Development of a Method Based on the Needle-trap Microextraction Filled with Hydroxyapatite and Polyaniline Nanocomposite for Determination of Volatile Organic Compounds in the Air

Nasim Sanaei[a], Abdulrahman Bahrami[a,*], Farshid Ghorbani Shahna[a], Majid Habibi Mohrez[a]
and Maryam Farhadian[b]

[a]*Center of Excellence for Occupational Health, Occupational Health and Safety Research Center, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran*

[b]*Department of Biostatistics, School of Public Health and Research Center for Health Sciences, Hamadan Uni versity of Medical Sciences, Đamadan, Iran*

In this study, the efficiency of packed needle trap with hydroxyapatite/polyaniline (NTD-HAP/PA) nanocomposite was assessed in air sampling and analysis of a hazardous group of VOCs such as benzene, toluene, ethylbenzene and xylenes. The effects of main parameters, including desorption temperature and time were evaluated on the performance and carryover of the prepared NTDs. Moreover, the repeatability, reproducibility and stability of the developed sampler were investigated for the sampling and determination of the interest analytes. The results of experiments indicated that the highest peak area was obtained at desorption temperature and time of 250 °C and 3 min, respectively. The reproducibility of the proposed method was investigated with three distinct NTDs with similar structure. The weight of the adsorbent was also obtained. The results showed that the relative standard deviation (RSD) of experiments was in the range of 0.2-9.7%. The RSD of repeatability was obtained at four different concentrations with three times replications less than 15%. The limit of detection and quantitation (LOD and LOQ) for the studied VOCs ranged from 0.01 to 0.14 ng ml^{-1} and 0.04 to 0.48 ng ml^{-1}, respectively. Also, the storage stability of the analytes of interest in the NTD-HAP/PA after 3 and 7 days at 4 °C was above 95 and 93%, respectively. It can be concluded that the proposed method could be applied as a desirable and powerful tool for air sampling and microextraction of volatile organic compounds.

Keywords: Needle trap device, Volatile organic compounds, Air, Hydroxyapatite, Hydroxyapatite/polyaniline nanocomposit

INTRODUCTION

Recently, there has been a growing concern regarding human exposure to air pollutants in the world, especially in developing countries, which pose great adverse health effects on humans [1,2]. Among these substances, volatile organic compounds due to their particular characteristics, including high evaporation rate and rapid diffusion into the environment are considered as the main group of air pollutants. Human exposure to these compounds has adverse and irreversible effects on human health in various occupations [3,4]. Benzene, toluene, ethylbenzene, and xylene isomers (BTEX) are among the most important and widely used volatile organic compounds (VOCs) [4-6]. BTEX are naturally present in some materials such as crude oil, natural gas and other derivatives of petroleum. They are mainly released into the environment through industrial activities and vehicle emissions. These compounds are widely used in various industries, such as rubber, dye, toy, plastic, and leather manufactures [5,6]. Inhalation is the main route of exposure to BTEX compounds. However, the exposure to these compounds through the skin and ingestion routes (swallowing) is also possible [7].

So far, various methods have been used to quantify the

*Corresponding author. E-mail: bahrami@umsha.ac.ir

VOCs in the workplaces and ambient air. The national institute for occupational safety and health (NIOSH) and the occupational safety and health administration (OSHA) have proposed several methods with similar principles for the air sampling and determining the VOCs in workplaces. Amongst them, solid sorbent tubes are generally used with a low-flow sampling pump [8]. Despite the widespread use of these methods, they have several disadvantages, such as spending a long time for the preparation step, requiring hazardous solvents, posing adverse environmental effects caused by solvent use, and low precision or sensitivity [9, 10].

In the past few years, the use of microextraction methods followed by rapid analysis has received much research interest due to problems concern to the use of the conventional methods for the sampling and determination of BTEX. Among the microextraction techniques, solid-phase microextraction (SPME) and needle trap device (NTD) have recently emerged as solvent-less microextraction technology [8,10,11]. Despite the benefits of SPME, it still has a variety of drawbacks including fiber fragility, limited capacity, and high cost, limiting its applications for various purposes [10,12,13]. Recently, there has been an increasing research interest in the use of NTD as an alternative technique for SPME to address the limitations of conventional methods. Therefore, the NTD offers various advantages over the SPME method, such as low cost, increased adsorption capacity by increasing the amount of packed adsorbent inside the needle, high strength due to the use of a strong stainless steel needle as the main body of the sampler [10,14]. This microextraction method is based on the passing air containing the pollutants through the NTD and then the adsorption of the analytes on the adsorbent surface. After direct sampling with the NTD, inserting its needle into the injection port of the gas chromatograph (GC) at a suitable desorption temperature, analyte desorption occurs. Then, the desorbed analytes are delivered by carrier gas from the adsorbent bed into the GC column [15]. On the other hand, the selection of a suitable sorbent in the NTD, as the most important factor affecting the adsorption rate of the analytes, has a significant effect on improving the efficiency of NTD.

Recently, the synthesis of nanometer-sized solid compounds has received much attention due to their specific physical and chemical properties [15]. Hydroxyapatite

with formula $Ca_{10}(PO_4)_6OH_2$ and stoichiometric ratio Ca:P = 1.67 can be used as packing material in NTD [16]. Hydroxyapatite offers unique properties including high thermal tolerance even up to 1200 °C, high capacity, availability, and low cost of synthesis over other previous absorbents. Due to these advantages, some studies have investigated this sorbent for the absorption and elimination of pollutants from water, air, and soil [17,18]. To date, no study has focused on the use of hydroxyapatite as a packing sorbent in the NTD [19].

Moreover, combining polymers with the packed adsorbent can enhance the performance of the adsorbent, and subsequently improve the sampling and analytical efficiency of prepared NTDs [20]. Polyaniline is one of the polymers that has been successfully used in several studies in combined with hydroxyapatite [21]. Polyaniline has a wide variety of applications due to its special advantages, including great stability at environmental conditions, high conductivity, easy fabrication, and low cost [20].

To the best of our knowledge, this adsorbent has not yet been used in the needle trap method for sampling air pollutants. Therefore, in the present study, hydroxyapatite in the combination of polyaniline (HAP/PA) was applied as a packing adsorbent for the air sampling and determination of benzene, toluene, ethylbenzene and xylene isomers (BTEX). Moreover, the influences of various analytical parameters, including desorption time and temperature, were investigated on the efficiency of the prepared sampler. Also, the storage stability, memory effect, reproducibility, and accuracy of the developed method were evaluated to validate its application for the compounds of interest. Finally, the efficiency of adsorbent was compared with the NIOSH-1501 method.

MATERIALS AND METHODS

Materials

Benzene, toluene, ethyl benzene, and xylene isomers compounds with the highest purity were purchased from Merck Co. High purity carbon disulphide (CS_2) was purchased from Merck Co. Calcium nitrate $Ca(NO_3)_2.4H_2O$ phosphorus pentoxide (P_2O_5), ethanol (gradient grade for liquid chromatography) and sodium hydrate (NaOH) were purchased from Merck Co. For the synthesis of polyaniline, aniline, hydrochloric acid and potassium dichromate were

purchased from Merck Co. DMF solution (N'N-dimethylformamide) was obtained from Merck Co. and was used for the synthesis of hydroxyapatite/polyaniline nanocomposite. Also, solid sorbent tube containing coconut shell charcoal (100 mg/50 mg) from Sigma Aldrich was used. All experiments were performed under a laboratory hood.

Instruments

In this study, a flame ionization detector (FID) equipped with gas chromatograph (Shimadzu GC-2010) was used to analyze the compounds. An RTX-624 capillary column with a specification (column length and inner diameter 30 m and 0.25 mm, respectively) was used to separate the analytes. The operational condition of GC was as follows: split ratio: 8:0, SPL pressure (injection port pressure): 150 kPa. Nitrogen with high purity was applied as the carrier gas. The column temperature began at 90 °C and after that increased to 150 °C at the thermal gradient of 3 °C min^{-1}. Therefore, the entire time of the program was 14 min and the temperature of the detector was adjusted at 280 °C.

For side by side sampling with NTD-HAP/PA and solid sorbent tube from the standard chamber, a low-flow sampler (SKC 222-3, USA) was applied. A high flow discharge pump (Biolite High-volume Sample Pump, SKC) was also used to create a steady-state airflow with a desired flow rate inside the standard chamber. Disposable medical syringe (3 mL, Luer lock, AVAPEZESHK, Ashtian, Iran) was used to pass carrier gas through the packed NTD, and deliver the desorbed analytes into the column of GC. The proposed NTDs were prepared by using synthesized HAP/PA packed medical spinal needles (22G × 90 mm, Dr-J, Japan). 50 ml medical syringes were provided from Varid Company (Mashhad, Iran) and used to inject analytes with a constant flow rate through a syringe infusion pump into the standard test chamber. The automated syringe infusion driver (syringe pump SP-510) was used to provide the desired amount of the compounds in the prepared test chamber. Glass wool was purchased from Merck Company to hold the adsorbent inside the spinal needle. A digital thermo-hygrometer (TFA Dostman Ltd, Germany) was used in the pilot to monitor the relative humidity and temperature in the standard chamber during sampling.
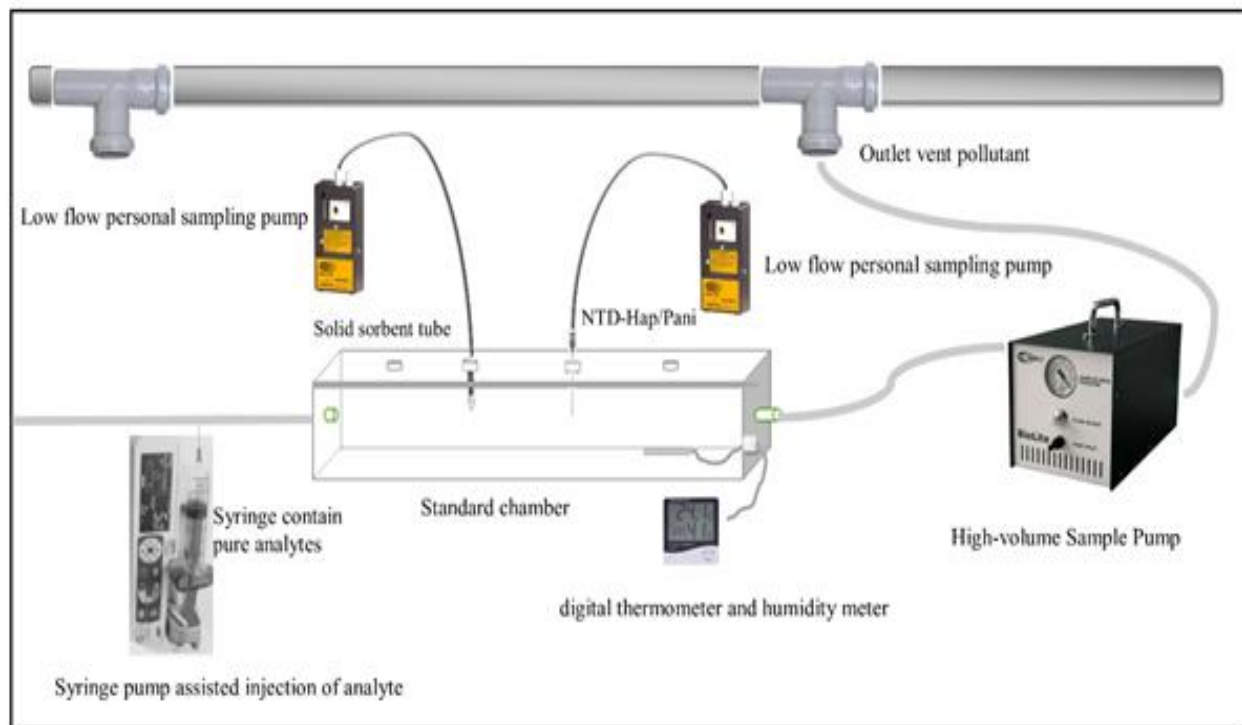
Standard Chamber

In this research, a glass chamber with internal dimensions of 30 × 15 × 15 was used to create conditions similar to workplace conditions. The syringe infusion pump device was connected to the inlet of the chamber to inject a certain amount of the interest analytes to the entering air into the chamber. The sensors of the digital thermometer and hygrometer were installed inside the reactor to control the levels of air temperature and its relative humidity in the test chamber. The temperature and relative humidity inside the chamber was set in the range of 27-29 °C and 30-35%, respectively, at all stages.

Before sampling, the holes were sealed with Teflon septum, and the chamber was purged through passing a constant stream of nitrogen gas. Air sampling with prepared NTDs was done by a calibrated low-flow pump at 1 ml min^{-1} after preparing the chamber for the test. Following air sampling, the needle trap was detached from the pump and injected with 1 ml of nitrogen gas into the GC injection port. Also, in this step, an activated charcoal tube (100 mg/50 mg coconut shell charcoal) was used to measure the concentration of analytes according to the NIOSH-1501 method. The obtained samples were extracted by one mL of CS_2, and then, one microliter of the extracted solution was injected into the GC and analyzed. Figure 1 presents a schematic image of the used test rig.

Preparation of HAP/PA Nanocomposite

Synthesis of nano-hydroxyapatite by hydrothermal method. The required compounds for the synthesized nano sorbent included calcium nitrate $Ca(NO_3)_2.4H_2O$, phosphorus pentoxide (P_2O_5), ethanol, and sodium hydroxide. Due to the stoichiometric ratio of Ca:P = 1.67, a mixture of calcium nitrate (0.2 M), pentoxide phosphorus (0.12 M), and ethanol were prepared for the formation of the hydroxyapatite phase. The resulting mixture was sonicated for 30- 40 min. After preparation of the solutions, 60 ml of calcium nitrate was poured into a beaker. Then, 60 ml of phosphorus pentoxide was added (drop by drop from a burette) into the calcium nitrate solution under constant stirring. Afterward, the sodium hydroxide solution (2 M) was used to adjust the solution pH at the desired level (about 10). The solution was poured into Teflon autoclave

Fig. 1. Schematic image of the standard chamber.

with a stainless steel liner and maintained at 150 °C for 24 h. After cooling the autoclave, the final product was washed with distilled water three times, and kept at 50 °C for 24 h to dry the nano hydroxyapatite [22,23].

Synthesis of polyaniline. In this step, aniline-hydrochloric acid and potassium dichromate were used for the synthesis of polyaniline. For this purpose, 20 ml of hydrochloric acid, 25 ml of potassium dichromate, and 2 ml of aniline were poured in a flask, and then a few drops of distilled water were added into the flask. Next, hydrochloric acid was slowly added into the flask content, and then aniline was added to the resulting mixture. Nitrogen gas passed through it for 30 min. The contents were transferred to the flask, and 25 ml of potassium dichromate solution was added to the flask with constant agitation. The products formed were separated using a filter and rinsed with distilled water. The washing operation continued until the outlet water became completely clear and colourless. The final products were collected using a filter and dried under vacuum at room temperature over

48 h [24].

Synthesis of HAP/PA nanocomposites. To synthesize the HAP/PA nanocomposites, 100 mg of hydroxyapatite was dispersed in 10 ml of DMF at a bottle flask. In another flask, 100 mg of polyaniline was dispersed in 10 ml of DMF. Then, the resulting mixture was placed in ultrasonic for one hour. Afterward, the hydroxyapatite solution was slowly added to the polyaniline mixture by a burette under constant stirring. The resulting mixture was agitated for 24 h at 25 ºC. Eventually, the contents were dried at 50 °C for 24 h and 85 °C for three hours [21].

Characterization of HAP/PA. After synthesizing the HAP/PA adsorbent, the structural properties of the adsorbent were investigated. A Fourier-transform infrared spectroscopy (FTIR) (FT-IR: 4000-400 cm^{-1}) was used to generate the infrared spectrum of the synthesized HAP/PA nanocomposites using Varian 670-IR spectrometer (Santa Clara, USA). Moreover, to investigate the adsorbent surface properties and absorbent morphological features, scanning electron microscopy (SEM) analysis was used. X-Ray

diffraction (XRD) was also applied to evaluate the formed phases of the HAP/PA nanocomposites. The composites were thermally decomposed by a differential thermal/thermo-gravimetric analysis (DT/TGA) in the temperature range of 50-800 °C with a device at a thermal gradient of 10 °C min^{-1} to evaluate the final phases of the generated hydroxyapatite and hydroxyapatite/polyaniline nanocomposite.

Preparation of Needle Trap Device

In this research, the NTDs was prepared using Gage 22 spinal needle, because of the diameter that is easily injected into the injection port and causes less damage to the septum. In this work, 1 mg of the prepared adsorbent was packed, and both sides of the adsorbent were protected by glass wool as a preservative to fix the adsorbent tightly inside the needle. Two layers of glass wool (3-5 mm) were packed in both sides of the adsorbent. The packed were evaluated in terms of airflow passing. In this regard, a soap bubble flow meter was used to calibrate the sampling airflow before sampling. Due to the low airflow rate of the packed NTDs, a 1 ml pipette was used to determine the sampling airflow instead of using the standard burette in the soap bubble set. The prepared NTDs were selected with a flow rate value of 1 ml min^{-1} for the next experiments. To eliminate any contamination in the packed adsorbent, the NTDs were first kept in the injection port of the GC device at 200 °C for two h. Figure 2 shows a schematic of the prepared NTDs.

Desorption Parameters

In the present research, to reduce the time of analysis, increase the usability of the adsorbent, and determine optimum desorption conditions, the effects of desorption time and temperature on the efficacy of proposed NTDs were investigated. The optimal desorption time and temperature were obtained to ensure that all analytes were desorbed from the adsorbent bed with the lowest memory effect. Accordingly, the desorption time and temperature for NTD packed with HAP/PA adsorbent were evaluated at four different levels of desorption times range from 1-4 min, and three temperature levels ranged from 220-280 °C. Finally, the lowest desorption time and temperature corresponding to the highest peak area response were chosen as the optimum desorption conditions.

Breakthrough Volume Investigation

Adsorbent capacity plays a crucial role in the application of NTD for various purposes. Adsorbent capacity directly affects the breakthrough volume of the NTD. Hence, the breakthrough volume of a new developed method must be determined to avoid measurement errors. For this purpose, two needles with similar conditions were selected and used for sampling and determination of the analytes from the chamber. To evaluate the breakthrough volume of the proposed method, two NTDs with the same packing conditions were connected in series by a connector. The end of the second NTD was connected with a flexible tube to a low flow pump. Then, air sampling was conducted by serried NTDs. Upon completion of sampling, in addition to the first NTD, the second NTD was also analyzed to determine the amount of analytes passed. Breakthrough volume was obtained when the ratio of the analytes in the second NTD to the first NTD was greater than 10%.

Carryover Effect

Carryover effect in a single-step microextraction method such as NTD occurs as a result of incomplete desorption. In this case, the residual analytes of packed sorbent bed interfere with the subsequent uses of the sampler and effects in a severe measurement error. Furthermore, it is necessary to determine the optimal desorption conditions, before sampling and analysis of the compounds with each sampling method. For this purpose, the analysis of the compounds trapped on the adsorbent bed of NTD was repeated twice. After the completion of sampling, the sampled NTDs were inserted in the injection port of the GC in two consecutive cycles to evaluate the residual analytes on the NTD after the first desorption cycle. In the present work, the carryover effect was evaluated under optimal conditions in the concentration range equal to the threshold limit values (TLV) of analytes.

Storage Time

The stability of analytes on the sorbent bed of NTD is one of the most essential issues that indicate the ability of samplers to retain the analytes for an adequate storage time without significant losses of analytes. In the present research, an absolute concentration of the analytes was made inside the test chamber, and air sampling was
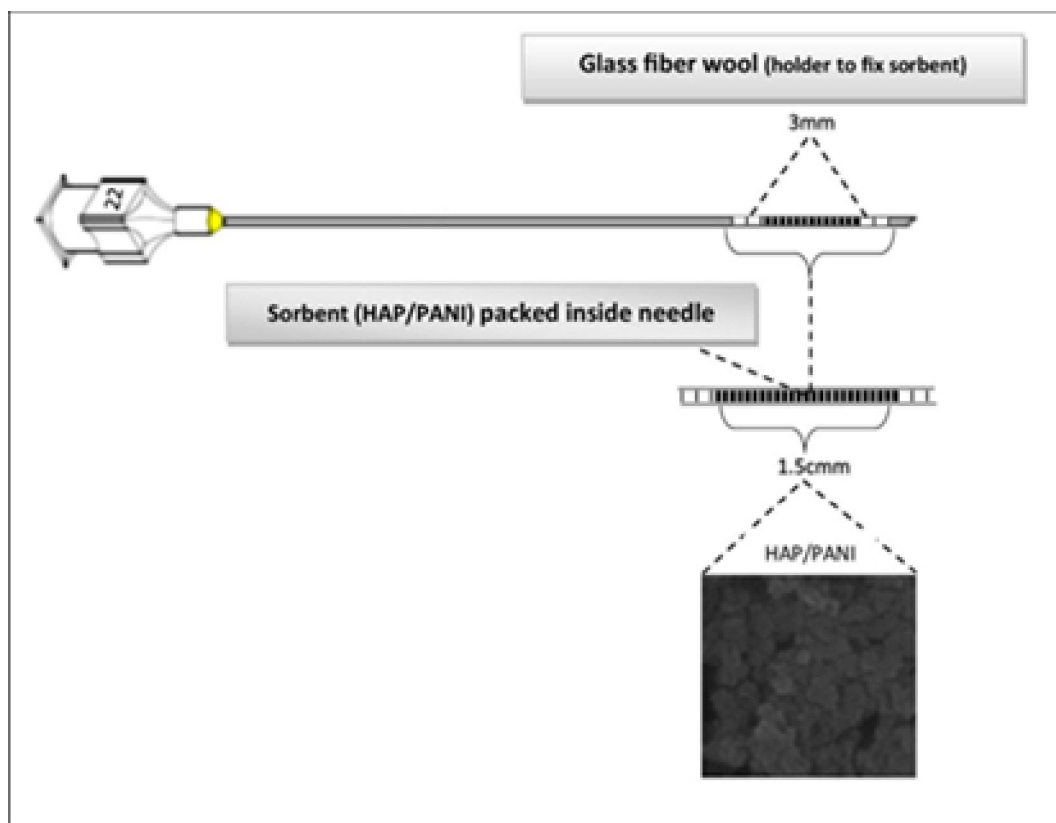
Fig. 2. Needle trap prepared with HAP/PA nanocomposite for sampling BTEXs compounds.

conducted by prepared NTD. Then, both sides of the NTD were covered by silicone septa. The sealed NTD was stored in a cylindrical glass holder for 1-7 days to prevent airflow through the NTD. After storing for a specified time, the NTDs were analyzed to evaluate the amount of missing analytes. Moreover, to assess the influence of temperature on storage stability of the NTD, these experiments were conducted at both lab and fridge temperatures (25° and 4° C).

Method Validation

In this study, repeatability of the proposed NTD was evaluated at four different concentrations, and this process was repeated three times for all concentrations. Relative Standard Deviation (RSD) was measured for each analyte and used as an index for judging the repeatability of the method. In this step, three NTDs packed with HAP/PA adsorbent (labelled as NTD-A, NTD-B, NTD-C) with

similar structural characteristics (*e.g.*, passing air flow rate and adsorbent amount) were used to sample a constant concentration of analytes from the test chamber. This procedure was repeated three times for each NTD (NTD-1, NTD-2 and NTD-3). The RSD values were calculated for each analyte to evaluate the repeatability of the proposed method.

To validate the method, limits of detection and quantitation (LOD and LOQ) were identified as the most common parameters in determining the sensitivity of a sampler and the analytical method. So, their values were calculated according to the signal-to-noise ratio. For determining LODs and LOQs, the concentration of the studied analytes inside the chamber was reduced to find the concentrations corresponding to the signal to noise ratios of 3 and 10, respectively.

Accordingly, the concentrations of the analyte in the standard chamber were decreased to the lowest detectable

level. After sampling with NTD packed with HAP/PA adsorbent, it was injected into the GC. The resulting peak area in the chromatogram with a signal-to-noise ratio of 3 was considered as LOD value (S:N = 3), and the resulting peak with a signal-to-noise ratio of 10 was considered as LOQ value. In this study, the linear dynamic range (LDR) was also investigated as another validation parameter.

In this research, the actual concentration of analytes in the test chamber was determined to evaluate the precision of the measurements with the proposed method. For this purpose, a solid sorbent tube (coconut shell charcoal, 100 mg/50 mg) was used according to the NIOSH 1501 method to measure the concentrations of the studied analytes (BTEX compounds) in the standard chamber.

Field Sampling by NTD-HAP/PA Device

After optimization of all parameters of NTD-HAP/PA sampling in the laboratory, the NTD-HAP/PA was used to analyze the concentration of volatile compounds in some petrol stations. Three calibrated NTD-HAP/PA were used for air sampling at about 1.70 m above the ground level. Immediately after sampling, all samplers were capped with a new and clean silicone septum and placed on a dry ice bed. As the BTEXs were highly volatile, all NTD-HAP/PA were analyzed over maximum 1 h after sampling in order to avoid volatilization.

RESULTS AND DISCUSSION

Characterization of HAP/PA

After synthesizing the HAP/PA adsorbent, the structural properties of the adsorbent were investigated. FTIR was used to study the functional groups on the surface of the adsorbent. The absorption wavelength for hydroxyapatite was measured in the range of 400-4000 cm^{-1}. The FTIR spectra confirmed the formation of hydroxyapatite. Asymmetric tensile and flexural modes appeared at 1043.64, 605.37, and 561.03 cm^{-1}, assigned to the phosphate group (See Fig. 3A). The peak at 1384.68 cm^{-1} corresponds to the carbonate group [25,26].

The absorption wavelength for polyaniline was recorded in the range of 400 to 4000 cm^{-1}. The peaks appeared at 1590 and 1480 cm^{-1} were attributed to the tensile vibration of the quinoid rings and the benzenoid rings, respectively.

The peak observed at around 1300 cm^{-1} was allocated to the vibration of the C-N bond stretch, so FTIR confirmed the structure of polyaniline [21,24,27].

In the FTIR HAP/PA study, the structure of hydroxyapatite and polyaniline is visible. Some peaks (100, 1700 cm^{-1}) appear to have changed slightly due to the interaction with the composite Fig. 3A.

Moreover, to study the morphological features of the adsorbent, scanning electron microscope (SEM) was applied. As shown in Fig. 3C, the prepared powder hydroxyapatite has nanometer-sized particles with uniform dispersion.

SEM images of the HAP/PA (Fig. 3D) showed that the coating of hydroxyapatite with polyaniline led to a change in the structure of the hydroxyapatite. Figure 3C shows that there was a large rod in the raw hydroxyapatite. After formation with polyaniline, the surface of the HAP/PA composite had porous micro-structure and agglomerates of typical shapes (Fig. 3D), which can improve its capacity for adsorption of the analytes of interest.

In this step, X-ray diffraction (XRD) was also applied to evaluate the phases formed in the proposed adsorbent. As observed in the XRD analysis of the hydroxyapatite (Fig. 3F), the peaks of hydroxyapatite are clearly identifiable in the range $2\theta = 25\text{-}35°$.

Figure 3E shows the XRD pattern of hydroxyapatite with polyaniline. Polyaniline peaks cannot be clearly observed in the XRD pattern of the HAP/PA nanocomposite, because the polyaniline peaks were weak and covered with hydroxyapatite peaks in the background. This spectrum (Fig. 3E) is consistent with the spectrum reported in the study of Li Huixia *et al.* [21].

The thermal stability of the adsorbents was tested by thermal analysis. The results of the TGA-DTA curve showed that the adsorbent had a weight loss of less than 6% up to 250 °C, and this weight loss is usually related to the loss of moisture. The percentage of weight loss absorber up to 800 °C is less than 22%, and this shows that the adsorbent has excellent thermal stability, and at high temperatures, it can maintain its structure. The results of the thermal analysis of the adsorbent are shown in Fig. 3B.
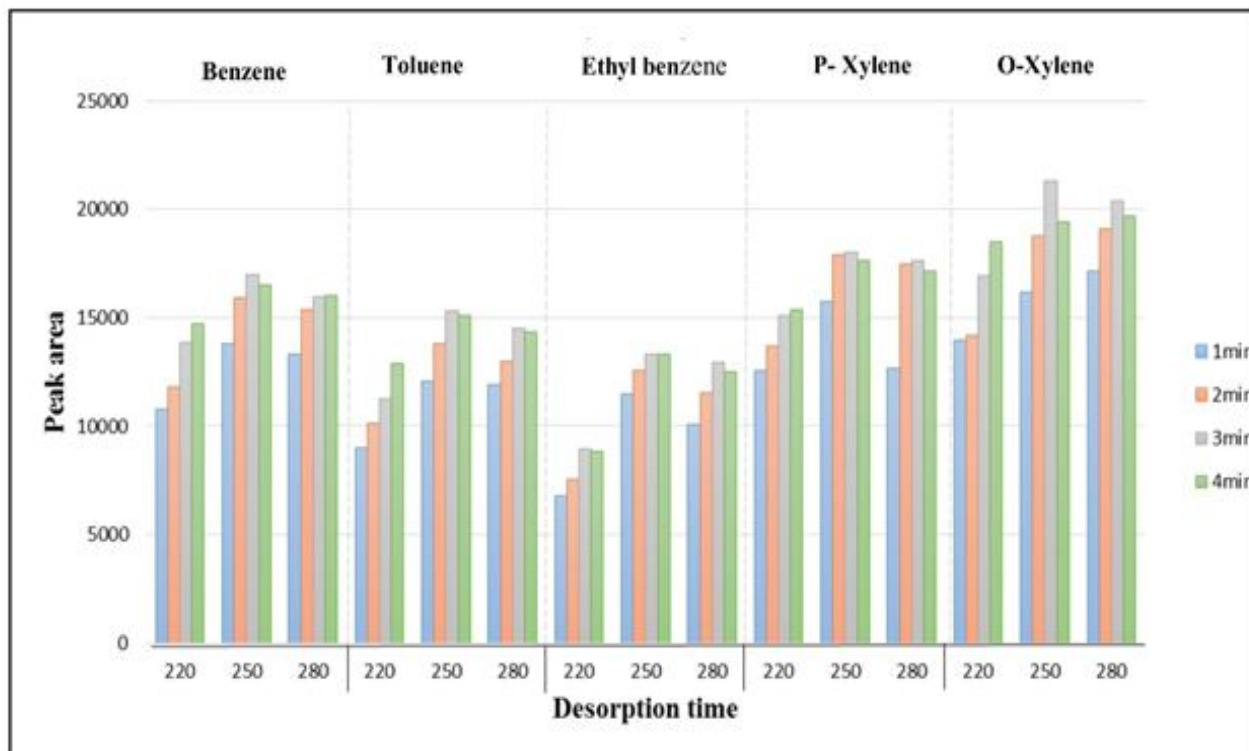
Desorption Parameters

As mentioned above, determining the optimal
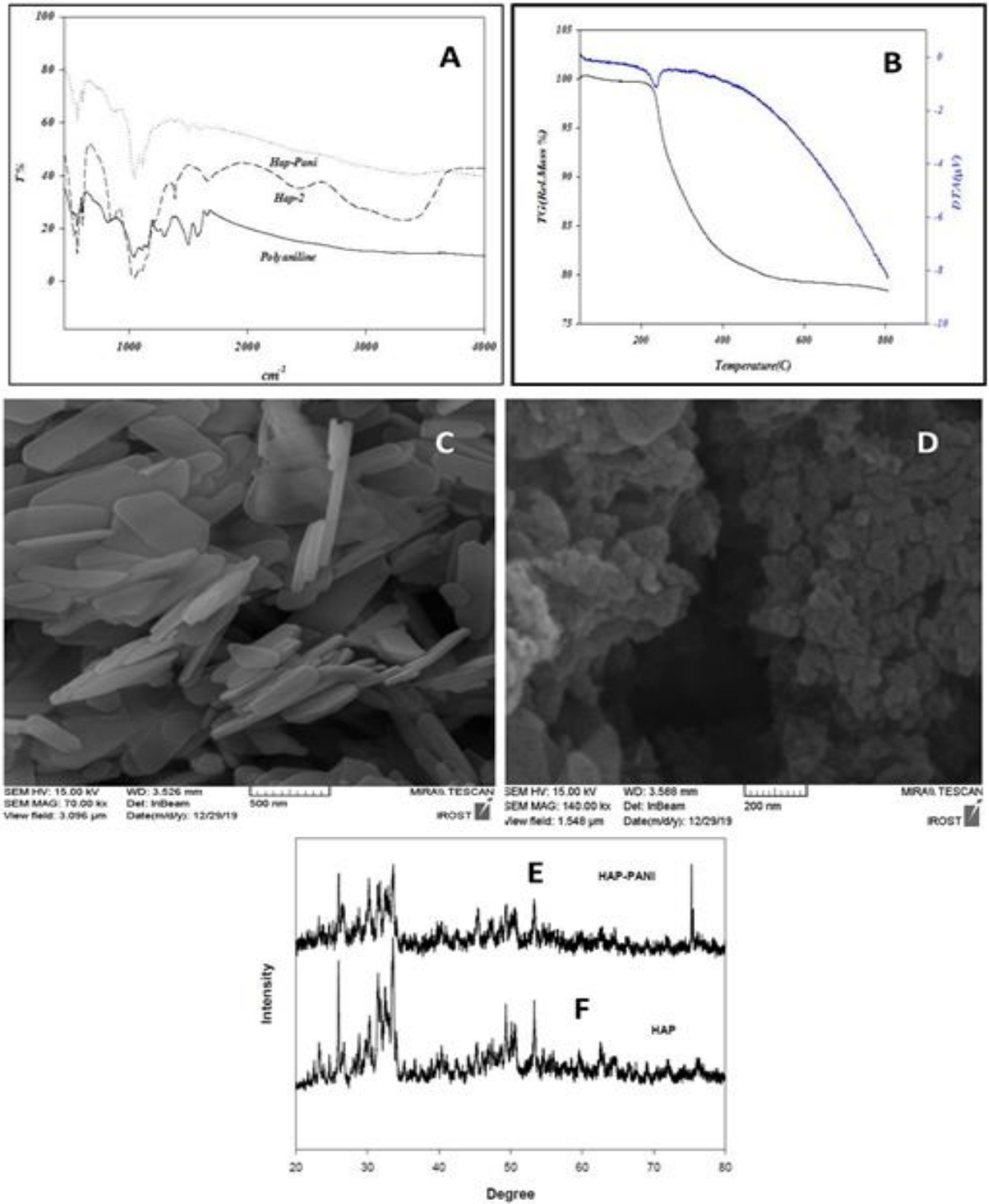
Fig. 3. (A) FT-IR spectra of HAP/PA, HAP and PA. (B) TGA-DTA curve of HAP/PA. (C) SEM images of hydroxyapatite. (D) SEM images of HAP/PA. (E) XRD pattern of HAP/PA. (F) XRD pattern of hydroxyapatite.

Fig. 4. Optimum desorption temperature and time.

desorption conditions is necessary to ensure that all analytes are separated from the adsorbent bed with the lowest carryover effect. Thus, the extraction time was evaluated at various desorption times in the range of 1-4 min. According to the results, the highest peak area of the analytes was obtained at 3 min of desorption time, and a further increase in desorption time did not enhance the desorption efficacy of the analytes. Also, three temperature levels of 220, 250, and 280 °C were investigated on the desorption efficiency to determine the appropriate desorption temperature. The highest peak area of the compounds of interest were obtained at 250 °C. It should be noted that no significant difference was found between the results obtained at 250 and 280 °C. Based on what was said, the optimum extraction temperature for the target pollutants in this study was at 250 °C, and the appropriate desorption temperature for the studied compounds was determined at 3 min. The finding of the optimization of desorption parameters is displayed in Fig. 4.

Breakthrough Volume Investigation

As mentioned above, to estimate the breakthrough volume of the prepared NTD, two adsorbent loaded NTDs were connected in series, and sampling from the chamber was performed by the first NTD, while the second one was connected to a small pump to pass a determined volume of air through the both NTDs. The results of the second NTD analysis showed that no analyte was detected in the second NTD after even > 4 h of sampling at concentrations several times higher than the TLV. Findings indicated that the proposed adsorbent could be successfully used to detect the analyte in the environmental concentration range.

Carryover Effect

The prepared NTD was used for the collection of the analytes from the test chamber (in the concentration range of TLV-TWA). In this regard, the NTDs sampled were injected into a GC injection port along with 1 ml of nitrogen gas. To calculate the amount of carryover effect, the NTD

Table 1. Results of Repeatability, Reproducibility, LOD, LOQ and LDR (R^2) of the NTD Packed with HAP/PA Compared with the NIOSH-1501 Method for Sampling and Analysis of the Studied Compounds Using the NTD-HAP/PA

Analyte	Repeatability (RSD% for one NTD with HAP/PA - 4 different concentrations with three replications				Reproducibility (RSD% for three NTDs HAP/PA - of a constant concentration with three replications)			LOD	LOQ	LDR	R^2	LOD-NIOSH 1501
	0.1	1.5	3	8	NTD-A	NTD-B	NTD-C	ng ml^{-1}	ng ml^{-1}	ng ml^{-1}	-	ng ml^{-1}
Benzene	0.39	0.17	0.47	3.5	0.36	0.20	0.36	0.01	0.04	0.7-5.33	0.96	500
Toluene	0.2	0.7	1.13	3.7	0.4	1.18	2.03	0.01	0.05	0.6-13.55	0.98	500
Ethyl benzene	0.24	0.32	1.3	2.3	1.62	0.77	9.69	0.02	0.09	0.6-27.18	0.97	700
P-Xylene	0.32	0.92	3.4	12.07	4.68	1.79	4.19	0.14	0.48	22.4-130.25	0.86	700
O-Xylene	0.27	0.26	4.09	10.95	4.55	3.78	5.43	0.13	0.45	21.4-151.96	0.86	800

was analyzed for the second time. The obtained results implied that the carryover effect was less than 10% for all of the cases analyzed.

Method Validation

To investigate the accuracy of NTD packed with the proposed absorbent (HAP/PA), as one of the most essential parameters invalidation, side by side sampling of BTEX was performed with two methods (the proposed NTD and the NIOSH recommended method) under optimized conditions. Before performing this step, the calibration curves for all the analytes were prepared separately in the range of 5-100 µg ml^{-1}. As can be seen in Table 1, there was an acceptable correlation between the two methods. Based on the obtained results, the R^2 values were in the range of 0.86-0.98 for all of the analytes. The examination of the repeatability of the proposed NDT implied that at all concentrations, the RSD was less than 15%, indicating that

the NTD packed with the HAP/PA had acceptable repeatability (Table 1).

The findings of the present study on the reproducibility of packed needles with HAP/PA adsorbent showed that the percentage of RSD was in the range of 0.2-9.7%. Therefore, it can be concluded that the packed NTD with the HAP/PA adsorbent offered a suitable reproducibility (Table 1).

As described in the materials and methods section, to investigate the performance of packed needles with HAP/PA adsorbent in the adsorption process of the target compounds, the LOD, LOQ and LDRs values for each analyte were determined separately and are presented in (Table 1).

The results demonstrated that the LOD and LOQ values for the studied compounds using HAP/PA adsorbent ranged from 0.01-0.14 ng ml^{-1} and 0.04-0.48 ng ml^{-1}, respectively. According to the results, the R^2 values of the calibration curve for each analyte indicated a wide LDRs for the

Table 2. Concentration of BTEXs in Petrol Station Using NTD- HAP/PA

Analyte	Concentration (ng ml^{-1}) No sample				$\bar{x}$	σ
	1	2	3	4		
Benzene	0.8	1.14	1.00	0.69	0.91	0.20
Toluene	1.18	1.64	1.36	1.01	1.30	0.27
Ethyl benzene	3.74	1.67	3.40	1.66	2.62	1.10
P-Xylene	11.11	14.25	14.83	14.50	13.67	1.72
O-Xylene	9.46	8.68	13.64	10.70	10.62	2.17

Table 3. Comparison between NTD-HAP/PA Method and other NTD Studies for Volatile Organic Compound

Matrix	Analyte	Sorbent	LOD (µg l^{-1})	LOQ (µg l^{-1})	RSD (%)	R^2	Ref.
Air	n-Hexane	Nano-carbon aerogel	0.013	0.04	0.12-3.19	0.998-0.9986	[10]
Air	Hexane	DVB/Carboxen	0.013	0.043	(Inter) 19.20 (Intra) 4.16	0.99	[28]
Air	o-Xylene	PDMS/Carboxen	0.015	0.051	(Inter) 67.66 (Intra) 8.55	0.99	[28]
Air	Toluene	PDMS/Carboxen	0.039	0.131	(Inter) 35.16 (Intra) 10.45	0.90	[28]
Air	HVOCs	UiO-66-NH$_2$	0.01-0.03	0.02-0.05	(Inter) 3.8-10.2 (Intra) 2.3-9.1	0.98-0.99	[29]
Air	VOCs	DVB/carbopack X/ carboxen	0.0003-0.194	0.0001-0.647	2.67-19.52	0.89-0.99	[28]
Air	VOCs	Carbotrap B	0.03-0.04	0.1-0.13	4.28-15.63	0.84-0.99	[30]
Air	VOCs	HAP/PA Nano-composite	0.01-0.14	0.04-0.48	0.2-9.69	0.86-0.98	This study
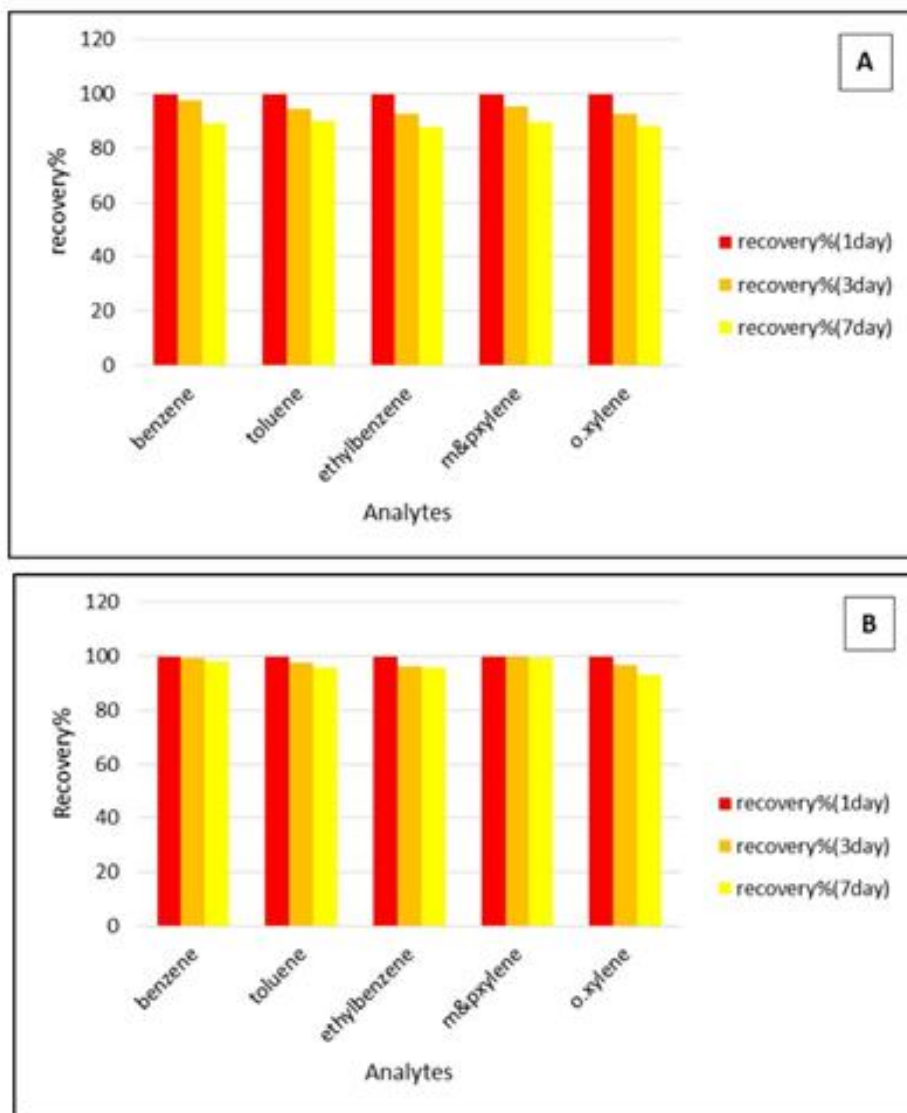
Fig. 5. The storage capability of NTD-HAP/PA for BTEX. A) at 25 °C, and B) at 4 °C.

studied compounds. It should be noted that the LOD values of the standard NIOSH method for BTEXs compounds were in the range of 500-800 ng ml⁻¹, whereas in the present study, LOD values of the proposed NTD ranged from 0.01-0.14 ng ml⁻¹.

Analysis of Real Samples in Petrol Stations

The results of field sampling of BTEXs are shown in Table 2. At the petrol station, the concentrations of toluene, ethyl benzene and xylenes were lower than those

recommended by NIOSH recommended exposure limits (RELs). However, benzene concentration in petrol station was higher than the recommended value (0.32 mg m⁻³).

Storage Time

The evaluation of storage stability indicated that the NTD- HAP/PA containing target analytes (BTEXs) was capable of maintaining the compounds of interest for seven days at 4 °C and three days at 25 °C. The storage stability results of the NTD-HAP/PA are displayed in Fig. 5.

Comparative Study

To investigate the efficacy of HAP/PA packed NTD, the findings of the present study were compared with other relevant studies. The results showed that the NTD- HAP/PA performance is comparable with the results of other studies. However, by comparing the results of the storage stability of the compounds with the HAP/PA adsorbent and the NIOSH recommended method, it was found that the solid sorbent tube offered higher storage stability during 30 days compared with the proposed NTD for the studied analytes. Comparison results with other studies are shown in Table 3.

CONCLUSIONS

In this study, the efficiency of NTD-HAP/PA, as a new sorbent, was investigated for sampling and analyzing volatile organic compounds. The performance of the NTD-HAP/PA was comparable with the NIOSH-1501 method. The findings showed that the NTD packed with HAP/PA adsorbent had a much higher sensitivity than that of the standard NIOSH-1501 method for the sampling and analysis of the compounds studied in this research.

There are unique features of this adsorbent including availability and low cost of synthesis method, excellent thermal resistance, high accuracy and repeatability, high sensitivity compared with NIOSH-1501 method, caused NTD-HAP/PA as a suitable tool, powerful, swift, sensitive, and reusable compared to conventional sampling and analysis methods of volatile organic compounds at low concentrations in the workplaces.

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