studied as a SPME fiber coating in homemade SPME unit because the fine and smooth fibers were produced.

Table 4.1 SEM images of the electrospun PAN fibers coating on SPME fiber at difference concentration of PAN.

PAN concentration	SEM images of electrospun PAN fibers	SEM images of SPME fiber coating	Average diameter of PAN fibers
3% w/v	(x10,000)	(x300)	165 ± 69 nm
5% w/v	(x8,000)	(x300)	276 ± 40 nm
7% w/v	(x8,000)	(x300)	351 ± 54 nm
10% w/v	(x7,000)	(x300)	464 ± 75 nm

4.2 The extraction of PAHs in water using the PAN fiber coating in SPME

SPME condition was optimized to obtain high extraction efficiency within a reasonable time. Parameters affecting the extraction of PAHs in water using electrospun PAN fibers as a SPME fiber coating were investigated including extraction time, extraction temperature, salt concentration, desorption time, and desorption temperature. 10 mL of ultrapure water samples spiked with 6 PAHs at 100 µg/L were extracted using 7-PAN SPME fiber.

4.2.1 Effect of extraction time

The extraction time was studied by varying the exposed time of the PAN fiber coating to the headspace of aqueous sample in the range of 10-60 min. As shown in Figure 4.1, the response for all PAHs increased when increasing the extraction time. However, the response was slightly changed except phenanthrene at the extraction time above 30 min. However, the suitable extraction time should relate with GC cycle time (approximately 30 min). Thus, an extraction time of 30 min was chosen as the optimum time in SPME process.

Figure 4.1 The adsorption time profiles of PAHs. Extraction condition as follows: a spiked aqueous sample (100 µg/L, 10mL), salt addition (10%w/v NaCl), adsorption temperature of 40°C, desorption time of 5 min at 200°C.

4.2.2 Effect of extraction temperature

Extraction temperature has a significant role in the SPME process as it affects the diffusion rate of analytes into coating. The effect of extraction temperature was evaluated by varying the temperature of sample solution from 30°C to 70°C (Figure 4.2). The increases in sample temperature would increase diffusion coefficient and then enhance the adsorbed number of PAHs on SPME fiber coating. Moreover, the volatile analytes were evaporated easily from aqueous phase to headspace phase at higher temperature. Nevertheless, at temperature above 40°C, there are the water film barrier at PAN fiber coating because the water evaporation occur leading to decrease of extraction efficiency. Therefore, in this study the extraction temperature was set to 40°C.
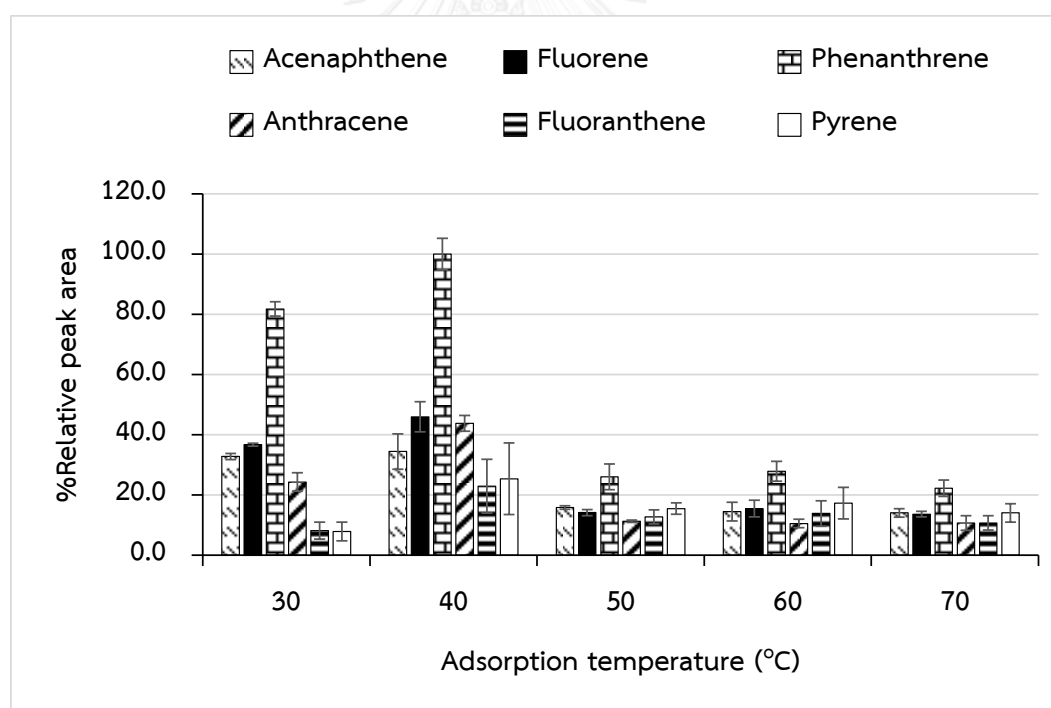
Figure 4.2 The extraction temperature profiles of PAHs. Extraction condition as follows: a spiked aqueous sample (100 µg/L, 10mL), salt addition (10%w/v NaCl), adsorption time of 30 min, desorption time of 5 min at 200°C.

4.2.3 Effect of desorption temperature

The highest desorption temperature without damaging the SPME fiber coating was evaluated. Because PAHs were desorbed from SPME fiber directly in the GC injection port by thermal desorption, the GC injection port was adjusted between 150°C to 220°C (Figure 4.3) for optimizing a desorption temperature. The result show that 220°C of desorption temperature gave the highest overall respond signal. However, when desorption temperature was set at 220°C, the PAN fiber coating rapidly change color from white to brown by operating only 3-5 times indicating the damage or change of PAN fiber coating. Therefore, the suitable desorption temperature for PAN fiber coating was optimized at 200°C.
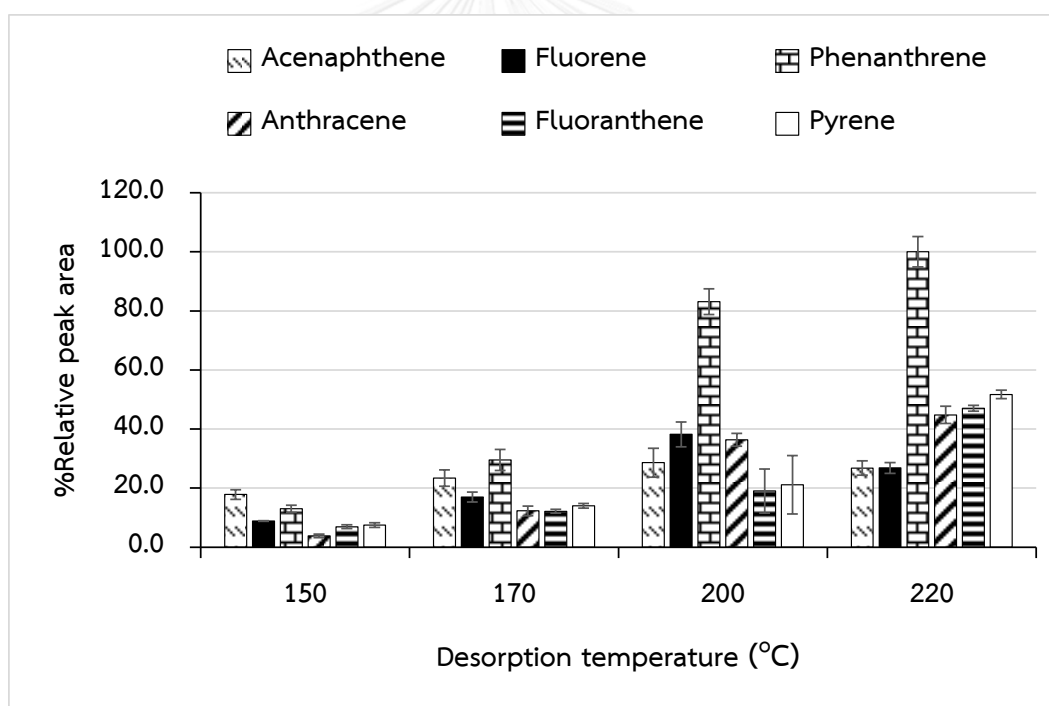
Figure 4.3 The desorption temperature profiles of PAHs. Extraction condition as follows: a spiked aqueous sample (100 µg/L, 10mL), salt addition (10%w/v NaCl), adsorption time of 30 min at 40°C, desorption time of 5 min.

4.2.4 Effect of desorption time

PAHs were desorbed from SPME fiber directly in the GC injection port by thermal desorption. Therefore, desorption time was also investigated at the time range of 1-5 min at 200°C (Figure 4.4). At 1 and 3 min, the small PAHs (2-3 rings) were completely desorbed from PAN fiber coating to GC. Nonetheless, fluoranthene and pyrene (4 rings) have a higher boiling point than 2-3 ring of PAHs. Hence, fluoranthene and pyrene could be more desorbed at 5 min. Consequently, desorption time of 5 min was selected.
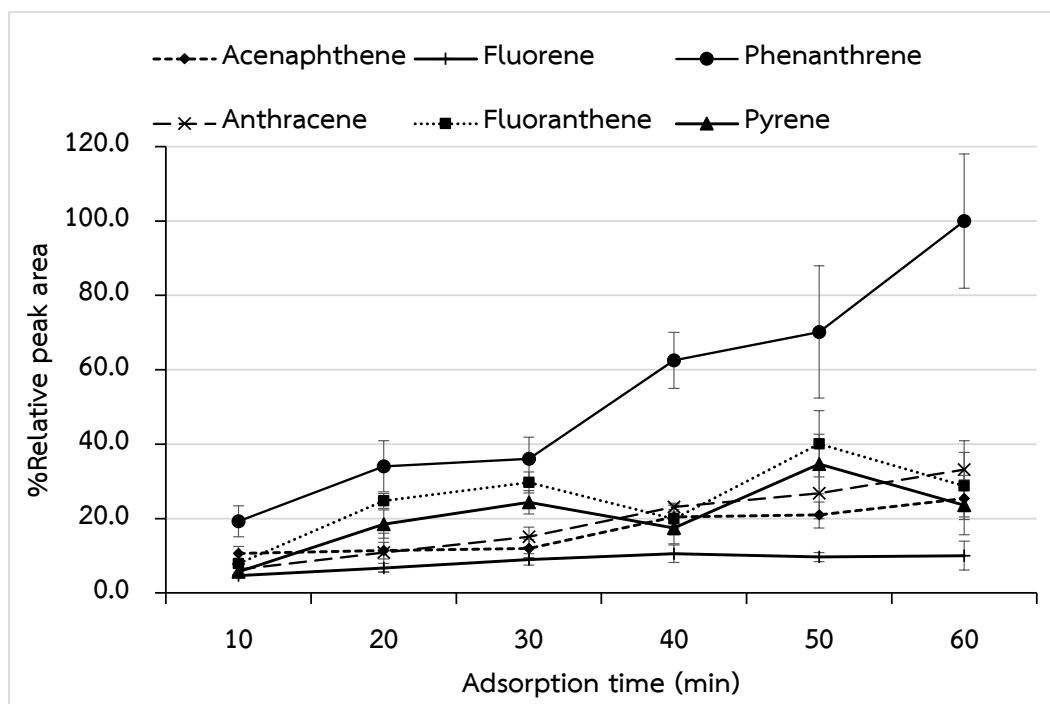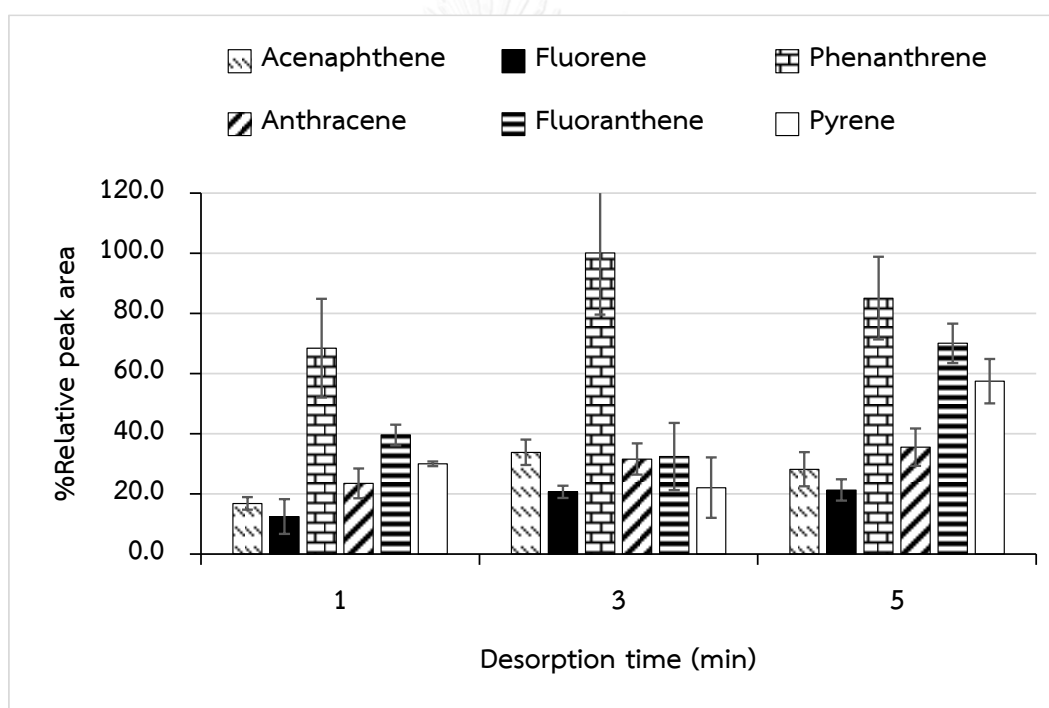

Figure 4.4 The desorption time profiles of PAHs. Extraction condition as follows: a spiked aqueous sample (100 µg/L, 10mL), salt addition (10%w/v NaCl), adsorption time of 30 min at 40°C, desorption temperature of 200°C.

4.2.5 Effect of salt

In order to decrease the solubility of organic compounds in aqueous phase, some salts were added into the aqueous sample to increase an ionic strength of aqueous phase. Therefore, the number of PAHs (nonpolar analytes) in headspace can be enhanced. This effect leads to the improvement of extraction efficiency. The influence of salt addition was studied by varying concentration of sodium chloride (0, 5 and 10 %w/v NaCl) in water samples. The results were shown in Figure 4.5. The increase in extraction efficiency was observed by increasing the amount of NaCl. Therefore, 10%w/v of NaCl was added in water sample in further experiments.
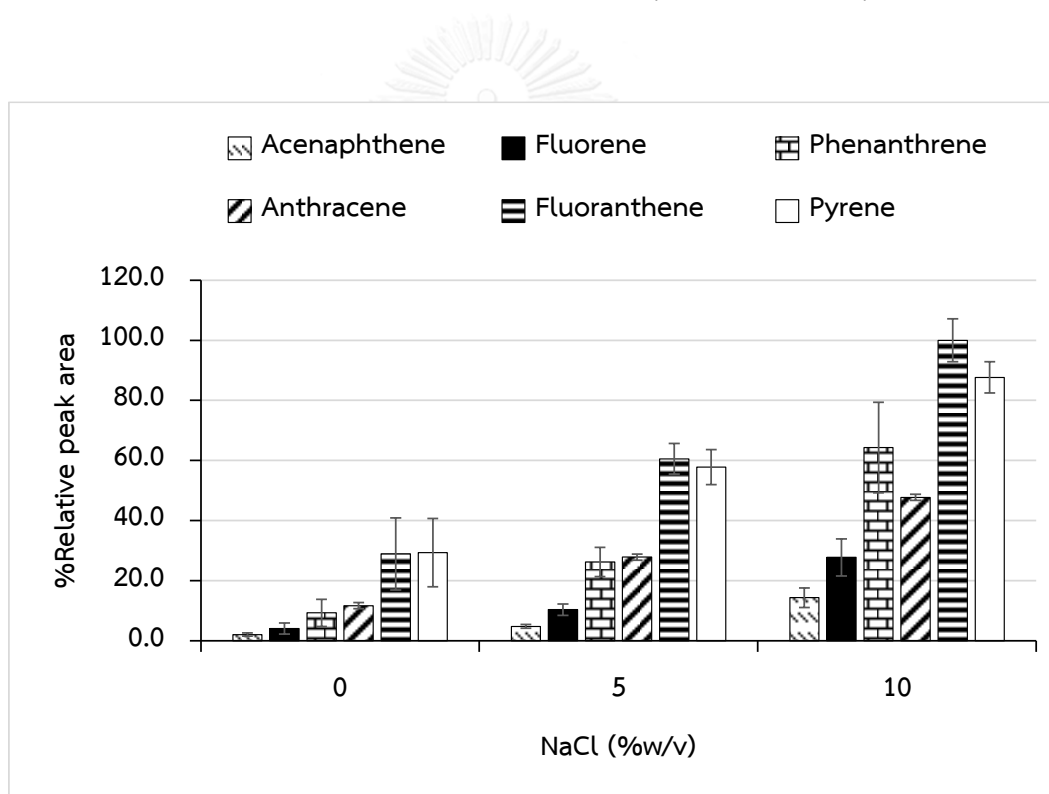
Figure 4.5 Effect of NaCl addition. Extraction condition as follows: a spiked aqueous sample (100 µg/L, 10mL), adsorption time of 30 min at 40°C, desorption time of 5 min at 200°C.

From the optimization study in 4.2.1 – 4.2.5, the optimum condition for extraction of PAHs in water using the electrospun PAN fibers as a SPME fiber coating was summarized in Table 4.2.

Table 4.2 The optimum condition for extraction of PAHs in water by using the electrospun 7-PAN fiber coating

Parameter	Condition
extraction time	30 min
extraction temperature	40°C
desorption temperature	200°C
desorption time	5 min
salt concentration	10 %w/v

4.3 Performance of electrospun PAN fibers in SPME fiber coating

The use of electrospun PAN fibers as SPME fiber coating in a homemade SPME unit was studied for determination of PAHs in water sample. Quantitative analysis of spiked water sample was performed using the optimum condition of SPME extraction in Table 4.2. Electrospun PAN nanofibers in SPME fiber coating fabricating from 5%, 7%, and 10% w/v of PAN were compared for the extraction efficiency of PAHs from water sample. Six PAHs which are acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene and pyrene were selected and determined in this study.

4.3.1 Calibration curve of PAHs

The calibration curve for determination of PAHs in water by electrospun PAN fibers as SPME fiber coating which fabricated from 5%, 7%, and 10% w/v of PAN are labelled as 5-PAN, 7-PAN and 10-PAN, respectively, was performed using an external standard method. The calibration curves were shown in FigurFigure 4.6-4.8. The linear ranges, correlation coefficients (R^2) and linear equations of each SPME fiber coating were reported in Table 4.3.

The calibration curve of PAHs by 5-PAN and 10-PAN SPME fibers showed a good linearity in the range of 5-75 µg/L with R^2 between 0.9697 and 0.9954 for 5-PAN and the range of 10-75 µg/L with R^2 between 0.8310 and 0.9787 for 10-PAN. The same linear range of 5-75 µg/L was also achieved for fluorine and phenanthrene by using 7-PAN SPME. But the other 4 PAHs (acenaphthene, anthracene, fluoranthene and pyrene) analyzed by 7-PAN SPME showed a good linearity in the range of 5-60 µg/L. However, 7-PAN SPME provide the best linear behavior in its linear range as excellent R^2 (between 0.9797 and 0.9956) was observed.

In addition, the slope value of the calibration curve can represent the sensitivity of the method. Among the studied SPME fibers, 7-PAN SPME fiber gave the highest sensitivity of all PAHs due to the morphology of the electrospun PAN fibers both size and fiber alignment. 10-PAN SPME fiber gave a low sensitivity and considering exclude on further studies. This indicated that the concentration of PAN for fiber fabrication has the impact on PAHs extraction via SPME technique.

Table 4.3 Linear equation and R^2 of calibration curve of PAHs by 5-PAN, 7-Pan and 10-PAN SPME fiber coating

Compound	5-PAN SPME fiber			7-PAN SPME fiber			10-PAN SPME fiber		
	LDR (µg/L)	R^2	Linear equation	LDR (µg/L)	R^2	Linear equation	LDR (µg/L)	R^2	Linear equation
Acenaphthene	5-75	0.9697	y = 0.3445x+5.5868	5-60	0.9956	y = 0.3503x+22.625	10-75	0.9191	y =0.2512x+0.9681
Fluorene	5-75	0.9774	y = 0.6366x+3.4047	5-75	0.9933	y = 0.9491+5.8864	10-75	0.831	y = 0.3261x+1.2931
Phenanthrene	5-75	0.9819	y = 1.4933x+12.724	5-75	0.9867	y = 2.5772+12.254	10-75	0.8942	y = 0.5096+8.0369
Anthracene	5-75	0.9833	y = 1.216x+23.35	5-60	0.9862	y = 2.4441+24.457	10-75	0.9787	y = 0.382x+14.492
Fluoranthene	5-75	0.9954	y = 2.2173x+32.496	5-60	0.9900	y = 4.2955+30.727	10-75	0.9151	y = 1.2117x+19.45
Pyrene	5-75	0.9851	y = 2.0800+37.182	5-60	0.9797	y = 4.1693+34.248	10-75	0.933	y = 1.2179x+21.508
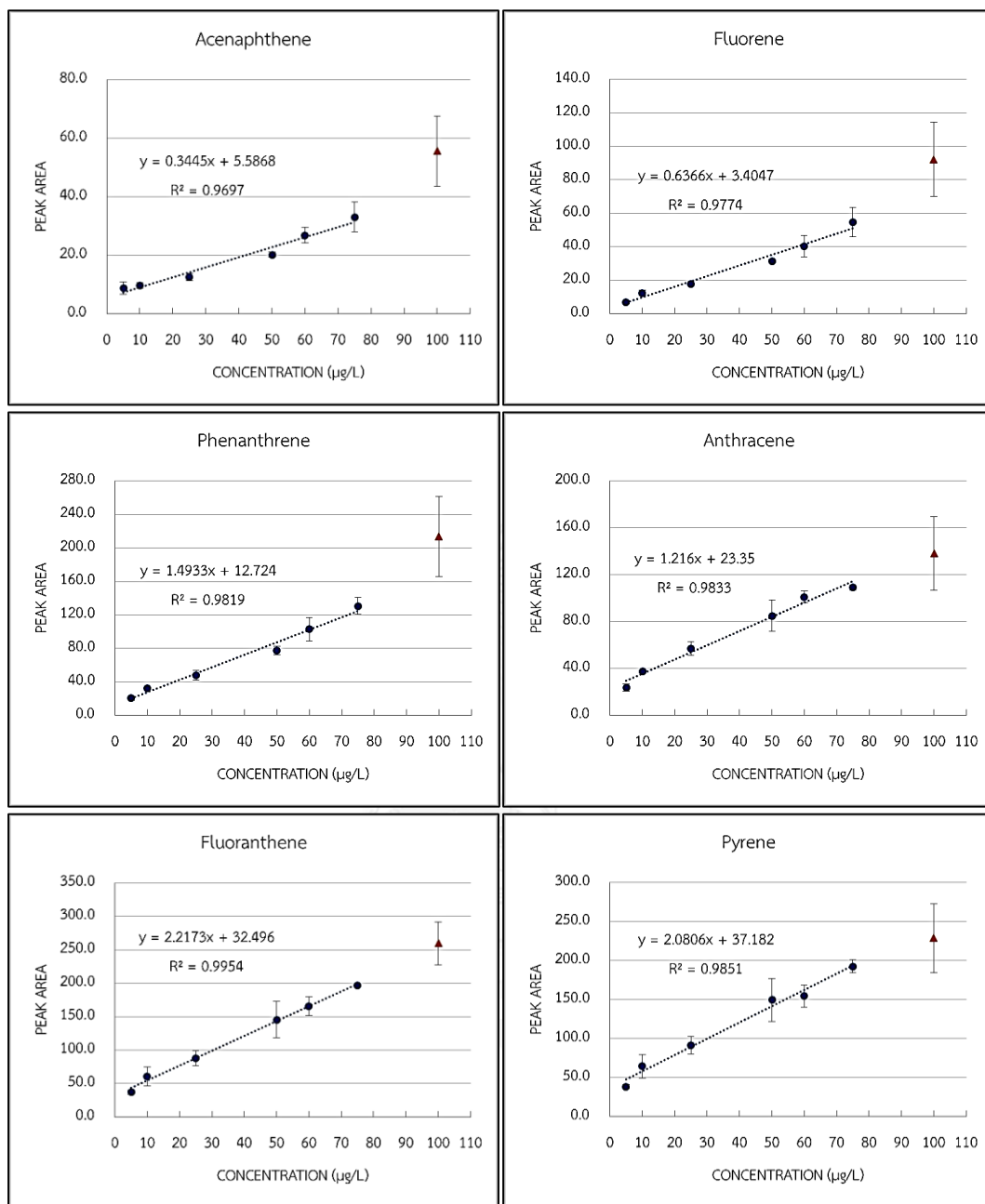
Figure 4.6 Calibration curve of PAHs by 5-PAN SPME fiber
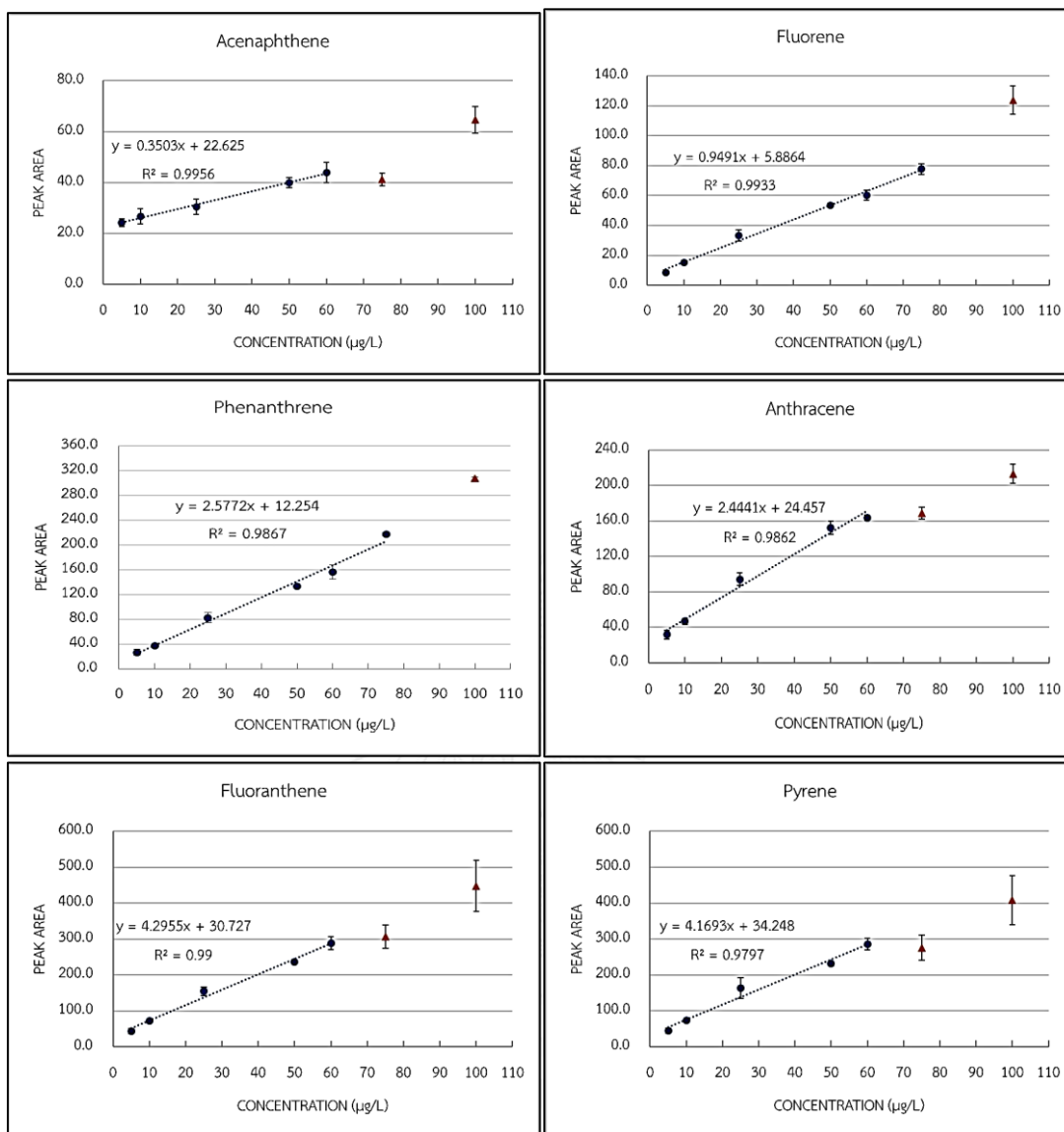
Figure 4.7 Calibration curve of PAHs by 7-PAN SPME fiber
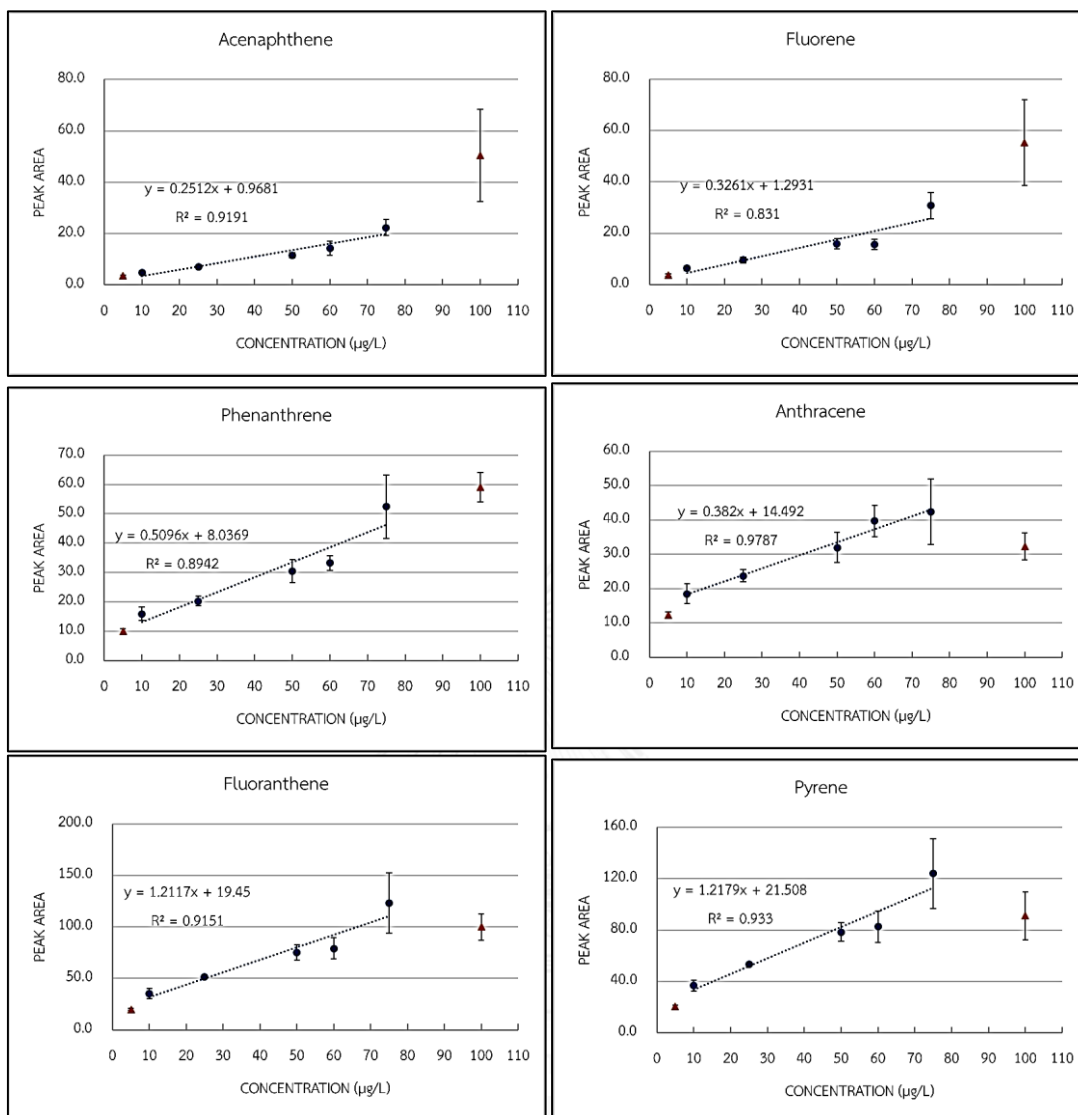
Figure 4.8 Calibration curve of PAHs by 10-PAN SPME fiber

4.3.2 Limit of detection and Limit of quantitation

Since 10-PAN gave a low sensitivity, only 5-PAN and 7-PAN were evaluated for limit of detection (LOD) and limit of quantitation (LOQ). Limit of detection was computed at signal to noise ratio (S/N) equal to 3 and limit of quantitation was computed at S/N equal to 10. The LODs and LOQs of six PAHs were summarized in Table 4.4.

Table 4.4 LODs and LOQs of the extraction of spiked water by 5-PAN and 7-PAN fiber coating.

Compound	5-PAN		7-PAN	
	LOD (µg/L)	LOQ (µg/L)	LOD (µg/L)	LOQ (µg/L)
Acenaphthene	0.5	4.0	0.9	4.0
Fluorene	0.5	3.0	0.6	3.0
Phenanthrene	0.4	0.6	0.4	0.8
Anthracene	0.4	0.7	0.5	0.6
Fluoranthene	0.1	0.4	0.1	0.4
Pyrene	0.1	0.4	0.1	0.4

4.3.3 Accuracy

The accuracy of 5-PAN and 7-PAN SPME fibers in homemade SPME unit was evaluated from the recovery of spiked water at 40 μg/L PAHs. The result was shown in Table 4.5. The acceptable range of recovery at μg/L level was 60 – 115 % by AOAC [39]. %Recovery of six PAHs using 5-PAN SPME fiber was in the range of 95.8-115.1 % indicating a good accuracy of the method. Moreover, the precision of 5-PAN SPME fiber was good (between 5.8% and 12.7%RSD). For 7-PAN SPME fiber, it also gave an acceptable range of %recovery (80.3%-108.6%) except acenaphthene that has only 41.7% of recovery. However, both 5-PAN and 7-PAN SPME fibers provided an acceptable accuracy to apply for extraction of PAHs in water sample by SPME.

Table 4.5 Percentage recoveries and RSD of the extraction of spiked water at 40 μg/L PAHs by 5% and 7% PAN fiber coating (n=3).

| Compound | 40 μg/L | | | |
| | 5%PAN | | 7%PAN | |
	%Recovery	%RSD	%Recovery	%RSD
Acenaphthene	103.9	12.6	41.7	13.7
Fluorene	99.6	12.7	108.6	7.3
Phenanthrene	115.1	5.3	105.5	4.8
Anthracene	99.0	9.5	80.3	7.4
Fluoranthene	108.4	5.8	101.4	4.5
Pyrene	95.8	7.7	93.8	6.9

4.3.4 Reproducibility of fiber production

The reproducibility was estimated by comparing the peak areas after extraction of spiked ultrapure water with 100 µg/L of six PAHs using three PAN SPME fibers which fabricated under the same condition (Figure 4.9). 7-PAN SPME fiber was selected for delegate of reproducibility test because in this polymer concentration, the electrospun fibers were facile fabricated and provide the good morphology fiber coating. The results show that the percentage of relative standard deviation (%RSD) values of reproducibility of three fibers were 2.4-7.4% (Table 4.6), leading to an acceptable reproducibility by AOAC (not more than 32%).

Table 4.6 %RSD of reproducibility of fiber production

Compound	Reproducibility of fiber production %RSD (n=3)
Acenaphthene	7.4
Fluorene	3.8
Phenanthrene	2.4
Anthracene	5.0
Fluoranthene	6.6
Pyrene	4.1
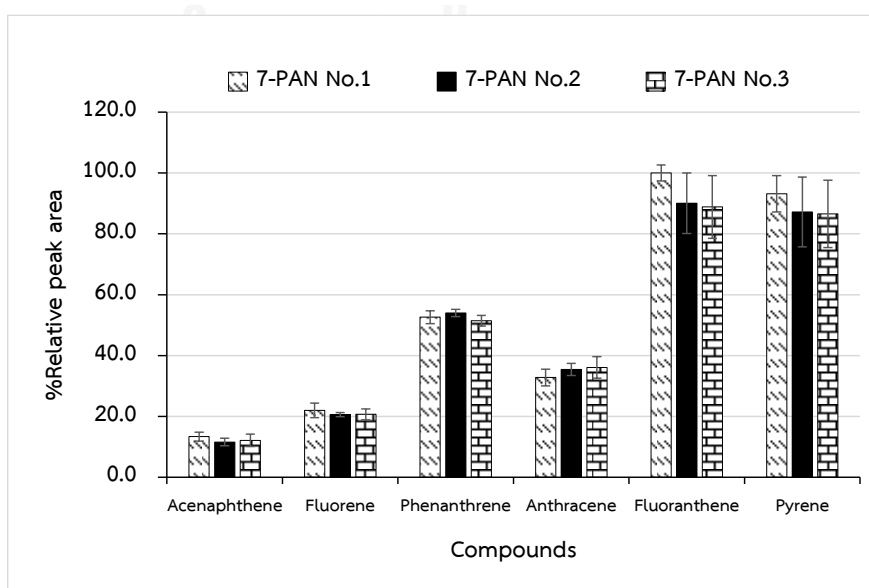
Figure 4.9 Reproducibility of fiber production

4.3.5 Durability

The durability of fiber coating is rather important factor of development of fiber coating. The fiber coating could damage at high temperature or drastic environment (acidic or alkaline). Nonetheless, the headspace mode can avoid that problem. In this work, durability of a fiber coating was studied by consecutive analysis of PAHs spiked into ultrapure water at 50 µg/L under optimum condition on single PAN fiber coating. In this study, only 7-PAN SPME fiber was evaluated since extraction performances of 5-PAN and 7-PAN SPME fibers were similar. The GC-FID responses of all analytes were shown in Figure 4.10. The electrospun PAN fiber coating was pretreated at 200°C for 20 min in GC injection port before used. The responses from GC-FID of all PAHs were increased after first analyses and contained stable responses. Until 20 analyses, the responses of all analytes were slightly increased. Therefore, a homemade SPME fibers can be reuse up to 20 times.
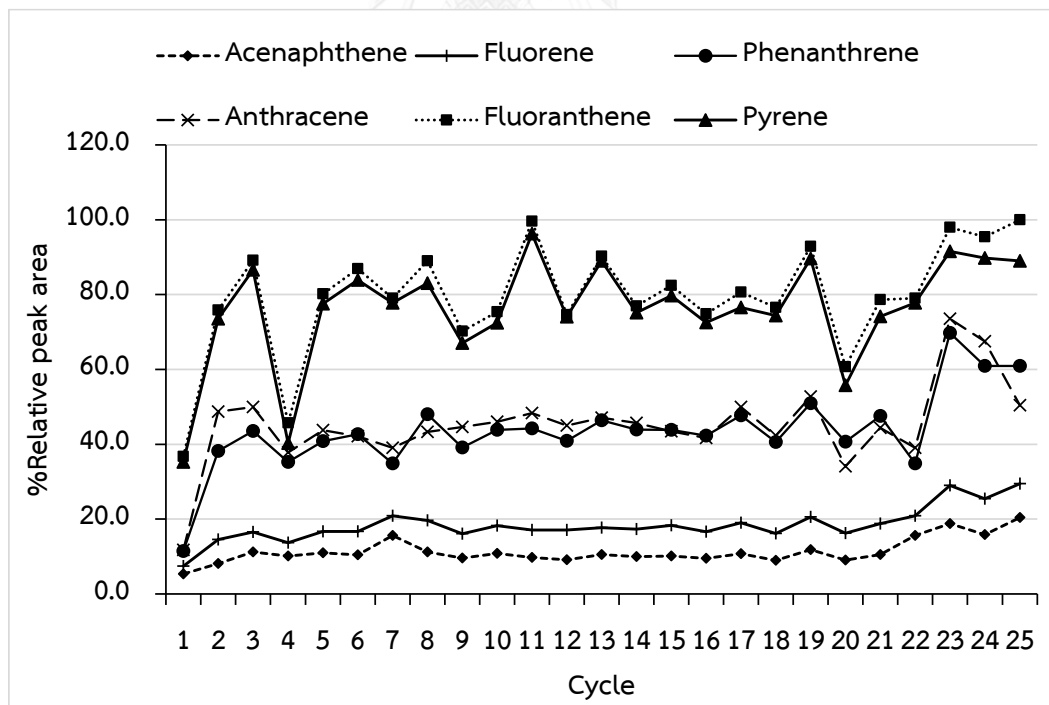
Figure 4.10 The GC-FID responses of PAHs by consecutive analysis on single 7-PAN SPME fiber.

4.4 Determination of PAHs in real water samples by PAN SPME fiber

Drinking water and pond water samples were extracted via headspace SPME technique under optimized extraction condition in this work. 5-PAN and 7-PAN SPME fiber were used in a homemade SPME unit. Moreover, the extraction efficiency of PAN SPME fiber was compared with commercial 100 µm PDMS SPME fiber. Since all PAHs were not detected in real water sample using all fiber coating. Therefore, the real water samples were spiked and %recoveries were calculated and compared. %Recoveries and %RSD of three analyses (n=3) of spiked drinking water at 60 µg/L PAHs were listed in Table 4.7. The extraction of spiked pond water was performed similar to drinking water and the data were shown in Table 4.8.

For spiked drinking water, 5-PAN SPME fiber provided an acceptable extraction result (%recovery of 99.6-111.8 and %RSD of 4.1-16.5) except anthracene with %recovery of 155.4. %recoveries of all PAHs using 7-PAN and commercial PDMS were comparable and in acceptable range (%recovery of 68.0-110.0 and %RSD of 0.9-22.4). The acceptable recovery at 10 µg/L level recommended by AOAC is 60%-115% [39]. For spiked pond water, similar to drinking water, %recovery of spiked pond water at 60 µg/L of PAHs were satisfactory. All three types of studied SPME fibers presented a comparable result.

Table 4.7 Percentage recoveries and RSD of the extraction of spiked drinking water at 60 µg/L PAHs.

Compound	5-PAN		7-PAN		PDMS	
	60 µg/L		60 µg/L		60 µg/L	
	%Recovery	%RSD	%Recovery	%RSD	%Recovery	%RSD
Acenaphthene	107.2	16.5	91.4	22.3	95.3	0.9
Fluorene	107.3	10.1	110.0	4.3	98.6	3.0
Phenanthrene	111.8	8.9	101.2	6.3	94.7	5.5
Anthracene	155.4	12.0	82.9	22.4	108.6	6.1
Fluoranthene	101.8	4.1	79.7	8.6	68.2	5.7
Pyrene	99.6	5.7	73.5	10.1	68.0	7.3

Table 4.8 Percentage recoveries and RSD of the extraction of spiked pond water at 60 µg/L PAHs.

Compound	5-PAN		7-PAN		PDMS	
	60 µg/L		60 µg/L		60 µg/L	
	%Recovery	%RSD	%Recovery	%RSD	%Recovery	%RSD
Acenaphthene	79.6	13.4	66.5	15.7	99.9	2.7
Fluorene	83.8	7.8	107.4	7.7	104.4	1.8
Phenanthrene	84.3	6.2	90.8	8.7	100.5	5.4
Anthracene	122.2	10.1	53.6	1.8	106.1	5.7
Fluoranthene	75.0	11.9	68.4	2.1	87.4	1.6
Pyrene	70.7	15.1	62.8	0.7	89.6	1.1

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The electrospun PAN nanofiber as fiber coating in SPME were successfully fabricated. The presence of nitrile group in PAN can form **π-π** interaction with aromatic compounds leading to good extraction efficiencies for PAHs. The fabrication of this work's fiber coating is simple, rapid inexpensive and reproducibility. The morphology of PAN SPME fiber was observed by SEM. When increasing the PAN concentration from 3 to 10 %w/v, the average diameter of PAN fibers was increased from 165 nm to 464 nm due to the increase in viscosity of PAN solution. The fiber coating's surface was a porous network with high surface area. But the alignment of electrospun PAN SPME fiber was improved when increased the PAN concentration leading to less extraction efficiency. Therefore, 5-PAN, 7-PAN and 10-PAN SPME fibers were chosen as a SPME fiber coating in a homemade SPME unit because the fine and smooth fibers were produced. Five parameters affecting extraction efficiency were studied. The optimal condition was extraction time of 30 min and extraction temperature of 40°C. NaCl was added 10% w/v. Desorption time and desorption temperature were optimized at 5 min and 200°C, respectively. The %recovery of spiked water at 40 µg/L PAHs at optimum conditions were in range of 95.8-115.1 % with %RSD less than 12.7% for 5-PAN SPME fiber and 80.3-108.6% with %RSD less than 7.4% for 7-PAN SPME fiber that were acceptable. The LODs of 5-PAN and 7-PAN SPME fibers were 0.08–0.5 µg/L and 0.1–0.5 µg/L, respectively. The linear range of 6 PAHs by 5-PAN and 7-PAN SPME fiber show a good linearity in the range of 5-75 µg/L with R^2 between 0.9697 and 0.9954 for 5-PAN and the range of 5-75 µg/L with R^2 between 0.9797 and 0.9956 for 7-PAN. The reproducibility of PAN SPME fiber production was estimated by comparing the peak areas after extraction of spiked PAHs in ultrapure water. The results show that %RSD values of reproducibility of three fibers were 2.4-7.4%, leading to an acceptable reproducibility by AOAC. Moreover, homemade SPME fibers can reuse up to 20 times. Finally, the electrospun PAN nanofibers as fiber

coating in SPME were applied to extract 6 PAHs which are acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and, pyrene in trace level (60 µg/L) from real water samples. The %recovery of extraction of PAHs ranged from 53.6–155.4 %.

5.2 Suggestion of future work

The electrospun PAN SPME fiber were a good material for extraction of PAHs. However, the selectivity between PAN SPME fiber and PAHs could be improved by adding carbon nanotubes that could interact with various forces e.g. π-π interaction and electrostatic force. Moreover, this material could be applied for extraction of other analytes with specified of the sorbent properties leading to improving the good extraction efficiency.

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APPENDIX

Table A.1 Physical and chemical properties of 8 types of PAHs in the present study

Compound name	Molecular weight (g/mol)	Boiling point (ºC)	Solubility in water (mg/L)	Vapor pressure (mmHg)
Acenaphthene	154.2	297	3.4	1.6×10^{-3}
Fluorene	166.2	295	1.9	7.1×10^{-4}
Phenanthrene	178.2	340	1-1.3	9.6×10^{-4}
Anthracene	178.2	339.9	0.05-0.07	1.7×10^{-5}
Fluoranthene	202.3	384	0.26	5.0×10^{-6}
Pyrene	202.3	404	0.14	2.5×10^{-6}

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Table A.2 Linear equation and R^2 of Calibration curve of PAHs by PDMS fiber coating

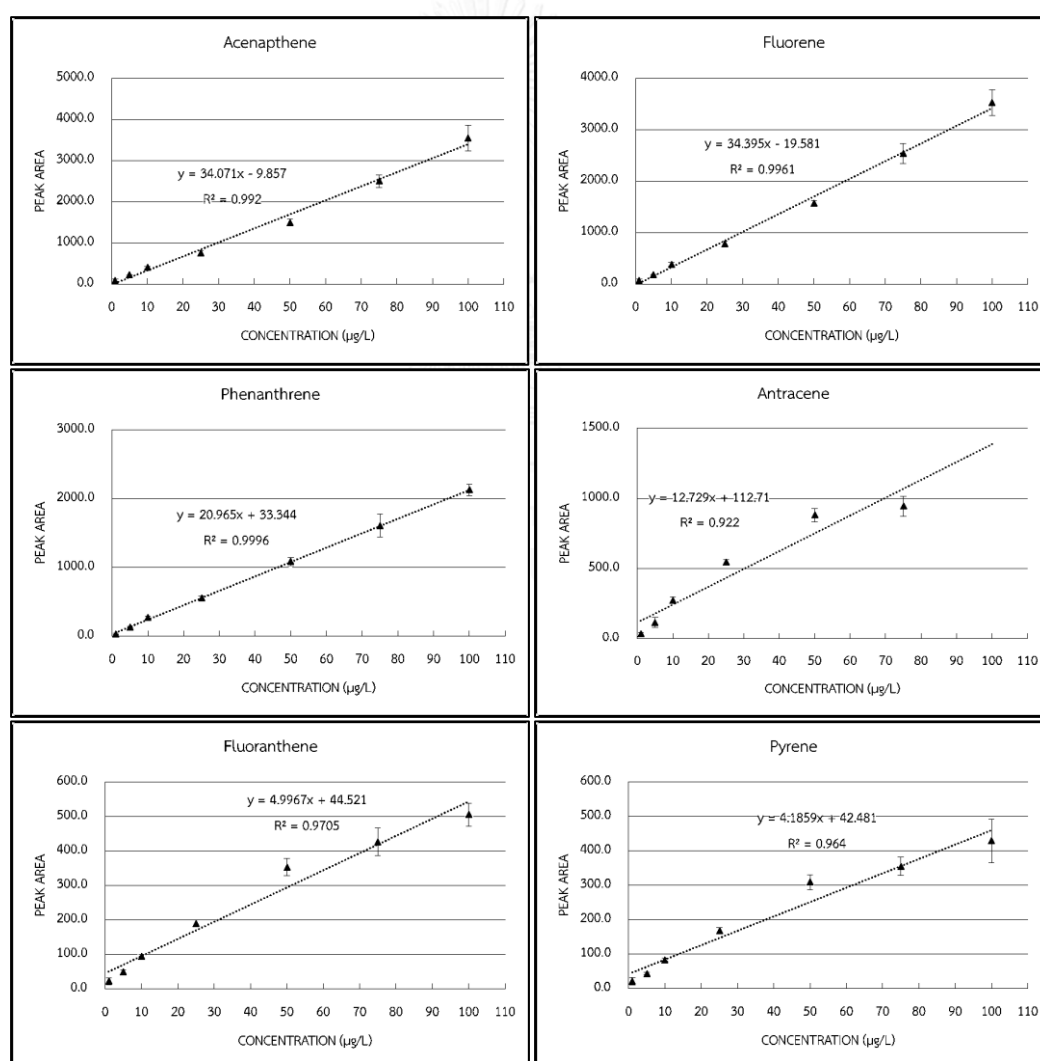| Compound	LDR (µg/L)	R^2	Linear equation
Acenaphthene	1-100	0.9920	y =34.071x-9.857
Fluorene	1-100	0.9961	y = 34.395x-19.581
Phenanthrene	1-100	0.9996	y = 20.965x+33.344
Anthracene	1-75	0.9220	y = 12.729x+112.71
Fluoranthene	1-100	0.9705	y = 4.9967x+44.521
Pyrene	1-100	0.9330	y = 4.1859x+42.481

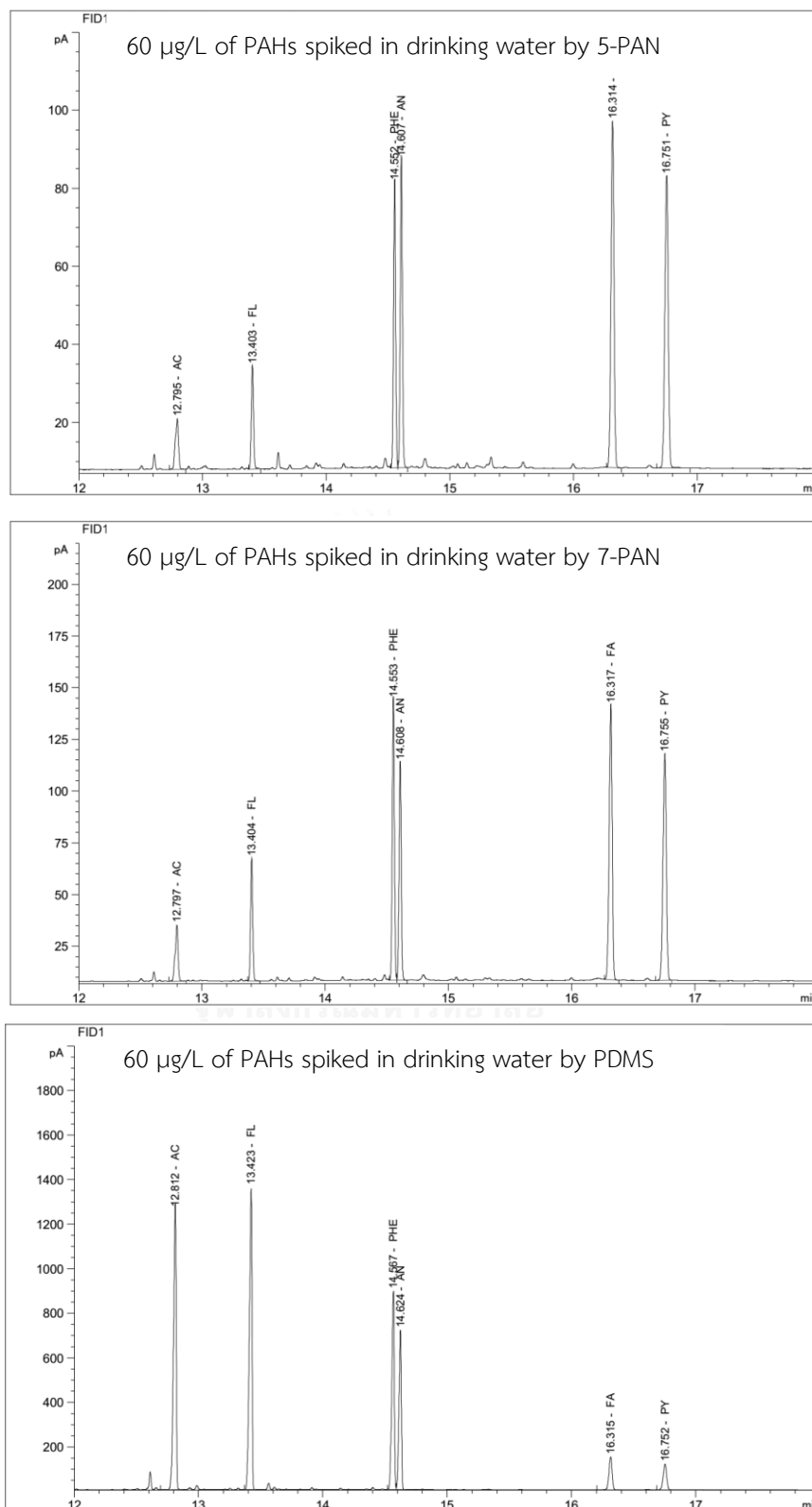**Figure A.1** Calibration curve of PAHs by PDMS fiber coating

Figure A.2 Chromatogram of PAHs from the extraction of 60 µg/L spiked drinking
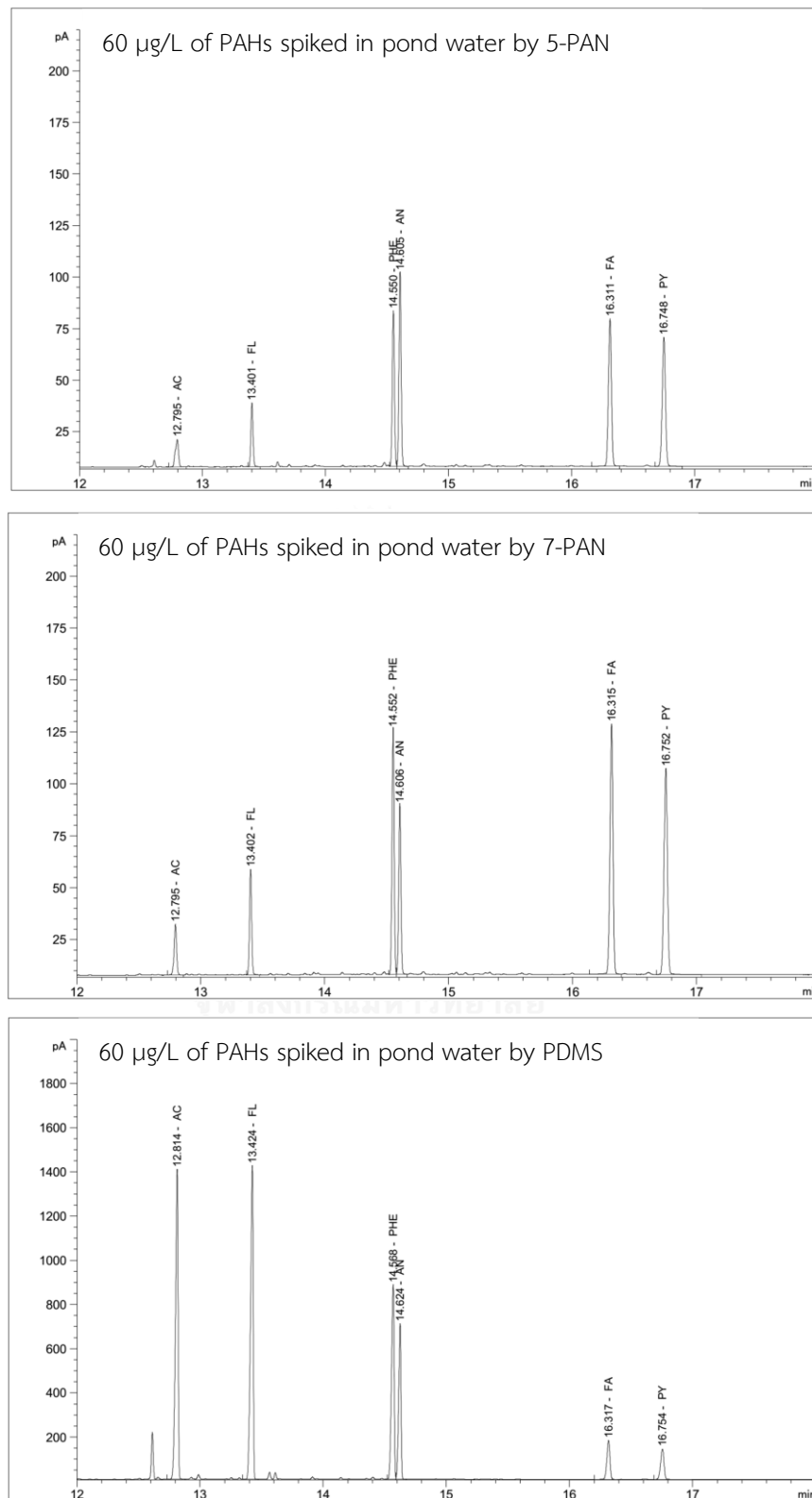
water by 5-PAN, 7-PAN and PDMS

Figure A.3 Chromatogram of PAHs from the extraction of 60 µg/L spiked pond water by 5-PAN, 7-PAN and PDMS

VITA

Miss Thichakorn Sungoradee was born on January 17, 1992 in Prachinburi province, Thailand. She graduated from Kasetsart University in March 2014 and hold a Bachelor degree from the faculty of Science in Chemistry field with second class honors. Then, she applied study for a master's degree in analytical chemistry, faculty of Science at Chulalongkorn University. She has been a graduated student under Asst. Prof. Dr. Puttaruksa Varanusupakul in Chromatography and Separation Research Unit (ChSRU). She finished her Master's degree of Science in 2017.

Poster presentation and proceeding

"Electrospun polyacrylonitrile nanofibers as fiber coating in solid phase microextraction" Thichakorn Sungoradee and Puttaruksa Varanusupakul. Poster presentation and proceeding, Pure and Applied Chemistry International Conference 2017 (PACCON 2017), Centra Government Complex Hotel & Convention Centre, Bangkok, Thailand, February 2-3, 2017.