

CHAPTER IV

RESULTS AND DISCUSSION

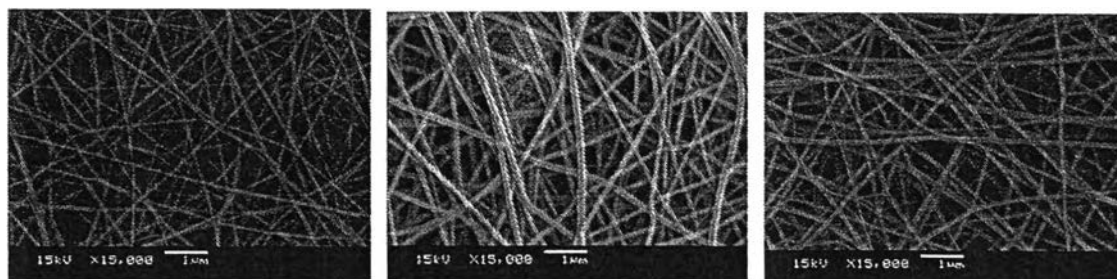
This chapter is divided into four major sections. First, the morphology and characterization of the electrospun polymer fibers was examined. Then, the optimization of coating DNPH onto electrospun polymer fibers was studied. Next, the extraction of aldehydes in water using DNPH-coated electrospun fibrous polymer membranes was optimized. Finally, the application of DNPH-coated polymer membrane in determination of aldehydes in drinking water was evaluated.

4.1 Morphology and characterization of the electrospun polymer fibers

4.1.1 Morphology of electrospun polymer fibers

The electrospun fibers of nylon6, polystyrene (PS) and polyacrylonitrile (PAN) prepared by electrospinning process were shown in Figure 4.1 and the fiber diameters were summarized in Table 4.1. All polymer fibers were uniform and the average diameters were 91-142 nm. Among three studied polymer fibers, the nylon6 fibers were smallest and PS fibers were largest. After coating the electrospun polymer fibers with DNPH, the fibers were still uniformed as shown in Figure 4.2 but the diameter of fibers were larger (Table 4.1). The fibers were larger because DNPH was coated onto the fibers.





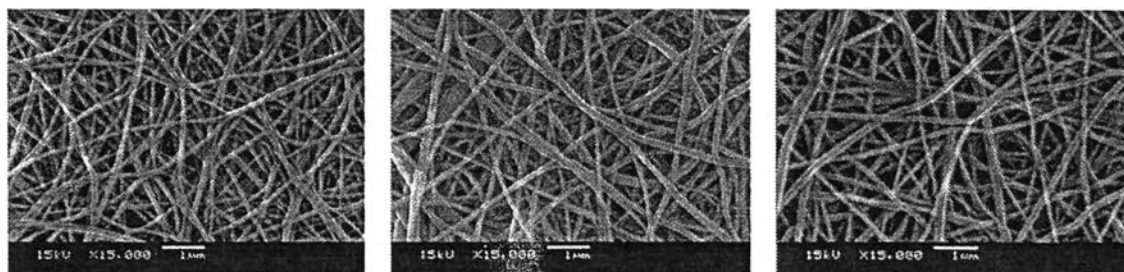
(a) Nylon6

(b) PS

(c) PAN

Figure 4.1 Scanning electron microscope (SEM) images of polymer fibers:

(a) Nylon6, (b) Polystyrene (PS) and (c) Polyacrylonitrile (PAN)



(a) Nylon6

(b) PS

(c) PAN

Figure 4.2 Scanning electron microscope (SEM) images of DNPH-coated polymer

fibers: (a) Nylon6, (b) Polystyrene (PS) and (c) Polyacrylonitrile (PAN)

Table 4.1 Average diameter of polymer fibers and DNPH-coated polymer fibers.

Polymer	Average diameter of fibers (nm) (n=30)	
	Polymer fibers	DNPH-coated polymer fibers
Nylon6	91±11	127±25
PS	142±20	174±30
PAN	129±19	182±22

4.1.2 Thermogravimetric analysis (TGA)

The TGA of electrospun polymer fibers were examined to determine and characterize the electrospun polymer fibers and DNPH-coated electrospun polymer fibers.

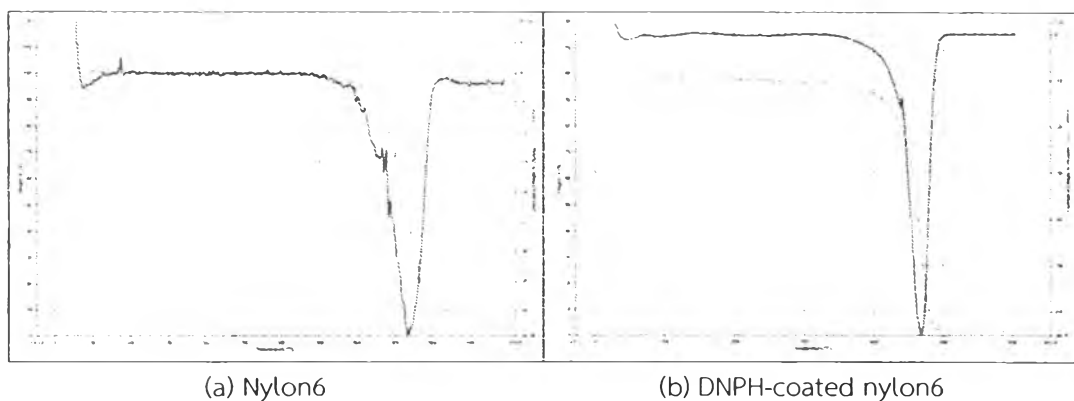


Figure 4.3 Thermogravimetric analysis (TGA) curves of (a) electrospun nylon6 fibers and (b) DNPH-coated nylon6 fibers.

TGA curves of the thermal decomposition of nylon6 are shown in Figure 4.3. The nylon6 fibers and DNPH-coated nylon6 fibers had the similar TGA curves in which nylon6 was decomposed in range 400-500 °C. However, the decomposition of DNPH was not clear observed for DNPH-coated nylon6 fibers (Figure 4.3 (b)). This might due to a low content of DNPH compared with the amount of polymer. Similar observations were perceived for electrospun PS and PAN fibers as shown in Figure 4.4 and Figure 4.5.

Nevertheless, the present of DNPH on polymer fibers were noticed from the yellow color of DNPH on the sorbent after DNPH coating. Further examination was done by eluting the DNPH-coated polymer fibrous membrane with acetonitrile and analyzed by HPLC. The DNPH peak was observed in the chromatogram and confirmed the coating of DNPH on the polymer fibers.



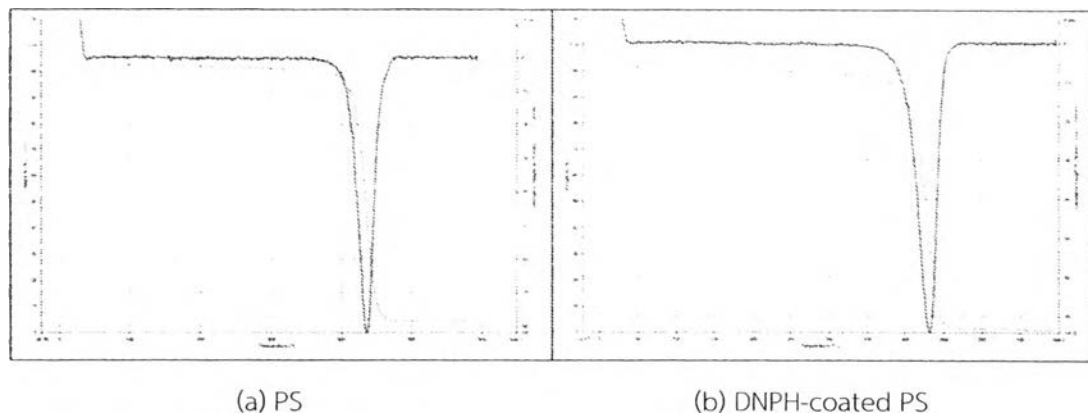


Figure 4.4 Thermogravimetric analysis (TGA) curves of (a) electrospun polystyrene (PS) fibers and (b) DNP-coated PS fibers.

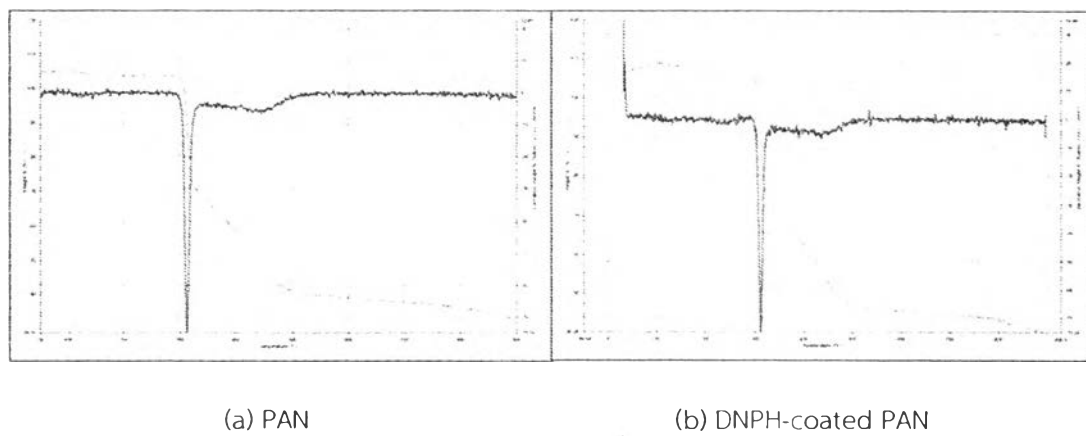


Figure 4.5 Thermogravimetric analysis (TGA) curves of (a) electrospun polyacrylonitrile (PAN) fibers and (b) DNP-coated PAN fibers.



4.2 Preparation of DNPH-coated membrane

Three parameters were optimized during DNPH coating on the polymer fibrous membrane: the solvent of DNPH solution, DNPH concentration and coating rate. Electrospun nylon6 fibers were used for all optimizations.

4.2.1 DNPH solvents

Several solvent systems were reported for preparation of DNPH solutions [15, 20]. Two solvent systems were compared in the experiment, acetonitrile and a mixture of water with acetonitrile (water-ACN). To ensure the result, concentration of DNPH solutions between 100 and 500 mg/L were compared. From Figure 4.6, peak areas of DNPH eluted from the sorbent coated with DNPH in water-ACN were higher than those of DNPH in acetonitrile. Thus, DNPH in water-ACN was coated on electrospun nylon6 fibers better than DNPH in acetonitrile. The degree of the sorbent "affinity" for the sorbate determines its distribution between the solid and liquid phases. In the other word, the affinity of DNPH on the polymer fibers involved the distribution of DNPH between the polymer fibers and DNPH solution. The DNPH dissolved in ACN better than in water (DNPH, ACN and water have the dipole moment of 7.06 D, 3.92 D and 1.85 D respectively) thus DNPH don't like to stay in water-ACN solution, hence, it can be adsorbed on polymer fibers better than DNPH in ACN. Therefore, the DNPH solution was prepared in water-ACN solution for the rest of this research.



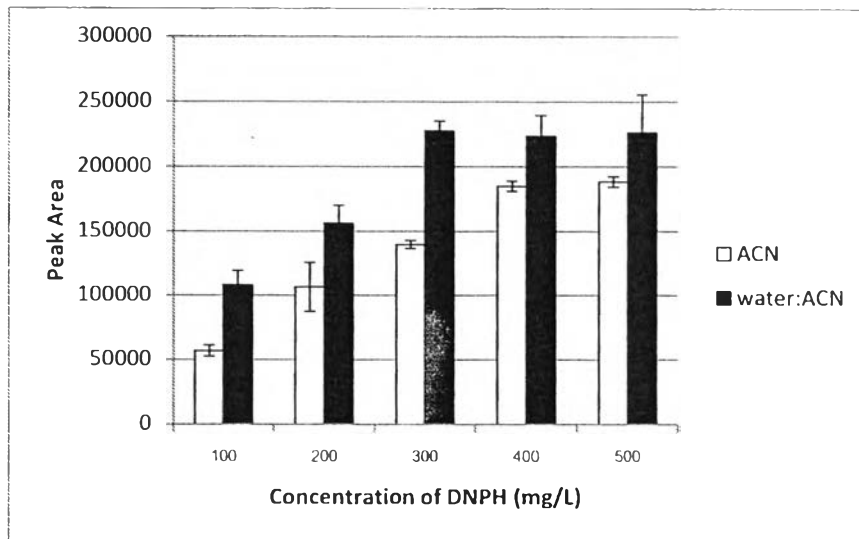


Figure 4.6 Peak area of DNPH eluted from the sorbent coating with DNPH in acetonitrile (ACN) and DNPH in the mixture of water with acetonitrile (water-ACN).



4.2.2 DNPH concentration

The concentration of the DNPH solution was optimized to ensure the full loading of DNPH onto polymer fibers. The concentrations of DNPH were varied to 100, 200, 300, 400 and 500 mg/L. From Figure 4.7, the amount of DNPH coating on the polymer fibers was increased when increasing the DNPH concentration. The highest peak area was obtained at 300 mg/L of DNPH, and continued constant when higher DNPH concentrations were used. At higher concentration, there was more amount of DNPH in the solution; therefore, there was more potency that DNPH will adsorb onto the sorbent. However, with a certain concentration, the sorbent became saturate with the DNPH. Even though more DNPH was added, DNPH cannot adsorb on the sorbent and therefore, the peak area was not increased any higher. Therefore, 300 mg/L of DNPH solution was used for coating DNPH on the polymer fibers.

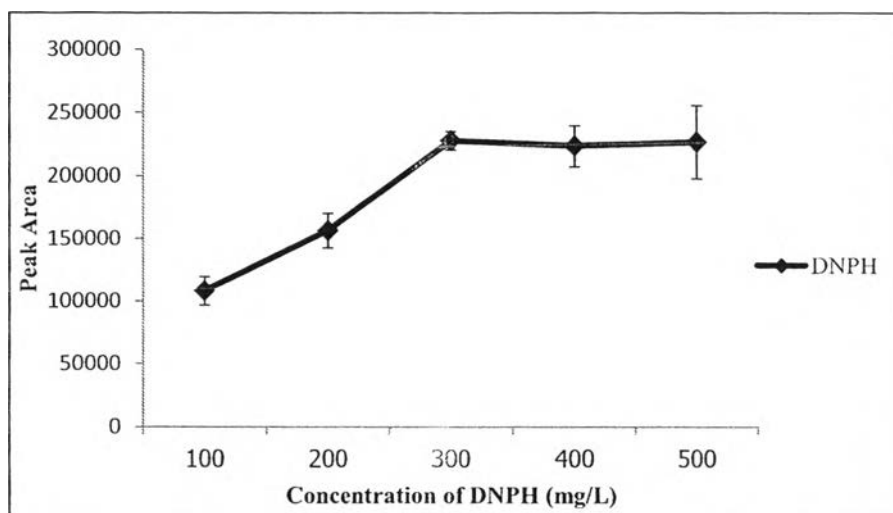


Figure 4.7 Effect of DNPH concentration on DNPH coating.

4.2.3 DNPH coating rate

The flow rate of coating DNPH onto the nylon6 sorbent was studied. The sorbent was coated with 3 mL of 300 mg/L of DNPH solution at coating rate of 60, 75, 100, 150 and 300 $\mu\text{L}/\text{min}$. From Figure 4.8, coating DNPH at high rate (>100 $\mu\text{L}/\text{min}$) was lower the efficiency of coating DNPH on the sorbent. At 100 $\mu\text{L}/\text{min}$, the peak area of DNPH was observed similar to those at low flow rates (60 and 75 $\mu\text{L}/\text{min}$). Therefore, 100 $\mu\text{L}/\text{min}$ was selected as the most suitable flow rate of coating since it offered a fast coating with high coating efficiency.

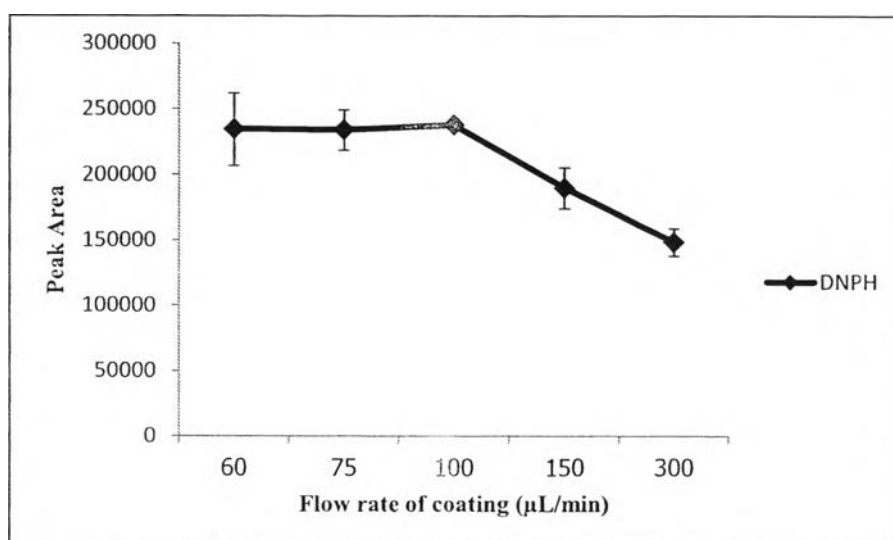


Figure 4.8 Effect of coating rate.

4.2.4 Efficiency of DNPH coating on electrospun polymer fibers

The optimized DNPH coating conditions were 3 mL of 300 mg/L DNPH in water-ACN solution and coating the membrane with the rate of 100 $\mu\text{L}/\text{min}$. As a result in Table 4.2, the efficiencies of DNPH coating on all electrospun polymer fibers (nylon6, PS and PAN) were not different. The peak areas were insignificantly different when statistically testing by t-test (ANOVA). Therefore, this optimized DNPH coating conditions were selected to apply with all three types of sorbents. Hence, the interaction between DNPH and sorbent was physisorption caused by weak van der waals force.

Table 4.2 Comparison of different sorbents in the DNPH coating.

Types of electrospun polymer fibers	Peak area			mean	SD
	Trial 1	Trial 2	Trial 3		
nylon 6	219129	231543	232425	227699	7435
PS	195738	214256	235463	215152	19878
PAN	209638	237542	215487	220889	14715

4.3 Extraction of aldehydes by DNPH-coated polymer fibers

In this section, 10 mL of aldehydes solution were analyzed. The aldehydes solution contained 10 $\mu\text{g}/\text{L}$ of formaldehyde, acetaldehyde, propanal, butanal and hexanal.

4.3.1 Sample flow rate

As mass transfer is a flow rate dependent process, the flow rate of sample solution was varied to determine if it had any effect on the extraction efficiency. Flow rates of extraction were varied between 0.33 and 2.00 mL/min. As shown in Figure 4.9, all three DNPH-coated electrospun polymer fibers had the same trend of effect. The amounts of aldehydes extract were not different at the sample flow rate between 0.33 and 1.00 mL/min. The amount of aldehydes-DNPH started to decrease at a sample flow rate of 2.00 mL/min, and hence, the aldehydes-DNPH were not derivatized and adsorbed on the sorbent completely. Thus, the sample



flow rate of 1.00 mL/min was selected for the extraction as the high extraction efficiency and short extraction time were achieved.

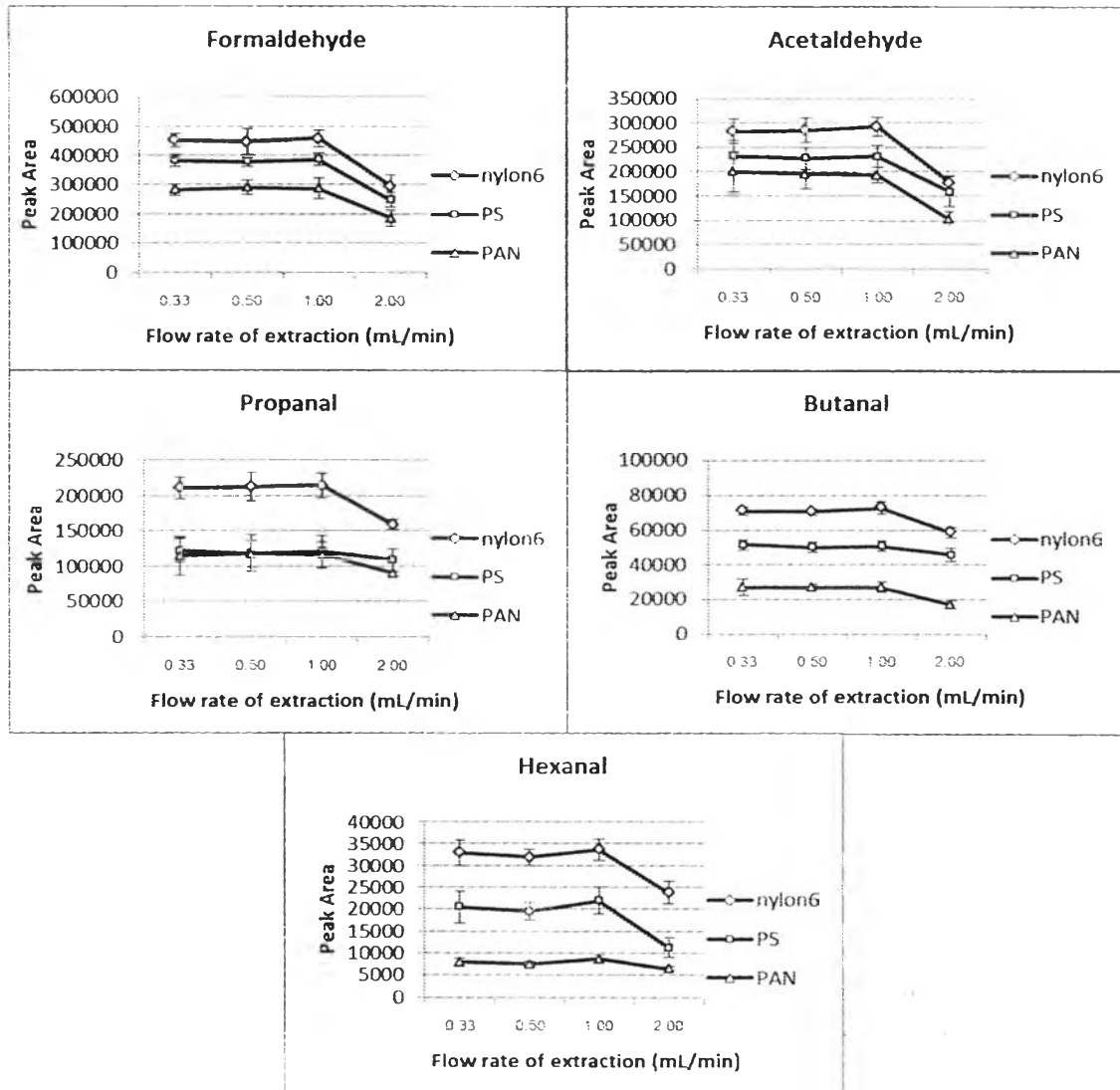


Figure 4.9 Effect of sample flow rate for extraction.

4.3.2 Desorption solvent

The analytes were desorbed in a suitable desorption solvent after extraction. The desorption solvents that were selected for the experiment are acetonitrile, methanol and hexane. Factors such as analyte solubility, solvent polarity, reactivity of solvents with the derivatizing agent affect the elution process. Since the aldehydes-DNPH derivatives were polar, polar solvents such as acetonitrile and methanol would have higher elution strength than non-polar solvent such as hexane. Therefore, solvent that has polarity is similar to the analytes, it can desorb analytes is the best according to the principle of like dissolves like. Figure 4.10 confirmed that acetonitrile was the best solvent in eluting aldehydes-DNPH derivatives. High desorption of all aldehydes-DNPH derivatives from nylon6, PS and PAN sorbents were achieved. Thus, acetonitrile was chosen as the elution solvent.

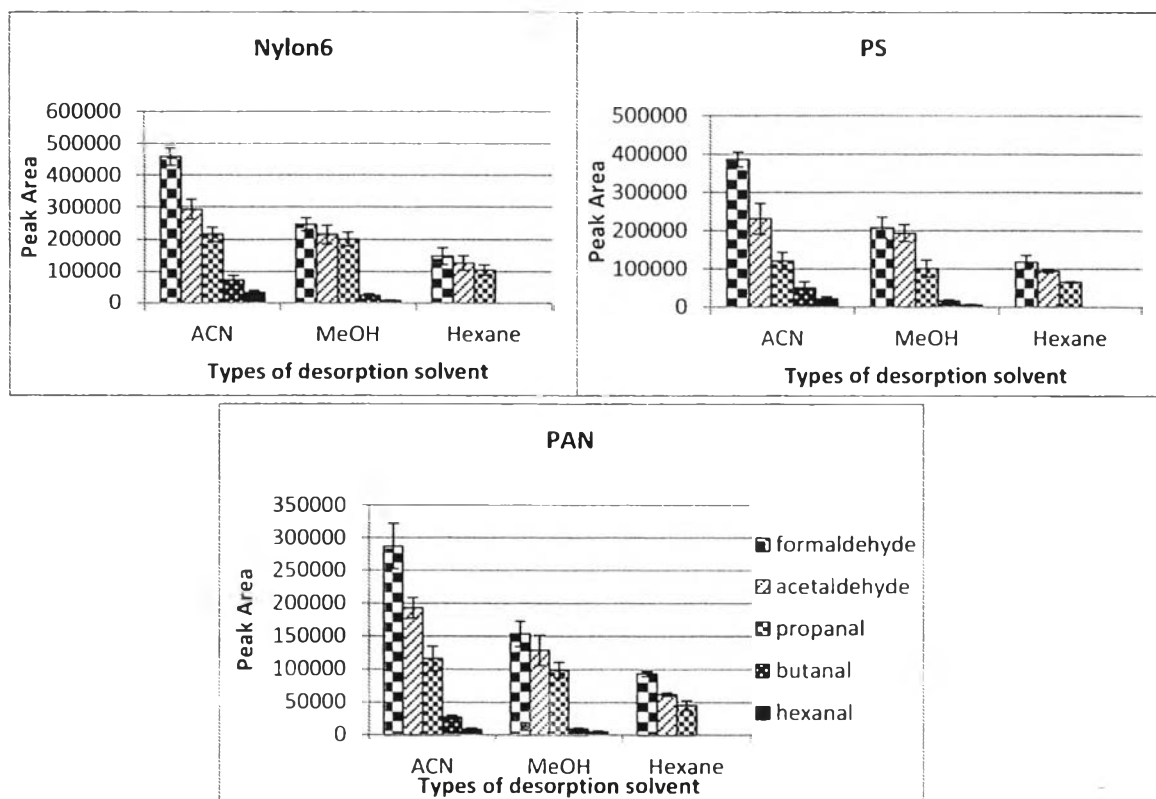


Figure 4.10 Comparison of different desorption solvents.

4.3.3 Desorption volume

The volume of acetonitrile as desorption solvent was studied to maximize extraction efficiency. Volume of desorption solvent was varied in the range of 100-300 μL . From Figure 4.11, volume of acetonitrile more than 100 μL caused a decrease in the peak area for all aldehydes and polymer fibers. This can refer that a 100 μL of acetonitrile is sufficient to elute the aldehydes-DNPH derivatives from the sorbent and more use of acetonitrile will result in a dilution of the analytes in the extract. In addition, the volume of the extract eluting with acetonitrile less than was difficult to collect and led to poor precision of the analysis. Therefore, 100 μL of acetonitrile was applied for the elution of aldehydes-DNPH from the polymer sorbent. Although, the standard deviation (SD) of peak area values at 100 μL were more than the other volume but it was the highest extraction efficiency.

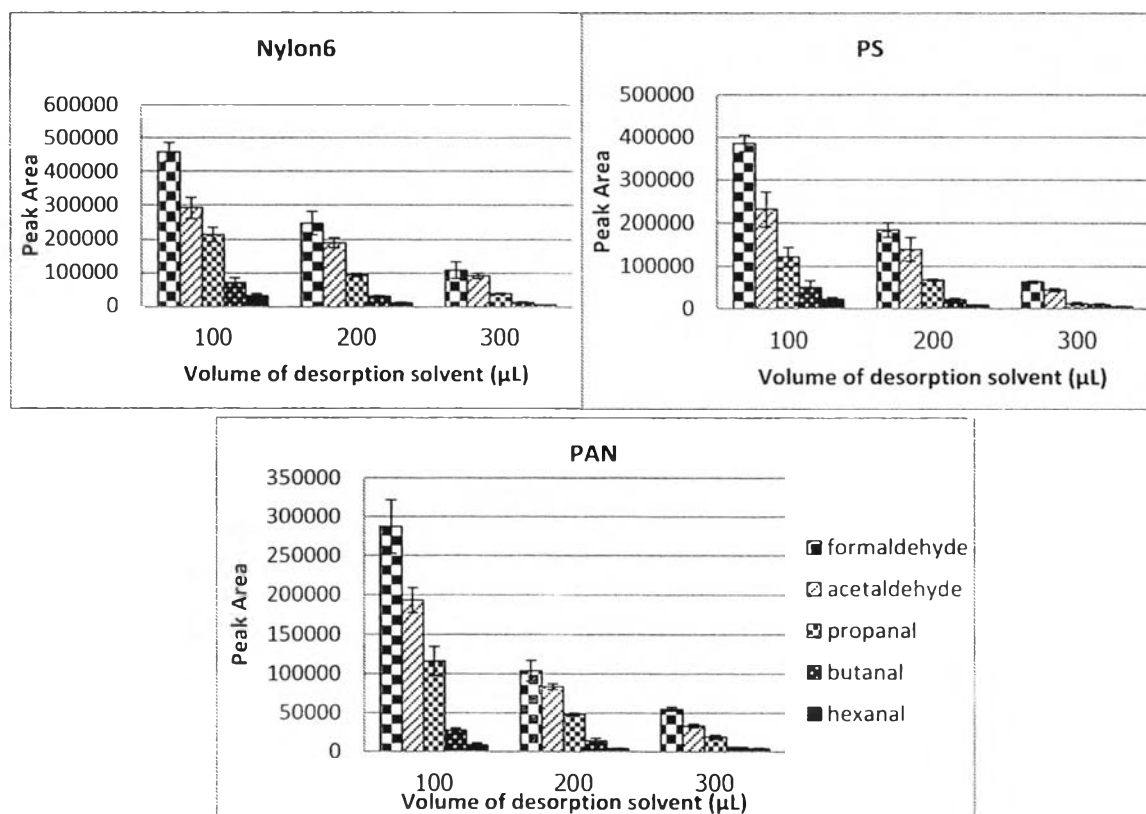


Figure 4.11 Effect of desorption volume.

Table 4.3 Mass of analytes in different desorption volume

Sorbents	Analytes	Mass of analytes at different desorption volume (ng)		
		100 μ L	200 μ L	300 μ L
Nylon6	formaldehyde	86.1	80.8	82.0
	acetaldehyde	96.3	118.5	93.0
	propanal	82.2	76.4	55.8
	butanal	43.9	38.0	26.1
	hexanal	50.0	45.2	45.3
PS	formaldehyde	72.9	71.8	68.1
	acetaldehyde	76.4	71.8	67.3
	propanal	47.8	56.4	44.7
	butanal	30.5	25.8	22.7
	hexanal	40.5	38.0	42.9
PAN	formaldehyde	54.8	42.2	45.6
	acetaldehyde	63.8	56.0	54.2
	propanal	46.0	42.0	39.8
	butanal	16.2	16.8	10.8
	hexanal	20.3	24.2	32.0

In 10 mL of water sample, it had 100 ng of aldehydes.

When the mass of analytes in each desorption volume was calculated as shown in Table 4.3, similar amount of analytes was obtained. This implied that the extract analytes on the electrospun polymer fibers were complete desorbed. Thus, the least volume of desorption solvent should be selected as the most concentration of analytes would obtain and gave the high peak area for quantitation.



4.4 Effect of membrane material

The selection of a sorbent is important as it determines the selectivity of the analytes. In this study, the amount of SPE disk was used in the range of 4.0-6.0 mg of different sorbents such as nylon6, PS and PAN membrane. Extraction of spiked water with the concentration of 10 $\mu\text{g/L}$ aldehydes was performed. The DNPH coated on nylon6 showed better performance than the other sorbents as shown in Figure 4.12. The peak area of all aldehydes extracted by nylon6 sorbent was higher than those extracted by PS and PAN sorbents. This could be due to the moderate polarity of the nylon6 which could interact with the polar DNPH and aldehydes. The average recoveries of five aldehydes from extraction with DNPH-coated polymer membrane were 43.9-96.3% for nylon6, 30.5-76.5% for PS and 16.2-63.8% for PAN as shown in Table 4.4. The recovery of aldehydes in water using electrospun nylon6 fibers was satisfied except butanal and hexanal (accepted recovery is 60-115% at 10 ppb level based on AOAC Peer-Verified Methods Program). However, the recoveries of this research using electrospun nylon6 fibers for formaldehyde, acetaldehyde and propanal were comparable to other researches as shown in Table 4.5.

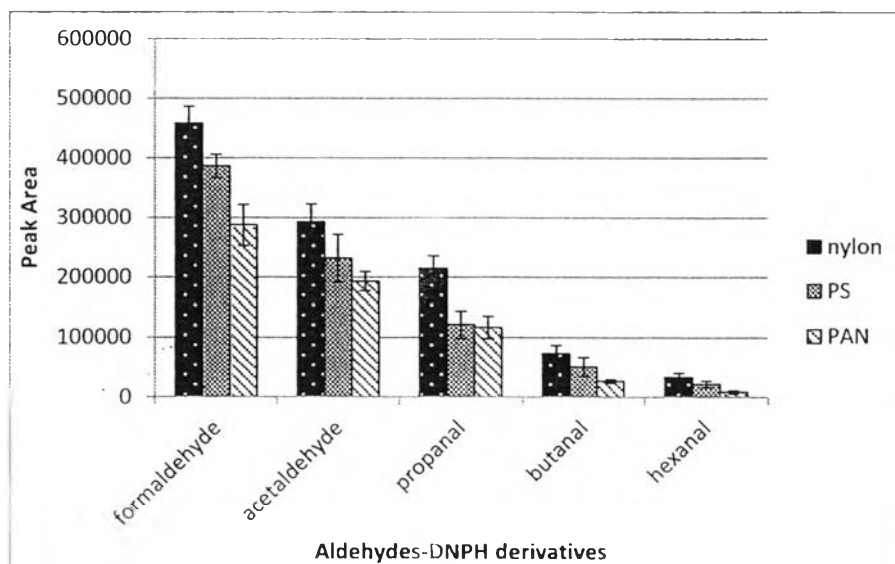


Figure 4.12 Effect of different sorbents in the extraction efficiency of SPE disk. The analytes were extracted from spiked water samples (10 $\mu\text{g/L}$) with DNPH-coated electrospun fibrous polymer membrane and eluted in 100 μL of acetonitrile

Table 4.4 Recovery percentage of derivatization and extraction of aldehydes (10 µg/L) in water by different sorbents.

Compound	Recovery (%)		
	Nylon6	PS	PAN
Formaldehyde	86.1±5.1	72.9±3.6	54.8±6.3
bentAcetaldehyde	96.3±9.9	76.5±13.1	63.8±5.2
Propanal	82.2±7.9	47.8±8.3	46.0±6.9
Butanal	43.9±8.6	30.5±9.8	16.2±1.8
Hexanal	50.0±9.1	35.1±6.8	18.0±3.1

Table 4.5 Comparison of aldehydes recovery from other research.

Sorbents	Matrix	Recovery (%)				
		Formal- dehyde	Acetal- dehyde	Propanal	Butanal	Hexanal
Si-C ₂ H ₅ [20]	rainwater	96.5	85.3	106.7	-	-
Silica gel [64]	air	92.0	94.3	-	-	-
MAA-EGDMA [21]	human saliva	81.4	84.8	-	83.1	-
MAA-EGDMA [65]	plasma	-	-	-	-	59.1



4.5 Extraction of aldehydes in drinking water

Drinking water was extracted using the optimized extraction conditions of the fibrous nylon6 SPE. Aldehydes were detected in the samples (Figure 4.13-Figure 4.18). To evaluate the suitability of the proposed method, drinking water was spiked and recoveries were calculated. The percentage recoveries of aldehydes at 10 µg/L spiked in drinking water ranged from 42-84% which indicates no matrix interferences (Table 4.6-Table 4.8).

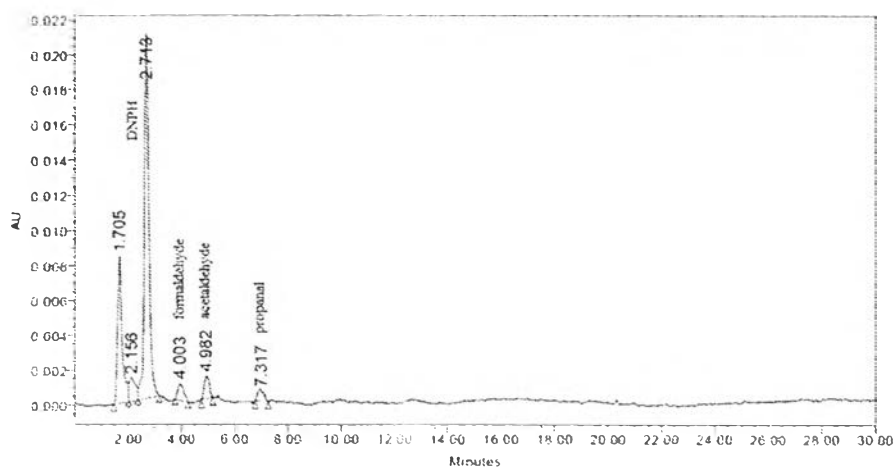


Figure 4.13 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample1.

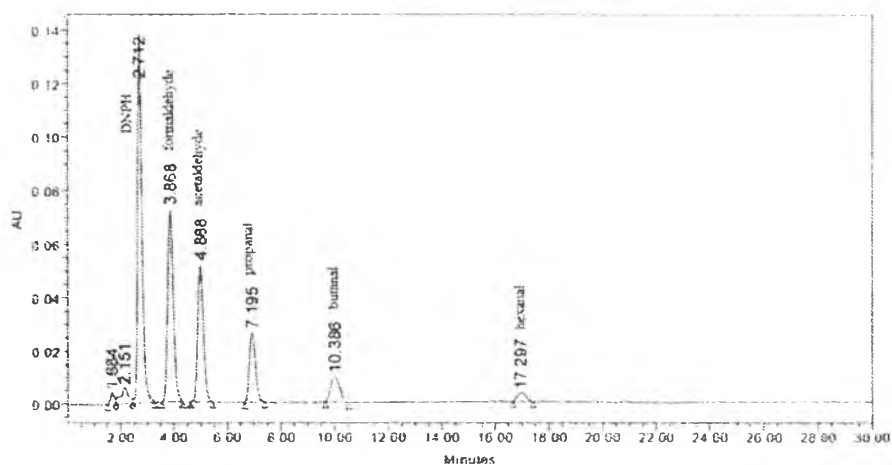


Figure 4.14 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample1 was spiked aldehydes at 10 $\mu\text{g/L}$.

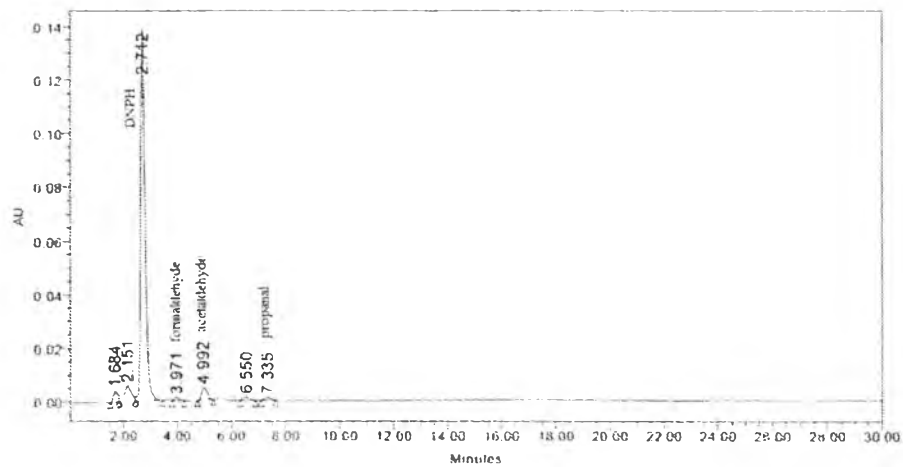


Figure 4.15 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample2.



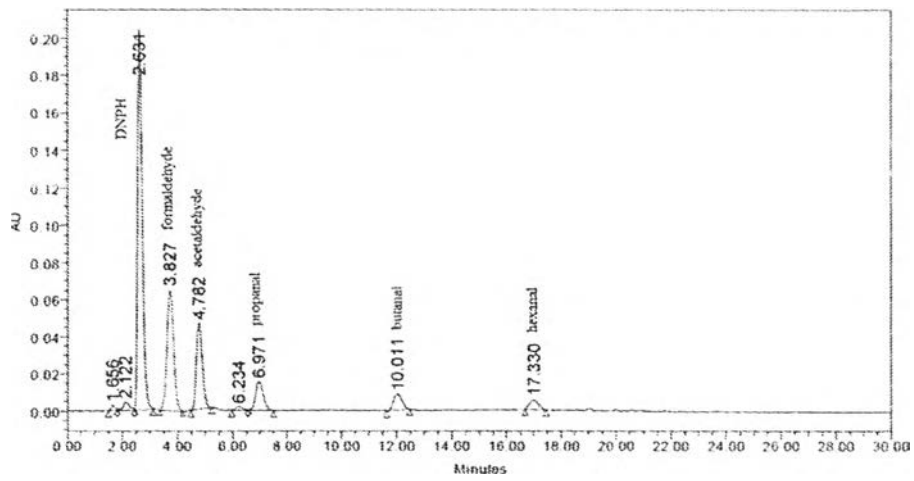


Figure 4.16 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample 2 was spiked aldehydes at 10 µg/L.

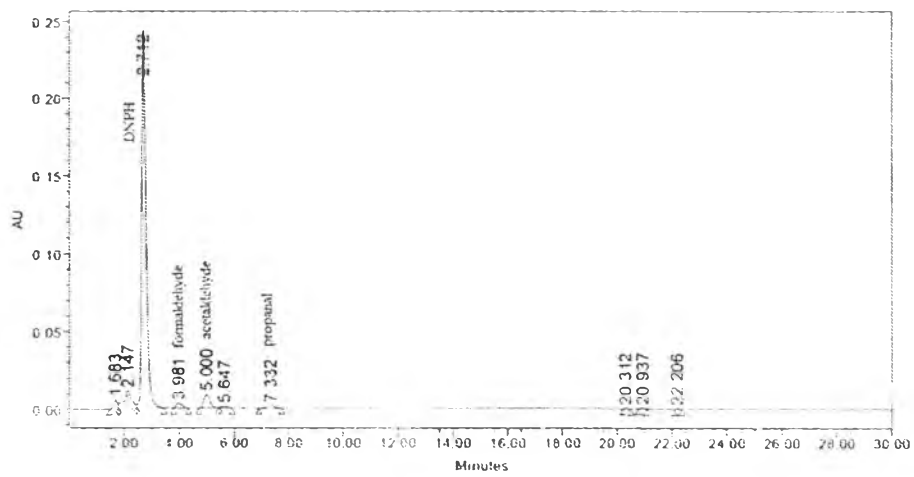


Figure 4.17 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample 3.



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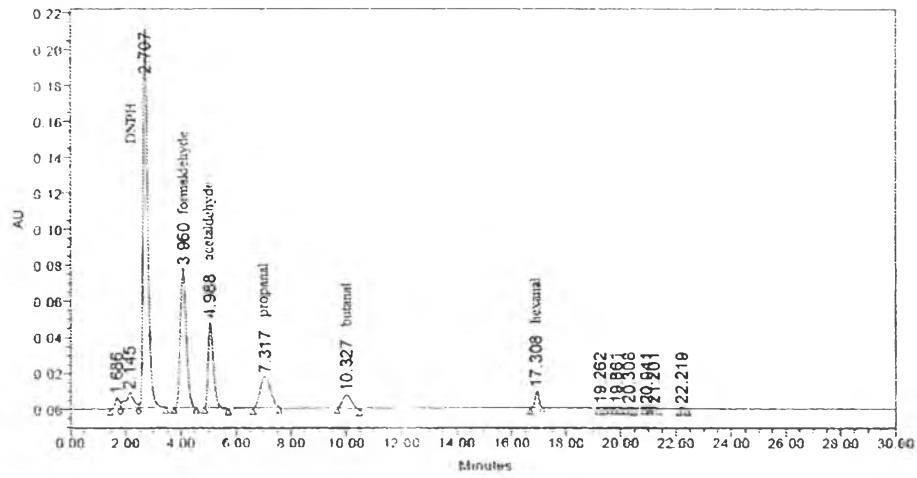


Figure 4.18 Chromatogram of eluted derivatized aldehydes from extraction of drinking water sample3 was spiked aldehydes at 10 $\mu\text{g/L}$.

Table 4.6 Percentage recoveries of aldehydes at 10 $\mu\text{g/L}$ spiked in to drinking water sample1.

compound	Concentration detected in drinking water ($\mu\text{g/L}$)	Concentration detected at 10 $\mu\text{g/L}$ spiked in drinking water ($\mu\text{g/L}$)	Recovery (%)
Formaldehyde	0.45	8.70	82.5
Acetaldehyde	0.81	9.11	83.0
Propanal	0.96	8.48	75.2
Butanal	ND	4.23	42.3
Hexanal	ND	4.46	44.6

ND: not detected.



Table 4.7 Percentage recoveries of aldehydes at 10 µg/L spiked in to drinking water sample2.

compound	Concentration detected in drinking water (µg/L)	Concentration detected at 10 µg/L spiked in drinking water (µg/L)	Recovery (%)
Formaldehyde	0.72	9.00	82.8
Acetaldehyde	1.34	9.72	83.8
Propanal	1.54	9.71	81.7
Butanal	ND	4.38	43.8
Hexanal	ND	4.81	48.1

ND: not detected.

Table 4.8 Percentage recoveries of aldehydes at 10 µg/L spiked in to drinking water sample3.

compound	Concentration detected in drinking water (µg/L)	Concentration detected at 10 µg/L spiked in drinking water (µg/L)	Recovery (%)
Formaldehyde	1.36	9.36	80.0
Acetaldehyde	2.82	10.1	72.8
Propanal	2.20	10.2	80.0
Butanal	ND	4.52	45.2
Hexanal	ND	4.87	48.7

ND: Not detected.

