Aniline-Naphthylamine Copolymer as Sorbent for Needle Trap Device

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Abstract
In current work, aniline-naphthylamine copolymers were prepared using electrochemical technique and then applied as a new sorbent for needle trap extraction of some volatile organic compounds from aqueous solution in headspace mode. The scanning electron microscopy and infrared spectrometry techniques were used to characterization of synthesized aniline-naphthylamine copolymers of aniline and naphthylamine. The results showed that aniline-naphthylamine copolymer compared to unmodified polymer, has higher porosity and non-uniform structures. The significant parameters of the sorbent preparation and extraction process such as the type and concentration of polymer, time and voltage of electrochemical deposition, the extraction time and temperatures and salt content were studied and optimized. The modified device is sensitive and fast providing good analytical parameters so that the detection limit of 0.9-2 ng L^{-1} and the quantification limit of 3-7 ng L^{-1} along with equilibrium time of 20 minutes were obtained. The linearity of method was obtained in the range of 15-1500 ng L^{-1} with $R^2 > 0.9996$. The method repeatability was considered at 50 ng L^{-1} and relative standard deviations of 3-5% were obtained. To finish, the performance of proposed device was studied via the extraction of selected analytes in real water samples and the relative recovery values were found to be in the range of 94-102%, showing no matrix effect.

Keywords: Aniline-Naphthylamine Copolymer, Solid Phase Microextraction, Volatile Organic Compounds, Gas Chromatography-Mass Spectrometry, Water Analysis

Introduction

Sample preparation of environmental pollutants in complex matrices is a fundamental stage for trace analysis purposes, because the goal compounds often have the low concentration or incompatibility between analytical instrument and sample matrix [1]. Therefore, the extraction of the goal compounds in complex matrices was essentially needed. Also, the quantitative analysis of trace analytes requires highly selective and sensitive preparations and analysis. Therefore, the sample preparation or pre-concentration of target analytes in real samples is essential to obtain accurate results. To complete this purpose, a number of sample preparation methods such as solid phase extraction and liquid-liquid extraction have been applied [2, 3]. However, they needed a lot of time and a huge volume of pure organic solvents. Recently, the needle trap device (NTD) method has been used as a solvent-less sample preparation approach that derived from solid phase microextraction [4]. In this technique, the sorbent is inserted between two glass wools or coated on the interior surface of a needle [5]. In the other type of needle trap device, the needle is packing with commercially available sorbents or chemically synthesized sorbents. All techniques derived from needle devices are cheap, reusable, mechanically stable and appropriate for sampling and sample preparation. In addition, by increasing the amount of sorbent in this device, it will improve the extraction efficiency and detection limit [6, 7].

Conductive polymers are a class of organic polymers that have the property of conductivity without the addition of any minerals. The conductivity of these polymers is due to the presence of a conjugated π-electron system along the structure of the polymer. A number of these polymers are flanked by negatively charged ions, because they have positively countered ionic. In the last decade, there have great growth in the progress of conductive polymers due to their multifactorial properties and various application potentials, such as ion exchangers, energy preservatives, corrosion resistant coatings, chemical sensors and isolation is done. A copolymer unlike a homo-polymer which only one monomer species is used has a combination of two (or more) monomer species. Copolymers usually have different chemical and physical properties (optical, conductivity, thermal stability, mechanical stability, color, solubility, morphology, etc.) from each of the constituent polymers. One of the methods of preparing a polymer with different properties is copolymerizing the polymers with each other [8].

Conducting polymers are widely used as sorbent for extraction of

organic compounds from aqueous samples. Also, polyaniline and its derivatives have particularly attracted a vast notice, because they have unique properties, including "polar functional group, hydrogen bonding, acid-base interaction, π-π interaction, hydrophobicity, electroactivity, ion exchange property". [9-14]. Aniline and its derivatives can conveniently polymerize using oxidation process via either a chemical method or an electrochemical technique. In electrochemical process, the coating of conducting polymer is electrochemically deposited on the surface of the working electrode from a water solution containing electrolyte and aniline. Electropolymerization process is usually chosen because it is easier to control the synthesis conditions (applied voltage, electrolyte content, and electrodeposition time), and obtained sorbent with higher porosity [15-23].

In this study, aniline-naphthylamine copolymers were prepared by electrochemical technique and then used as a new sorbent in the needle trap device for headspace extraction of some volatile organic compounds (VOCs) as model compounds from aqueous solution. The effect of diverse experimental conditions on the extraction efficiency of VOCs investigated and optimized.

Experimental
Reagents
Aniline and naphthylamine were obtained from Aldrich (Mississauga, Canada) and distilled before use. The volatile organic compounds such as "toluene, ethyl benzene, o-xylene and m- xylene along with sodium chloride" were purchased from Merck (Darmstadt, Germany). Standard solutions (1000 mgL^{-1}) of VOC mixture were prepared in methanol solvent (HPLC-grade) and stored in the refrigerator. The working solution was daily prepared via diluting the standard solution with double distilled water.

Apparatus
Volatile organic compounds were analyzed by an Agilent Technologies GC 7890A series couple to a 5973 mass spectrometer detector. The total data was recorded and analyzed using the ChemStation software. The separation of compounds was performed on a HP-5 capillary column (30 m, 0.25 mm, 0.25 µm film thickness). The temperature of desorption was carried out at 270 ºC. The flow rate of carrier gas (Helium) was justified at 1 mLmin^{-1}. The temperature of oven was initially held at 60 ºC for 4 min, and then, raised to 220 ºC by 20 ºCmin^{-1}. The transfer line from the gas chromatograph to the mass spectrometer was set at 280 ºC. The SIM detection method was used for VOCs (m/z of 91 and 92 for toluene, m/z of 91 and 106 for ethyl benzene, o-xylene and m- xylene) to improve the sensitivity.

The characterization of the synthesized sorbent was performed by a TESCAN VEGA II XMU (Brno, Czech Republic).

The extraction process was performed in 10 mL glass vials that sealed by a PTFE-faced septum and aluminum cap then it heated in a homemade bath connected to a circulating water bath (RTG-8 NesLab, USA) and stirred by a Gerhardt Bonn hot plate magnetic stirrer.

The electropolymerization process was performed using a power supply (Kepco, Flushin, NY, USA). The NTD was prepared in our laboratories by the spinal needle with gauge numbers of 23.

Preparation Aniline-Naphthylamine Copolymers Sorbent
Aniline and naphthylamine were distilled under reduced pressure and stored in the refrigerator before utilize. The electrolyte solution prepared with the addition of sulphuric acid into double distilled water. The electrochemical cell contained working and counter electrodes of stainless steel. Firstly, a certain mole of naphthylamine was added to 5 mL of aniline solution (0.1 M) and sonicated for 10 min. Subsequently, the end part of stainless plunger (1.5 cm) was located in the homogenous solution as the working electrode. Then, the constant potential (1.5 V) was applied between two electrodes for 30 min and the ANI-NAPH copolymer was directly synthesized on the working electrode.

Needle Trap Device
The needle trap device was made from the spinal needle with a length of 88 mm (o.d. = 0.65 mm, id =0.35 mm) and gauge number of 23. The diverse amount of synthesis sorbents such as polyaniline, polynaphthylamine, and aniline-naphthylamine copolymer were immobilized in the needle by two glass wools. Firstly, the glass wool inserted into the needle and then the aniline-naphthylamine copolymer was packed in the needle and finally the second glass wool was inserted in the tip part of the needle. In the thermal desorption stage, Helium (carrier gas) flowed through sorbent by the small hole was drilled on the side of the needle (40 mm from the opening).

Sampling by Needle Trap Device
7 mL of working solutions of volatile organic compounds (1 mgL^{-1} in distilled water) was placed into a 10 mL glass vial containing 2.1 g NaCl. Sample vials were heated in a water bath and the solution was stirred with magnetic stirrer while the needle trap device was hold at ambient temperature. The extraction was performed by exposing the sorbent to the headspace of the sample for 20 min at 45 ºC. Then, the NTD was inserted through the vial septum and placed in the headspace of the sample. A 23 G needle was also inserted into the sample solution to purge the circulating headspace into the sample. The NTD and the purging needle were connected to a peristaltic pump in away to aspirate the headspace sample through the NTD. The sampling flow rate was 2.5 mLmin^{-1}.

Results and Discussion
In the two recent decades, conducting polymers have particularly attracted a vast notice, because, they have unique properties including, "polar functional group, hydrogen bonding, acid-base interaction, π-π interaction, hydrophobicity, electroactivity and ion exchange property". Also, it is expected that the extraction efficiency will be improved by increasing the surface area and porosity of the polymer.

Due to the same method and conditions of polymerization of these polymers, it is possible to easily polymerize different conductive polymers with each other and prepare a copolymer with different properties. Among conducting polymers, copolymers derived from polyaniline (by one aromatic ring) and poly-1-naphthylamine (by two aromatic rings) is selected due to the presence of monomers with different sizes next to each other have a porous structure with a high surface area. In the first stage, it was needed to optimize the influence parameters on the synthesizing conditions to facilitate obtain the higher extraction efficiency. For this purpose, the effect of the amount of NAPH in the range of 0.00- 0.3 M was studied in 5 ml of aniline solution (0.1 M). The results obtained in Fig. 1 revealed that increasing the concentration of NAPH up to 0.1 M improves extraction efficiency. Therefore, NAPH and ANIL have the efficient role in the morphology of synthesized copolymer and subsequently in the extraction process.
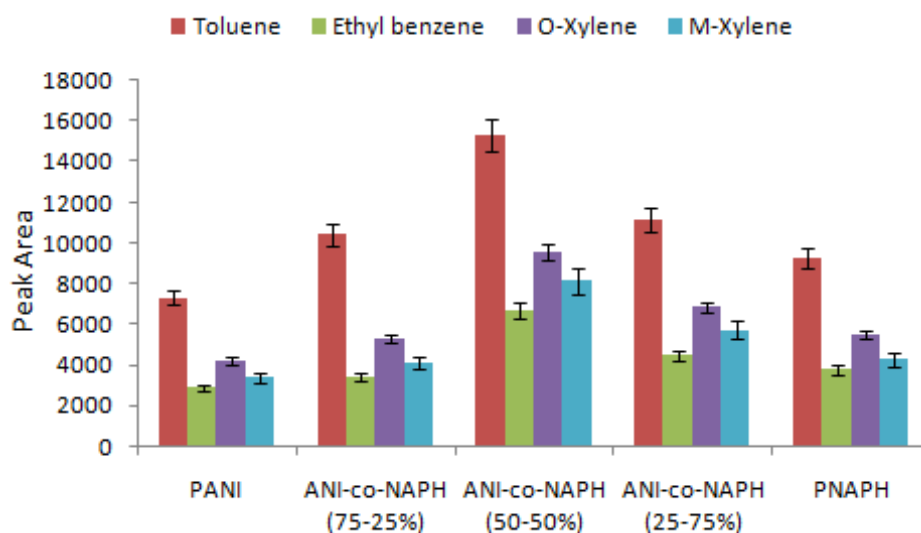
Figure 1: Effect of the Component Molar Ratios on the Extraction Efficiency

Characterization of the Aniline-Naphthylamine Copolymer

The characteristics of the aniline-naphthylamine copolymer were considered by SEM. The micrographs of polyaniline, polynaphthylamine, and aniline-naphthylamine copolymer are shown in Fig. 2. The synthesized copolymer has porous structure and non-smooth in comparison with the PANI and PNAPH.
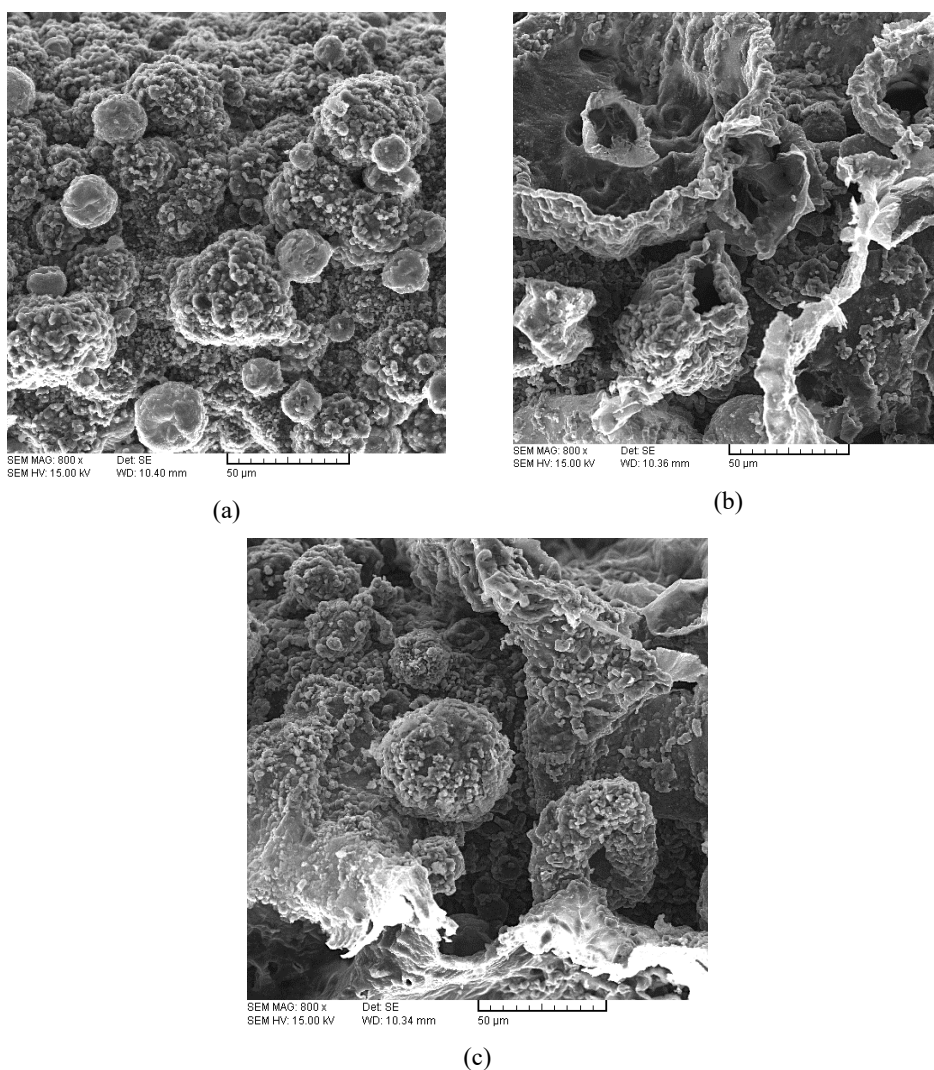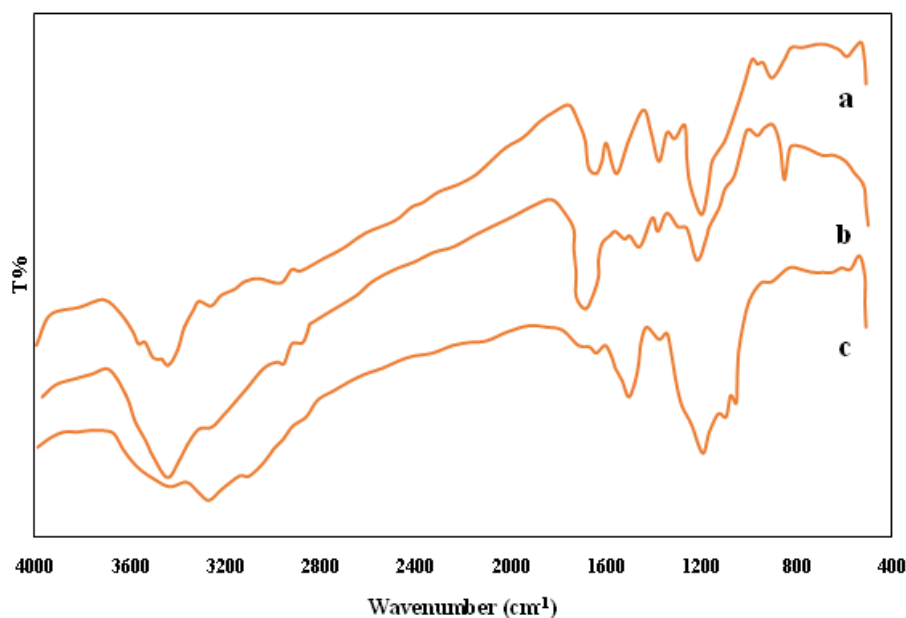
Figure 2: SEM of a) Aniline Polymer, b) Naphthylamine Polymer and c) the Aniline-Naphthylamine Copolymer in the Same Scale

The structure of ANI-NAPH copolymer (50-50) due to the formed spaces between two dissimilar NAPH and ANI monomers in the copolymer backbone has a rather coral form. The morphological dissimilarity between PNAPH or PANI and ANI-NAPH copolymer (50-50) is due to the co-polymerization of aniline and naphthylamine, in which, a resultant copolymer with different properties is anticipated.

The FTIR spectra of PANI (a), PNAPH (b) and ANI-NAPH (50-50) (c) are shown in Fig. 3. The spectrum of PANI (Fig. 3a) reveals to have some absorbance peaks at 1486, 1579 and 3418 cm^{-1} which are characteristics of PANI. The absorbance peaks at 1486 and 1579 cm^{-1} are attributed to C=C and C=N stretching mode for benzenoid and quinoid ring while the absorbance peak at 3418 cm^{-1} is attributed to the N-H band. The absorbance peaks at 1398, 1623 and 3410 cm^{-1} was found for PNAPH (Fig. 3b) that are characteristics of PNAPH. The peak of N-H stretching vibration mode was revealed at 3410 cm^{-1}. The peak at 1398 cm^{-1} is attributed to C-N stretching vibration mode. The IR spectrum of ANI-NAPH copolymer (50-50) (Fig. 3c) contains peaks at 1430, 1583 and 3418 cm^{-1} that are characteristic of ANI-NAPH copolymer. The peak at 3443 cm^{-1} is attributed to N-H stretching vibration mode. The peaks at 1430 and 1583 cm^{-1} are attributed to C=C and C=N stretching mode for benzenoid and quinoid rings.

Figure 3: FTIR a) Spectra of Aniline Polymer, b) Polynaphthylamine and c) the Aniline-naphthylamine Copolymer

Optimization of Sampling Condition

Significant factors on the extraction efficiency of modified NTD such as the temperature of extraction, the concentration of salt, sorbent amount and time of extraction were studied and optimized. Salt addition to the aqueous solution causes to enhance the ionic strength and decrease the solubility of organic compounds. The effect of increasing NaCl salt was investigated in the range of 0-30% (w/v). The peak area of response was increased up to 20% and then it almost remained constant. Consequently, further experiments were carrying out in the adding of 20% (w/v) of NaCl salt.

Other considerable parameter in head-space mode is the temperature of extraction, since it has significant effect on the equilibrium of the extraction process. The increasing the temperature of ex-

traction has two effects on the efficiency of extraction. The positive effect of increasing temperature, the separation of organic compounds from their matrix can enhance and their concentration in the head space of the sample was increased so that higher extraction rates could be achieved. The coefficient of distribution of sorbent/sample headspace can be decreased in high temperature and the extraction efficiency is reduced. The efficiency of extraction of VOCs in the range of 25-75°C was considered. The obtained results discovered that the extraction efficiency was enhanced by increasing the temperature to 45 °C and then decreased (Fig. 4b). When the extraction time was constant in different temperatures, the effect of these two phenomenon's caused to decreasing the performance of NTD at temperature higher than 45 °C.

(a)

(b)
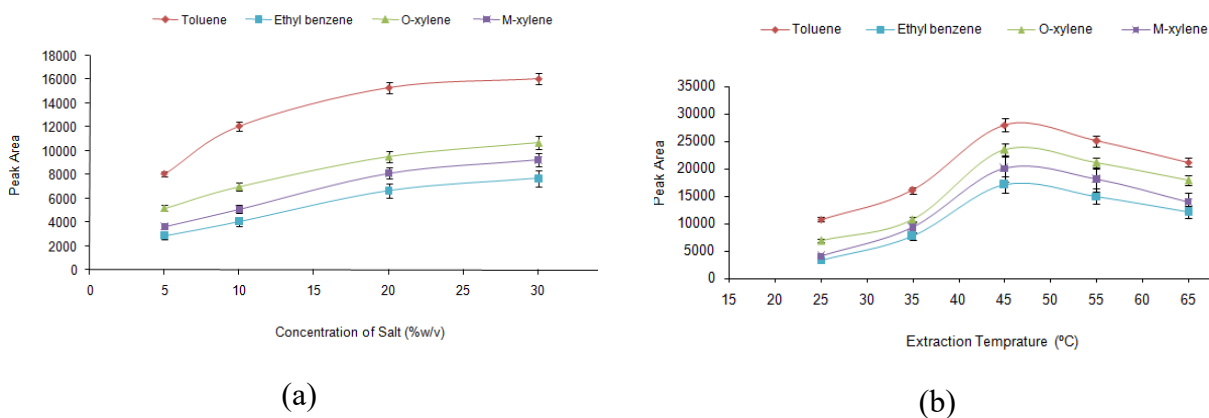
Figure 4: (a) Effect of Ionic Strength (b) and Extraction Temperature on the Extraction Efficiency

The efficiency of extraction depends on the time that the sorbent is exposed to the analytes in the headspace of the sample. The effect of extraction time was studied in the range of 5 - 45 min. The obtained results revealed a sharp increasing in the efficiency of extraction within the first 10 min of the contact time, continued by a gradual enhancement in the extraction efficiency until the adsorption equilibrium was achieved at 20 min. After this time, insignificant change was observed in the extraction efficiency at extraction times more than 30 min, because, the all active sites of sorbent were saturated by VOCs, so that, the equilibrium time was obtained at 20 min. Numerous active sites on the sorbent surface are easily available in the initial stage of the adsorption process, thus the adsorption occurred faster, caused a sharp increase in the amounts removed. Finally, the extraction time of 20 min is selected to ensure attaining the extraction equilibrium.

The needle trap device was evaluated in terms of repeatability, accuracy, linearity, the limit of quantification and detection. The RSD% at a level of 50 ng L^{-1} were obtained in the range of 3-5%. The linearity of method was obtained at a number of spike levels from 15 to 1500 ng L^{-1} and the coefficients of correlation (R) from 0.9996 to 0.9998 were obtained (Table 1). The detection limit and quantification limit values were in the rage of 0.9-2 ng L^{-1} and 3-7 ng L^{-1}, respectively. Also, the relative recovery of the proposed method was performed on the tap water and Calan dam sample spiked (at 50 ng L^{-1}) compared by the non-spiked Calan dam and Tehran drinking. Relative recoveries obtained for the spiked real aqueous samples (at 50 ng L^{-1}) in the range of 94–102% (Table 1), indicating no matrix effect. Table 2 compares analytical data obtained in the current study with previously works, showing that the time of analysis is rather lower and comparable LODs were obtained [24-27].

Table 1: Analytical Parameters Obtained from HS-NTD of Selected VOCs Using the Aniline-naphthylamine Copolymer Sorbent and GC-MS

compound	LDR (ng L^{-1})	(R^2)	LOD (ng L^{-1})	Intra-day RSD[a]% (n=3)	Inter-day RSD[b]% (n=3)	Intra-day Relative recovery% (n=3)	
						Kalan dam water	Tap water
Toluene	15-1000	0.9997	0.9	3	6	102	101
Ethyl benzene	15-1000	0.9996	2	5	9	96	94
O-Xylene	15-1000	0.9997	1	3	7	101	98
M- Xylene	15-1000	0.9995	1	4	9	99	99

[a,b] at 50 ng L^{-1}

Table 2: Comparison of Analytical Characteristics for Needle Trap Device with Other Work

Sorbent	LDR[a]	LOD[b]	RSD[c]%	Matrix	Ref.
Polydimethylsiloxane	10-25,000 µg L^{-1}	0.75–10 µg L^{-1}	< 8	Water	[24]
Cobalt oxide nanoparticles	10–300,000 µg L^{-1}	1–11 µg L^{-1}	< 11	Water	[25]
Sol–gel-carbon aerogels	1–1500 µg L^{-1}	8–47 µg L^{-1}	< 4.6	Water	[26]
Graphite	0.6–11090 µg L^{-1}	0.19–3.29 µg L^{-1}	2-4.5	Water	[27]
Aniline-naphthylamine copolymer	0.015-1.5 µg L^{-1}	0.9-2 ng L^{-1}	3-5	Water	Current work

[a] Linear dynamic range
[b] Limits of detection (S/N = 3)
[c] Relative standard deviation (n = 3)

Concluding Remarks

In this work, NTD-GC/MS method based on ANI-NAPH copolymer was developed for trace determination of trace organic volatile compounds as model compounds in aqueous samples. The comparison of ANI-NAPH copolymer sorbent with PANI and PNA sorbents revealed that ANI-NAPH copolymer has higher extraction efficiency. This benefit is more probably due to the porous structure of the ANI-NAPH copolymer. In addition, the analytical data along with relative recovery demonstrated that the ANI-NAPH copolymer is a suitable sorbent for extraction of organic compounds. The modified device based on the use of ANI-NAPH copolymer is rapid, solvent-less, simple and cheap to use for deter-

mination of VOCs with reproducibility and satisfactory sensitivity.

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