

## DEVELOPMENT OF A NEEDLE TRAP DEVICE PACKED WITH HKUST-1 SORBENT FOR SAMPLING AND ANALYSIS OF BTEX IN AIR

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**Abstract.** In this study, we developed a needle trap device packed with HKUST-1 (Cu-based metal-organic framework) for the sampling and analysis of benzene, toluene, ethylbenzene, and xylene (BTEX) in ambient air for the first time. The HKUST-1 was synthesized *via* the electrochemical process. Afterwards, the adsorbent was packed into 22 gauge needles. To provide the different concentrations of BTEX, the syringe pump was connected to the glass chamber to inject a specific rate of the BTEX compounds. Design-expert software (version 7) was used to optimize the analytical parameters including breakthrough volume, desorption conditions and sampling conditions. The best desorption conditions were achieved at 548 K for 6 min, and the best sampling conditions were determined at 309 K of sampling temperature and 20 % of relative humidity. According to the results, the limit of quantification (LOQ) and limit of detection (LOD) of the developed needle trap device (NTD) were in the range of 0.52–1.41 and 0.16–0.5 mg/m<sup>3</sup>, respectively. In addition, the repeatability and reproducibility of the method were calculated to be in the range of 5.5–13.2 and 5.3–12.3 %, respectively. The analysis of needles stored in the refrigerator (>277 K) and room temperature (298 K) showed that the NTD can store the BTEX analytes for at least 10 and 6 days, respectively. Our findings indicated that the NTD packed with HKUST-1 sorbent can be used as a trustworthy and useful technique for the determination of BTEX in air.

**Keywords:** air, HKUST-1, metal-organic framework, electrochemical, needle trap device, volatile organic compounds.

### 1. Introduction

Benzene, toluene, ethylbenzene, as well as *m*-xylene, *o*-xylene, and *p*-xylene (BTEX), as a major group of air pollutants, are classified as priority contaminants.<sup>1</sup> The International Agency for Research on Cancer (IARC) has classified benzene as a human carcinogen (group A) and ethylbenzene as possibly carcinogenic to humans (Group 2B).<sup>2</sup> Acute exposure to benzene is associated with nervous disorders, and ingestion of high levels of benzene can cause seizures, dizziness and nausea, vomiting, coma, and eventually death. Chronic exposure to benzene is also associated with lymphoid leukemia, multiple myeloma, non-Hodgkin lymphoma and lung cancer.<sup>2</sup>

Various methods have been proposed to evaluate the exposure to BTEX such as NIOSH 2549, NIOSH 1500, EPA TO-17, EPA TO-14A, and OSHA 1005. These methods are commonly used for pre-concentration of BTEX followed by chromatography analysis.<sup>3</sup> Despite excellent reliability, the main drawbacks of these methods include complexity, time-consuming, and requiring sample preparation equipment. This notably delimits their application for monitoring of air pollutants in many developing countries with severe air problems.

To accurately measure volatile organic compounds (VOC) in the air, suitable sampling and pre-concentration techniques are required to detect tiny amounts of these compounds with high sensitivity. In recent years, various sample preparation techniques have been used for determination of organic contaminants in air, such as solid-phase extraction (SPE) and solid-phase micro-

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extraction (SPME). SPE is a common extraction technique, which requires large sample volume and long sampling time. In recent years, a lot of efforts have been made to improve the characteristics of the SPE.<sup>4,5</sup> The extraction capacity of SPME fibre is typically based on equilibrium. Until now, this method has been used in various sciences.<sup>6,7</sup>

Needle trap device (NTD) is a new tool for air sampling, which combines the advantages of SPE and SPME. The NTD was first introduced by Pawliszyn team work in 2001. This microextraction technique has received much interest from researchers in recent years.<sup>8</sup> In the NTD technique, all steps including sampling, extraction, preparation, and analysis of pollutants existing in workplaces are performed in one step and it requires no additional preparation and solvent extraction steps. Nowadays, the NTD is applied for extraction of analytes from different matrices such as water, biological and air samples.<sup>9-17</sup>

Metal-organic frameworks (MOFs) are a new class of porous materials that have high absorption capability and unique catalytic properties.<sup>18,19</sup> The MOFs offer many advantages for measuring of trace analytes in complex matrices such as high selectivity, high specific surface area and large porous volume.<sup>20</sup>

Selective absorption of the target analytes by MOFs is based on their molecular geometry, size, hydrophilic, and hydrophobic properties. Also, MOFs are quite flexible against different target molecules,<sup>21</sup> while many conventional sorbents have a relatively low selectivity or limited adsorption capacity for environmental pollutants. In this study, Cu<sub>3</sub>(BTC)<sub>2</sub> (other names: MOF-199 and HKUST-1, BTC = 1,3,5-benzene-tricarboxylic acid) as a MOF sorbent was first synthesized using the electrochemical method, and then packed inside steel needle for sampling and analysis of tiny amounts of BTEX in air.

In HKUST-1, Cu(II) ions make dimmers, where a copper atom is coordinated by oxygen from 1,3,5-benzene-tricarboxylic acid linkers and water molecules.<sup>22</sup> HKUST-1 was first introduced by Chui *et al.* in 1999.<sup>23</sup> So far, many efforts have been made to improve its properties.<sup>24</sup> Despite our literature review, there was no study on the use of NTD packed with HKUST-1 as a sorbent for sampling and analysis of pollutants in the air.

Therefore, this paper focused on the development and validation of a noncomplex and valid method for determining BTEX in air using NTD packed with HKUST-1. In this regard, the influences of different

analytical parameters, including desorption temperature, desorption time, sampling temperature, and sampling time were evaluated and optimized using response surface methodology (RSM) based on the central composite design (CCD). Moreover, in order to investigate the field applicability of the proposed method, it was used for the detection of BTEX in a real field.

## 2. Experimental

### 2.1. Materials

All analytes used in this study including benzene, toluene, ethylbenzene, *ortho*-, *meta*-, and *para*-xylene were purchased from Merck Co. (Germany). For the synthesis of HKUST-1, trimesic acid (H<sub>3</sub>BTC, Merck, 95 %), potassium nitrate (KNO<sub>3</sub>, Sigma-Aldrich, 99 %), ethanol (Merck, 99 %) were used without further purification. All solutions were prepared with distilled water at room temperature.

### 2.2. Instruments

Chromatographic analyses were conducted using a gas chromatography device (GC, Shimadzu GC-2010) equipped with a capillary VOCOL (R) column (60' 0.53mm, DF: 3.00 μm) and flame ionization detector and injection port (up to 723 K). The GC system was operated under the following conditions: split mode 1:8.5, SPL pressure 150.9 kPa, column flow 1 mL/min, purge flow 3 mL/min, linear velocity 22.4 cm/s and total flow 12.5 mL/min. Nitrogen gas with high purity of 99.99 % was used as carrier gas in the GC device. The temperature program of the GC device was started at 363 K, and then increased to 453 K with the rate of 6 K/min. Total run time was 15 min and detector temperature was set at 473 K.

The characterization of the synthesized MOF was investigated with different analytical tests. For this reason, a field emission scanning electron microscopy (FE-SEM, Hitachi S-4160) using an APD 2000 (ItalStructures, Riva Del Garda, Italy) was used for the powder X-ray diffraction (XRD) patterns. The apparatus was equipped with a linear sensitive detector (SAINT-GOBain). FTIR spectra of the synthesized MOF were obtained on a Perkin-Elmer GX FT-IR spectrometer.

A hotplate (D500, Iran) was employed for heating the standard module for the optimization of sampling parameters. The packed NTD was attached to a low-flow

sampling pump (SKC, model 222-3) and then used for the sampling of the analytes of interest from the standard chamber. The charcoal sorbent tubes (SKC, No. 226-1) were also used for side-by-side sampling of the analytes. The studied Cu-MOF was packed inside the needle (22G×90 mm, Dispo, Japan). Luer lock syringes (3 mL, Ava-Iran) were used to transfer the adsorbed BTEX from the NTD: Cu-MOF into the GC injector. A high-volume sampling pump (SKC, Biolite) was applied along with the standard glass chamber for preparing the desired concentrations. To adjust the temperature of air flow inside the glass chamber a digital thermometer (model SUN15-TI) was used, and its humidity was controlled by a hygrometer (model SUN25-H).

### 2.3. Pilot Study

Fig. 1 shows the pilot used in the present study to generate the constant concentrations of BTEX compounds at laboratory scale. The constant stream of air in the chamber was provided using a high-volume vacuum pump. Also, the syringe pump was connected to the glass chamber to inject a specific rate of the BTEX compounds into the standard chamber.

The temperature and relative humidity of the passing air were monitored using a digital thermometer and hygrometer mounted inside the chamber. The concentration of the BTEX compounds inside the glass chamber was also determined in accordance with the standard NIOSH manual of analytical methods.<sup>25</sup>

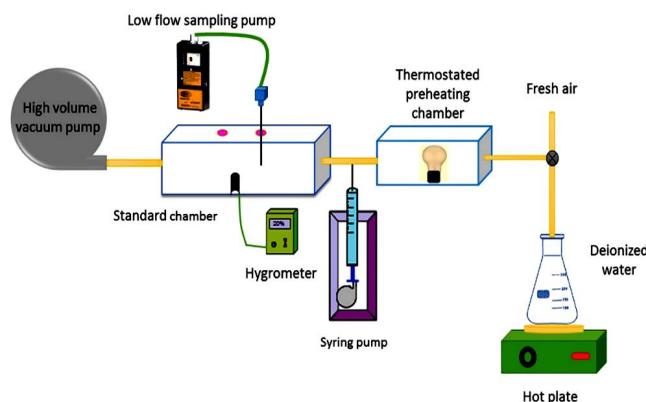


Fig. 1. A simple schematic of the standard chamber

### 2.4 Synthesis of HKUST-1

Cu-MOF was synthesized in a glass bottle. The bottle contained a precursor solution and tow-electrodes. The auxiliary electrode was made up of a stainless steel

sheet and the working electrode was made of copper plate with the dimensions of 20×10×3 mm.

In this study, we synthesized the Cu-MOF according to our previous study [19] with some changes. A supporting electrolyte (0.127 g) of sodium nitrate (0.1M) was dissolved in 15 mL of deionized water and considered as solution A. Furthermore, to prepare solution B, 0.525 g (2.5 mmol) of trimesic acid (H<sub>3</sub>BTC) was dissolved in 15 mL of ethanol. Then, while solution B was stirred, the solution A was added and used for the electro-synthesis process.

In order to prepare the precursor solution, the copper plate was inserted into solution, and the adsorbent synthesis was carried out using constant current electrolysis (1 mA·cm<sup>-2</sup> for 10800 s). The solution was filtered to separate the precipitated sorbent, and then washed with ethanol and distilled water to remove impurities.

The stability of the frameworks was achieved at room temperature for about 8 h. Then, the ensnared solvent molecules were removed from adsorbent at 423 K for 24 h. The adsorbent was activated in a vacuum oven at 473 K for 5 h before packing inside the needle.

### 2.5. NTD Preparation

In this study, medical spinal needles (22G×90 mm) were used as the main body of the proposed sampler and then packed with a mixture of 1.5 mg of Cu-BTC and 1 mg of glass powder (to prevent the clogging inside the NTD). Finally, both sides of the packed sorbent were sealed with 3 mm of fiberglass. After preparation, the needle was attached to the personal sampling pump, and the airflow through the NTD was determined using a soap bubble flow meter. A passing flow rate of about 3 ml/min was selected for the packed NTDs as an optimal flow rate through the NTD.<sup>26</sup>

### 2.6. Sampling and Desorption Parameters

Design expert software (v.6.0) was used to investigate the influences of several parameters and their interaction effects on the sampling efficiency of the NTD: Cu-MOF. RSM is a preferable method for the optimization of analytical agents that includes mathematical and statistical techniques.<sup>27</sup>

CCD is frequently applied in RSM empirical design.<sup>28</sup> This design consisted of a total of 14

experiments in 2 blocks (two days). In the present study, equation 1 was applied to predict the optimal conditions.

$$Y = B_0 + \sum_{i=1}^n B_i X_i + \sum_{i=1}^n b b_i x_i^2 + \sum_{1 \leq i \leq j}^n b_{ij} x_i x_j \quad (1)$$

where  $Y$  is the peak area response;  $B_0$  is the constant of model;  $B_i$  is the coefficient of the variable;  $x$ ,  $n$ ,  $b_{ij}$  and  $b_{ii}$  are the coded variables, number of variables, coefficient of variable interactions and coefficient of quadratic model variable, respectively.

In the first step, the influences of desorption temperature (493, 513, 533, 553, and 573 K), time (1, 3, 5, 7, and 9 min) and their interactions were investigated on desorption process under constant sampling conditions (298 K, 20 % of relative humidity). Afterwards, the sampling conditions were optimized. For this reason, the factorial point levels of independent variables including five levels of sampling temperatures (288, 298, 308, 318 and 328 K), five levels of relative humidity (20, 30, 40, 50, and 60 %) and their interactions were evaluated on the sampling efficiency under optimum desorption conditions. The variables examined for optimization of sampling and desorption conditions are shown in Table 1. The concentrations of BTEX in the standard chamber were made almost equal to the time-weighted average (TWA) concentration. After sampling, NTD was placed into the injection port of the GC device and after the predetermined desorption time, 3 ml of nitrogen gas was

injected into the NTD through a medical syringe to deliver the trapped analytes into the GC column.

**Table 1.** Variables in the matrix of CCD for optimization of sampling and desorption conditions of the NTD: Cu-MOF

Independent variables		Levels				
		$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Desorption condition	Temperature, K	493	513	533	553	573
	Time, min	1	3	5	7	9
Sampling condition	Temperature, K	288	298	308	318	328
	Humidity, %	20	30	40	50	60

## 2.7. Breakthrough Volume Investigation

At this stage, two NTDs were first connected by a plastic tube and then the sampling was conducted at a flow rate of 3 mL/min from the standard chamber. For assessing the breakthrough volume, various concentrations of the analytes were prepared inside the standard chamber ranging from 0.2 to 5 times the TWA values of BTEX, as the highest concentrations occurred in the workplaces. Table 2 presents the experimental steps (14 runs and 2 blocks) for determining and modelling breakthrough volume in NTD: Cu-MOF.

**Table 2.** Full factorial CCD matrix for assessing breakthrough volume

Independent variables		Range and levels				
		$-\alpha$	$-1$	$0$	$+1$	$+\alpha$
Benzene	Volume, mL	150	350	550	750	950
	Concentration, mg/m <sup>3</sup>	0.32	2.24	4.15	6.07	7.99
Toluene	Volume, mL	150	350	550	750	950
	Concentration, mg/m <sup>3</sup>	15.1	105.5	196	286	377
Ethylbenzene	Volume, mL	150	350	550	750	950
	Concentration, mg/m <sup>3</sup>	17	121.5	225.5	330	434
<i>m-, p-, o-</i> -xylene	Volume, mL	150	350	550	750	950
	Concentration, mg/m <sup>3</sup>	87	608	1129	1650	2171

In order to study the breakthrough volume, the percentage of the penetrated analyte in the second NTD was calculated according to Eq. 2.

$$I = \frac{I_{a_2}}{I_{a_2} + I_{a_1}} \times 100 \% \quad (2)$$

where  $I$  is the percentage of analyte penetrated to the second NTD;  $I_{a_1}$  is the peak area in NTD No. 1;  $I_{a_2}$  is the peak area in NTD No. 2.

The RSM method suggested multiple concentrations and volumes as optimal conditions prior to breakthrough, of which the volume corresponding to the highest concentration was selected as the break-through volume.

## 2.8. Carryover Effect

Desorption conditions such as time and temperature have an effective impact on memory effect or carryover

of a sampler. Memory effect is caused by the defective desorption. Factors affecting the carryover effect include analyte stability, analyte volatility and affinity of analyte molecules to sorbent. Also, increasing desorption temperature and time can cause a decrease in the lifespan of the packed sorbent. Hence, to select the best desorption conditions, the maximum tolerable temperature of the sorbent material and carryover effect must be considered.

Upon completion of desorption process under the optimal conditions, the NTD was again injected into injection port of the GC device to determine the BTEX residues on the sorbent. Sampling was carried out at the TWA concentration range.

## 2.9. Method Validation

Method validation is described as a proof-of-procedure (through scientific studies) to ensure that the developed method has an acceptable performance. In this study, in order to validate the developed method, some analytical parameters of the NTD were examined in accordance with the IUPAC guidelines.<sup>29</sup>

### 2.9.1. Accuracy

In this study, in order to determine the accuracy of the proposed method, the results of sampling and analysis of the analytes with the NTD were compared with standard method (NIOSH 1501). For this reason, side by side sampling was conducted using the Cu-MOF and charcoal sorbent tube from the standard chamber. The experiment was repeated six times, and eventually the measurement results were compared to those obtained by the NIOSH standard method using One-Sample T-Test.

### 2.9.2. Repeatability and reproducibility

To calculate the repeatability of the proposed method, three concentrations of the analytes were sampled using an NTD with six repetitions (18 samples). The reproducibility was also determined through measuring a specified concentration of the analytes using three NTDs with three replications (9 samples). Finally, the standard deviation (RSD) of the results was calculated.

### 2.9.3. Determination of LOD, LOQ, LDR

By reducing the amount of analytes in the glass chamber, the concentrations corresponding to the signal-to-noise ratios (S/N) of 3 and 10 were

considered as LOD and LOQ, respectively. The total sampling volume was 30 ml with the sampling flow rate of 3 ml/min.

### 2.9.4. Storage time

Since NTDs are used as a field sampler, the storage capability of the analyte in the NTDs is an important factor prior to the laboratory analysis. In order to evaluate this parameter, the storage capability of the NTD method was studied by 33 NTDs samples. The sample was taken under optimum sampling conditions while the concentration of the analytes was within the range of TLV-TWA, and then Teflon caps were used to seal both ends of NTDs. On the first day, three NTDs were analysed, and half of the remaining NTDs were stored at laboratory temperature (298 K), and other NTDs were stored in the refrigerator (277 K) for 1–10 days. Afterwards, the samples were injected into GC-FID under optimum desorption conditions. The peak area responses of the compounds of interest were plotted versus those obtained by the control NTDs, which were injected in the first day. The control NTDs were immediately injected into the GC system after sampling.

### 2.9.5. In-field measurements

Due to the importance of using the developed sampler in the real environment, in the second phase of the study, the proposed sampler was used for field monitoring of the analytes of interest under the optimal conditions obtained from the previous steps. For this purpose, six NTDs packed with Cu-MOF were used for the sampling of the BTEX concentrations in ambient air of fuelling stations for 30 min. The concentrations of BTEX were also determined using the charcoal sorbent tubes according to the NIOSH method, and eventually the measurement results were compared to those obtained by the proposed method.

## 3. Results and Discussion

### 3.1. Characterization of Cu-MOF

The function and bonding attributes of the Cu-MOF and H<sub>3</sub>BTC *via* IR spectra were indicated in Fig. 2. The lack of peaks at the range 3085–2554 cm<sup>-1</sup> in the

Cu-MOF pattern indicated that the carboxylic acid function contributed to the composition of Cu-MOF. The relocation of asymmetrical and symmetrical vibration coupled peaks of carboxylate anions (1646–1578 and 1443–1375  $\text{cm}^{-1}$ ) can be allocated to the coordination of ligand with the cation.

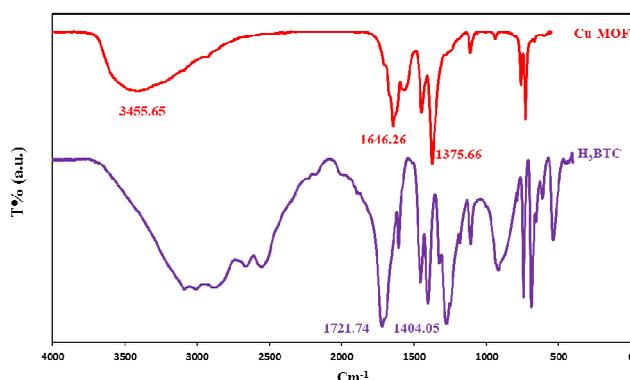


Fig. 2. FT-IR spectra of H<sub>3</sub>BTC and Cu-MOF

Fig. 3 demonstrates the crystallinity of the adsorbent by *ex-situ* powder X-ray diffraction. The survey of PXRD analysis showed that the broad corner of PXRD pattern corresponded to the well-distinctive crystallinity of the adsorbent compared with the simulated pattern.<sup>19</sup>

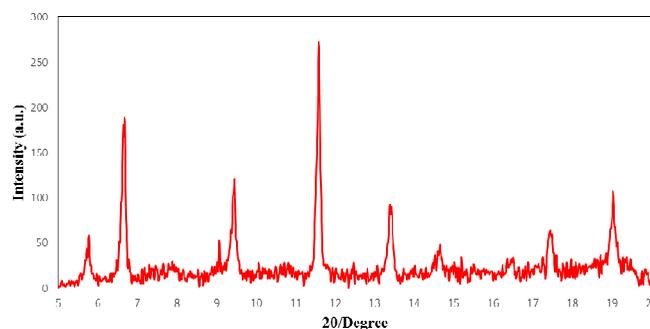


Fig. 3. PXRD pattern of the Cu-MOF

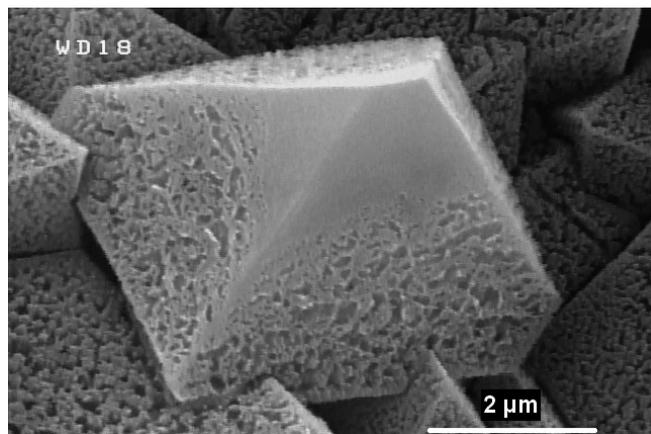
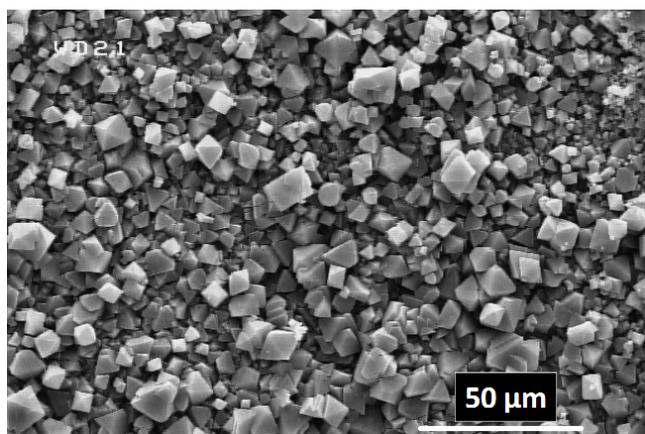


Fig. 4. FE-SEM picture of Cu-MOF

The FE-SEM pictures of the powder Cu-MOF in  $1 \text{ mA} \cdot \text{cm}^{-2}$  for 10800 s has been shown in Fig. 4. The images present the sponge pyramidal microcrystals of Cu-MOFs.

### 3.2. Desorption Parameters

In this stage, the effects of desorption time and temperature were modelled and optimized using CCD and RSM by Design-expert software (v 7.0; USA Stat Ease). Table 3 shows the ANOVA results of the offer model for desorption parameters. The features of the offer models were evaluated using  $p$ -value,  $F$ -value,  $R^2$ , and adjusted  $R^2$  (the adjusted determination coefficient).

The desorption conditions model  $F$ -value for all analytes, and corresponding  $p$ -value of  $<0.0001$  imply that the models are significant, and there are only less than 0.01 % chance that a model  $F$ -value of this value could occur due to noise.

The optimal values of desorption temperature and time of the proposed method are presented in Table 4.

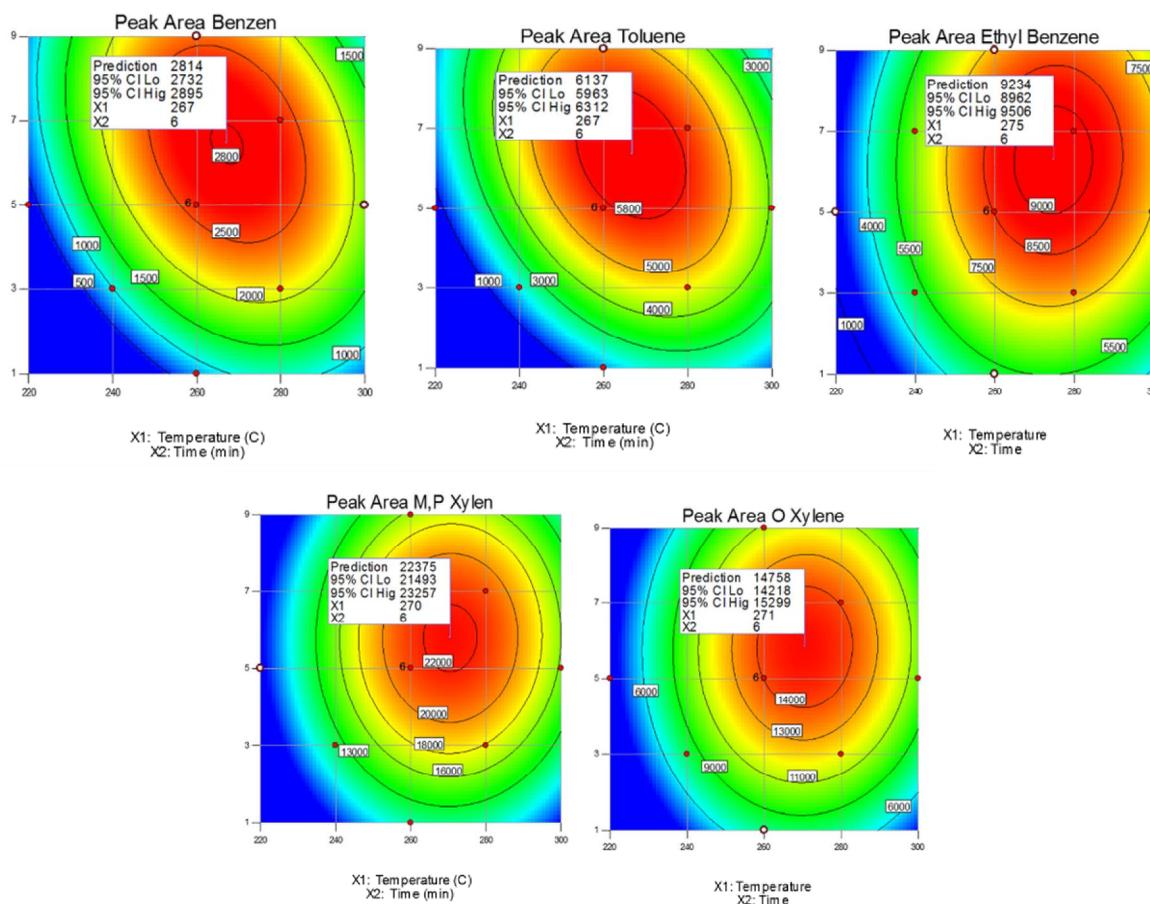
Fig. 5 illustrates the interaction effect between desorption temperature and time on the NTD efficiency. Since BTEX compounds are highly volatile, they require low time and temperature to desorb from the adsorbent surface. These results are consistent with the findings of other studies on sampling and analysis of BTEX with SPME.<sup>3,30,31</sup>

**Table 3.** ANOVA results of sampling and desorption variables

Source	Desorption conditions				Source	Sampling conditions			
	Sum of squares	D.F	F-value	p-Value		Sum of squares	D.F	F-value	p-Value
<b>Benzene</b>									
Square	$7.72 \cdot 10^6$	5	229.55	<0.0001	Square	$9.379 \cdot 10^6$	5	1585.16	<0.0001
A: Temperature	$1.853 \cdot 10^6$	1	275.41	<0.0001	A: Temperature	$73.50 \cdot 10^2$	1	6.21	0.0415
B: Time	$2.085 \cdot 10^6$	1	309.83	<0.0001	B: Humidity	$6.734 \cdot 10^6$	1	5690.41	<0.0001
AB	$1.076 \cdot 10^5$	1	15.99	0.0052	AB	$13.572 \cdot 10^3$	1	11.47	0.0117
A <sup>2</sup>	$3.255 \cdot 10^6$	1	483.71	<0.0001	A <sup>2</sup>	$8.312 \cdot 10^5$	1	702.42	<0.0001
B <sup>2</sup>	$1.358 \cdot 10^6$	1	201.73	<0.0001	B <sup>2</sup>	$1.002 \cdot 10^6$	1	846.36	<0.0001
$R^2 = 0.9239$ $R^2$ adjusted = 0.9896					$R^2 = 0.9991$ $R^2$ adjusted = 0.9985				
<b>Toluene</b>									
Square	$3.694 \cdot 10^7$	5	233.58	<0.0001	Square	$1.242 \cdot 10^7$	5	10958.42	<0.0001
A: Temperature	$8.123 \cdot 10^6$	1	256.80	<0.0001	A: Temperature	2821.33	1	12.44	0.0096
B: Time	$9.429 \cdot 10^6$	1	298.09	<0.0001	B: Humidity	$8.920 \cdot 10^6$	1	39342.51	<0.0001
AB	$6.176 \cdot 10^5$	1	19.53	0.0031	AB	18225	1	80.38	<0.0001
A <sup>2</sup>	$1.662 \cdot 10^7$	1	525.41	<0.0001	A <sup>2</sup>	$9.910 \cdot 10^5$	1	4370.98	<0.0001
B <sup>2</sup>	$6.922 \cdot 10^6$	1	218.83	<0.0001	B <sup>2</sup>	$1.448 \cdot 10^6$	1	6387.29	<0.0001
$R^2 = 0.9940$ $R^2$ adjusted = 0.9898					$R^2 = 0.9999$ $R^2$ adjusted = 0.9998				
<b>Ethylbenzene</b>									
Square	$4.93 \cdot 10^7$	5	170.14	<0.0001	Square	$3.928 \cdot 10^7$	5	16789.64	<0.0001
A: Temperature	$2.256 \cdot 10^7$	1	388.76	<0.0001	A: Temperature	28518.75	1	60.95	0.0001
B: Time	$4.887 \cdot 10^6$	1	84.23	<0.0001	B: Humidity	$2.875 \cdot 10^7$	1	61440.33	<0.0001
AB	14884	1	0.26	0.6281	AB	992.25	1	2.12	0.1887
A <sup>2</sup>	$2.046 \cdot 10^7$	1	352.60	<0.0001	A <sup>2</sup>	$3.407 \cdot 10^6$	1	7282.44	<0.0001
B <sup>2</sup>	$6.310 \cdot 10^6$	1	108.76	<0.0001	B <sup>2</sup>	$3.923 \cdot 10^6$	1	8385.75	<0.0001
$R^2 = 0.9918$ $R^2$ adjusted = 0.9860					$R^2 = 0.9999$ $R^2$ adjusted = 0.9999				
<b>m-, p-Xylene</b>									
Square	$3.596 \cdot 10^8$	5	85.85	<0.0001	Square	$3.612 \cdot 10^7$	5	$1.246 \cdot 10^5$	<0.0001
A: Temperature	$1.120 \cdot 10^8$	1	133.7	<0.0001	A: Temperature	507.00	1	8.75	0.0212
B: Time	$2.714 \cdot 10^7$	1	32.4	0.0007	B: Humidity	$2.884 \cdot 10^7$	1	$4.976 \cdot 10^5$	<0.0001
AB	$14762 \cdot 10^3$	1	0.018	0.8981	AB	36	1	0.62	0.4565
A <sup>2</sup>	$1.921 \cdot 10^8$	1	229.24	<0.0001	A <sup>2</sup>	$2.279 \cdot 10^6$	1	$39.322 \cdot 10^3$	<0.0001
B <sup>2</sup>	$8.595 \cdot 10^7$	1	102.6	<0.0001	B <sup>2</sup>	$2.803 \cdot 10^6$	1	$48.363 \cdot 10^3$	<0.0001
$R^2 = 0.9840$ $R^2$ adjusted = 0.9725					$R^2 = 1$ $R^2$ adjusted = 1				
<b>o-Xylene</b>									
Square	$1.544 \cdot 10^8$	5	98.98	<0.0001	Square	13.58	5	376.09	<0.0001
A: Temperature	$4.978 \cdot 10^7$	1	159.59	<0.0001	A: Temperature	6.38	1	883.45	<0.0001
B: Time	$1.037 \cdot 10^7$	1	33.24	0.0007	B: Humidity	5.89	1	816.13	<0.0001
AB	$21.316 \cdot 10^3$	1	0.068	0.8013	AB	1.09	1	151.21	<0.0001
A <sup>2</sup>	$8.616 \cdot 10^7$	1	276.20	<0.0001	A <sup>2</sup>	0.20	1	28.19	0.0011
B <sup>2</sup>	$3.037 \cdot 10^7$	1	97.37	<0.0001	B <sup>2</sup>	$1.43 \cdot 10^3$	1	0.20	0.6699
$R^2 = 0.9861$ $R^2$ adjusted = 0.9761					$R^2 = 0.9963$ $R^2$ adjusted = 0.9936				

**Table 4.** Optimum conditions of desorption and sampling parameters

Parameters/ Analytes		Benzene	Toluene	Ethylbenzene	<i>m</i> -, <i>p</i> -Xylene	<i>o</i> -Xylene
Desorption conditions	Temperature, K	540	540	548	543	544
	Time, min	6	6	6	6	6
Sampling conditions	Temperature, K	303	304	304	308	307
	Humidity, %	20	20	20	20	20

**Fig. 5.** The effect of desorption temperature and time

### 3.3. Sampling Parameters

The influences of temperature and humidity were investigated on the sampling performance of NTD: Cu-MOF based on CCD analysis. According to the optimization results of the sampling parameters, for the studied analytes, the quadratic model was highly significant from the evidence of the low  $p$ -value ( $< 0.0001$ ) and high  $F$ -value. The high  $R^2$  (determination coefficient between 0.9963 and 1) proved the goodness fit of the model. The value of the adjusted determination coefficient ( $R^2$  adjusted = 0.9936 to 1) was also high, which advocated a high significance of the model (Table 3). Table 4 reveals the optimal values of the

sampling temperature and relative humidity. Fig. 6 illustrates the interaction effect between sampling temperature and humidity on the NTD performance.

As observed in Fig. 4, the results of the sampling temperature and humidity effect implied that the efficiency of the NTD increased with the increasing sampling temperature from 288 to 303 K, and then decreased with further increasing in the sampling temperature up to 308 K. Moreover, the interaction effect of sampling temperature of 303 and relative humidity of 20 % is optimal. As observed in Fig. 4, the NTD performance decreased with increasing the relative humidity, because the adsorption sites on the HKUST-1 surface were occupied by water molecules.<sup>32</sup>

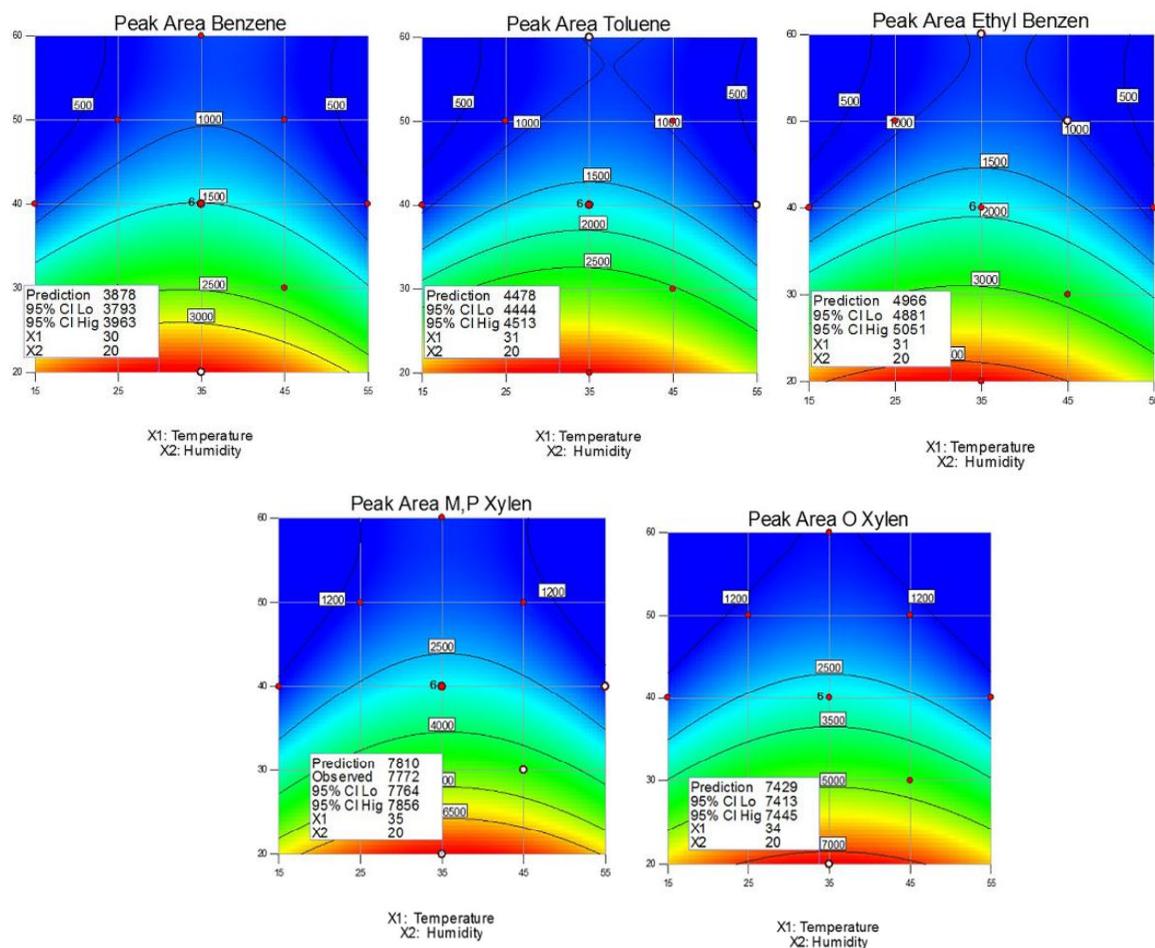


Fig. 6. Effect of sampling time and humidity on the proficiency of NTD: Cu-MOF

### 3.4. Breakthrough Volume investigation

NTD as a non-equilibrium method can adsorb all target analytes in the air passing through the sorbent bed (prior to the breakthrough). Various factors affect breakthrough, such as the amount of sorbent used in the NTD, volume of air passing through the sorbent bed, reaction between adsorbent and analyte, and analyte concentration.<sup>31</sup> According to the results, analyte concentration and sampling flow rate are inversely proportional to breakthrough volume. Fig. 7 demonstrates breakthrough volume at different sampling air volumes and analyte concentrations.

During the examination of the breakthrough volume of proposed method, the “P” values higher than 10 % (according to Eq. (2)) were considered as a point of breakthrough volume. Then, using Design-expert software, the maximum volume of sampling air was

determined at the greatest concentration of analyte before the incidence of breakthrough volume. With regard to the concentrations and volumes reported in Fig. 7, the other parameters were tested at lower concentrations and air sampling volumes before occurring breakthrough in the packed sorbent.

For a model to fit the experimental data, the  $R^2$  value should be close to 1. Use of adjusted  $R^2$  (adjusted determination coefficient) is preferred because  $R^2$  always increases on adding variables to the model but the adjusted  $R^2$  does not always increase as necessary variables are added to the model. According to Table 5 the  $R^2$  value indicates that the proposed regression model can be used to predict the % breakthrough volume within the experimental range for all analytes, and the values of adjusted  $R^2$  in Table 5 were also high. To sum up, these results show that the offer models are statistically significant, and can be used to predict the breakthrough volume.

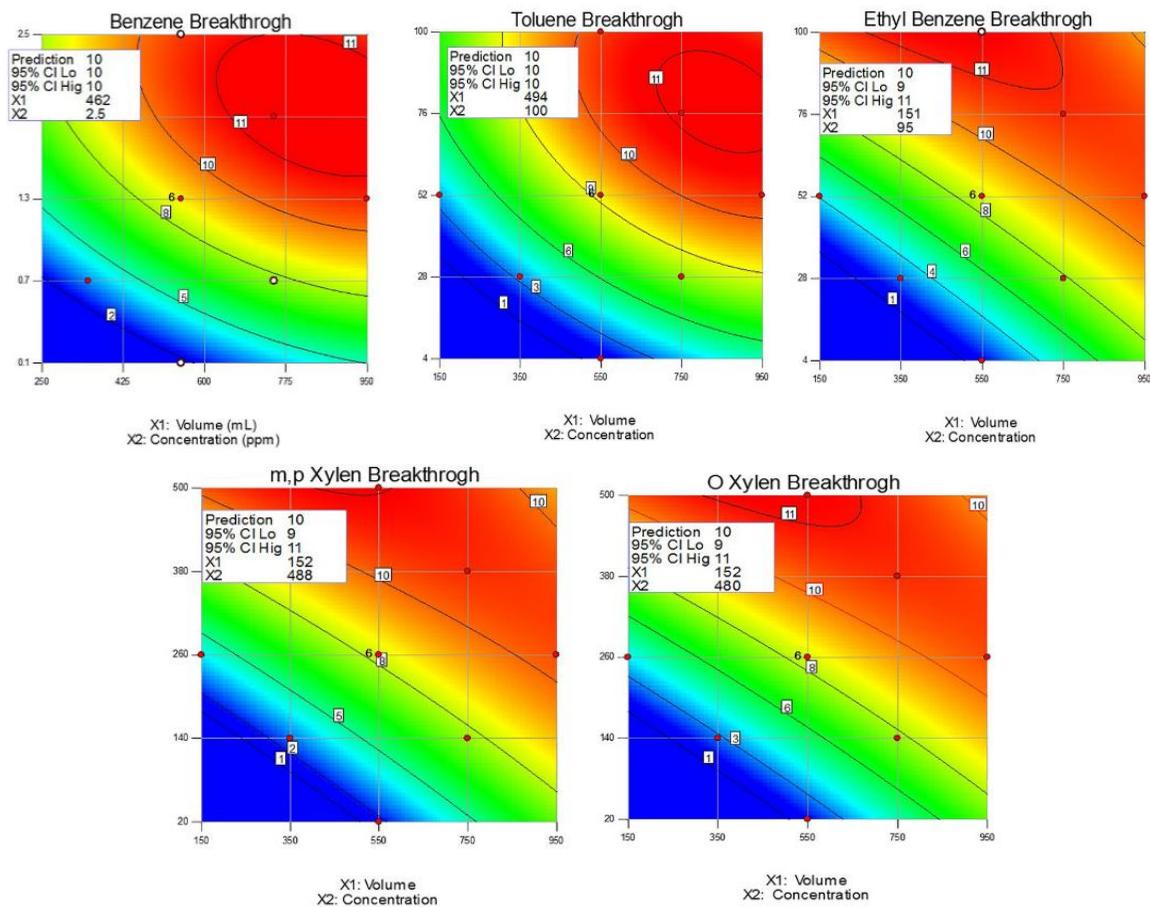


Fig. 7. Effect of sampling air volume and analyte concentration on the breakthrough volume

Table 5. ANOVA results of breakthrough variables

Source	Sum of squares	D.F	F-value	p-Value
1	2	3	4	5
<b>Benzene</b>				
Square	108.36	5	985.82	< 0.0001
A: Volume	36.75	1	1671.74	< 0.0001
B: Concentration	58.61	1	2666.10	< 0.0001
AB	0.64	1	29.11	0.0010
A <sup>2</sup>	4.25	1	193.35	< 0.0001
B <sup>2</sup>	11.14	1	506.68	< 0.0001
$R^2 = 0.9986$		$R^2$ adjusted = 0.9976		$R^2$ pred = 0.9958
<b>Toluene</b>				
Square	104.07	5	985.82	< 0.0001
A: Volume	35.29	1	1671.74	< 0.0001
B: Concentration	56.29	1	2666.10	< 0.0001
AB	0.61	1	29.11	0.0010
A <sup>2</sup>	4.08	1	193.35	< 0.0001
B <sup>2</sup>	10.70	1	506.68	< 0.0001
$R^2 = 0.9986$		$R^2$ adjusted = 0.9976		$R^2$ pred = 0.9958
<b>Ethylbenzene</b>				
Square	109.82	5	328.26	< 0.0001
A: Volume	31.36	1	468.75	< 0.0001

1	2	3	4	5
B: Concentration	69.12	1	1033.06	< 0.0001
AB	3.24	1	48.42	0.0002
A <sup>2</sup>	2.12	1	31.64	0.0008
B <sup>2</sup>	5.48	1	81.90	< 0.0001
$R^2 = 0.9958$ $R^2$ adjusted = 0.9927 $R^2$ pred = 0.9828				
<b><i>m-,p-Xylene</i></b>				
Square	103.33	5	328.26	< 0.0001
A: Volume	29.51	1	468.75	< 0.0001
B: Concentration	65.04	1	1033.06	< 0.0001
AB	3.05	1	48.42	0.0002
A <sup>2</sup>	1.99	1	31.64	0.0008
B <sup>2</sup>	5.16	1	81.90	< 0.0001
$R^2 = 0.9958$ $R^2$ adjusted = 0.9927 $R^2$ pred = 0.9828				
<b><i>o-Xylene</i></b>				
Square	107.50	5	328.26	< 0.0001
A: Volume	30.70	1	468.75	< 0.0001
B: Concentration	67.66	1	1033.06	< 0.0001
AB	3.17	1	48.42	0.0002
A <sup>2</sup>	2.07	1	31.64	0.0008
B <sup>2</sup>	5.36	1	81.90	< 0.0001
$R^2 = 0.9958$ $R^2$ adjusted = 0.9927 $R^2$ pred = 0.9828				

The breakthrough experiments showed that the HKUST-1 had a high capacity for the adsorption of BTEX compounds. Breakthrough volume of NTD was related to the affinity of the analyte to the adsorbent, amount of the sorbent packed inside the needle, sampling air volume, and analyte concentration. The maximum volumes of sampling air recommended by the NIOSH 1501 method for the sampling of benzene, toluene, ethyl benzene, and xylene are 45, 12, 35, and 35 l, respectively,<sup>25</sup> which are higher than the sampling air volume in the proposed NTD method. This difference is attributed to the small amount of packed adsorbent (1.5 mg) inside the needle. This result is in agreement with the findings of other studies on NTD application.<sup>30</sup>

### 3.5. Carryover Effect

The carryover effect of the developed method was examined under determined desorption conditions. The percentage of carryover effect was less than 5 % for all of the analytes under optimal desorption conditions (at 548 K and 6 min).

Therefore, after the completion of desorption cycle, the device was ready to reuse without any analyte remaining on the surface of the adsorbent packed inside the NTD. Due to the volatility of the analytes, they were completely desorbed at desorption temperature of 548 K and time of

5 min. The desorption temperature and time affect the NTD efficiency and the analyte affinity to sorbent. In a study conducted by Wang *et al.*,<sup>33</sup> the desorption temperature of BTEX from the carboxene 1000 was reported to be 573 K, which is higher than those obtained in the present study, because HKUST-1 has less affinity to BTEX compounds compared to the carboxene 1000.

## 3.6. Method Validation

### 3.6.1. Accuracy

The accuracy of the NTD: Cu-MOF *versus* the standard method (NIOSH 1501) was verified using One-Sample T-Test. Table 6 showed no significant difference between the two methods.

**Table 6.** Average difference between NTD: Cu-MOF and standard method- One Sample T-Test

Analyte	Average ( $N = 6$ ), ppm		$p$ -Value
	NIOSH 1501	NTD:Cu-MOF	
Benzene	0.53	0.51	0.052
Toluene	19.82	19.89	0.057
Ethylbenzene	20.21	20.19	0.062
<i>m-,p-Xylene</i>	105	104.3	0.053
<i>o-Xylene</i>	97.98	97.9	0.059

### 3.6.2. Repeatability and reproducibility

The relative standard deviation (RSD) was used to evaluate the accuracy of the developed method. According to the summary data in Table 7, this method had suitable accuracy for monitoring of BTEX in the air. The repeatability values of NIOSH method 1501 for BTEX are 11.4, 10.9, 17.1, and 12.2 %, respectively, which is consistent with our results.

### 3.6.3. Determination of LOD, LOQ and LDR

In order to validate the developed method, the concentrations corresponding to the chromatogram

with S/N ratios of 3 and 10 were considered as LOD and LOQ, respectively. The LOD, LOQ and linear dynamic range (LDR) are shown in Table 7. The LOD values reported in NIOSH 1501 for BTEX are 500, 700, 500, 800, and 700 ng/ml, respectively. The LOD value of the proposed method was lower than those reported in the NIOSH method. Hence, the NTD: Cu-MOF offered an acceptable way for the determination of BTEX in air. The results of the present study are comparable with other similar studies on the application of NTD for sampling and analysis of such compounds in air.<sup>34,35</sup>

**Table 7.** Values of different tests to validate the proposed method

Analyte	Repeatability, mg/m <sup>3</sup> RSD % <i>N</i> = 6 Injections		Reproducibility, mg/m <sup>3</sup> RSD% <i>N</i> = 6 injections		LOD, mg/m <sup>3</sup>	LOQ, mg/m <sup>3</sup>	LDR, mg/m <sup>3</sup>
Benzene	0.3	6.4	NTD1	8.1	0.16	0.52	0.2–22
	1.6	7.5	NTD2	10.1			
	8	7.9	NTD3	6.2			
Toluene	15	7.3	NTD1	6.3	0.38	1.1	0.4–380
	75	8.3	NTD2	8			
	377	5.7	NTD3	10.6			
Ethylbenzene	17	5.5	NTD1	5.3	0.5	1.4	0.5–435
	87	6.6	NTD2	9.4			
	434	9.4	NTD3	11			
<i>m</i> -, <i>p</i> -Xylene	87	7.4	NTD1	8.1	0.4	1.32	0.3–2200
	434	6.3	NTD2	12.3			
	2171	8.2	NTD3	9.4			
<i>o</i> -Xylene	87	8.6	NTD1	9.7	0.4	1.41	0.4–2200
	434	13.2	NTD2	8.9			
	2171	10.1	NTD3	12.3			

### 3.6.4. Storage time

Storage capability of the sampler was examined on 2, 4, 6, 8, and 10 days after sampling. The results of storage capability of NTDs were compared with the analysis results of the control NTDs. The control NTDs were immediately analysed after sampling (without storing). The analysis of NTDs stored in the refrigerator showed that after ten days there was no significant difference between the results of stored NTDs and control NTDs ( $p > 0.05$ ).

The NTD stored at 298 K for six days did not show a significant decrease in peak areas responses compared with the control NTDs ( $p > 0.05$ ). After eight days, there was a 6 % decrease in the adsorbed BTEX on the NTD: Cu-MOF.

As a result, BTEX compounds trapped in the NTD can be stored in the refrigerator and ambient temperature for at least 10 and 6 days, respectively, without analyte loss, while in Wang et al. study on the use of NTD packed with carboxene adsorbent, 6 % of

the benzene analyte was reduced after four days of storage time.<sup>33</sup> The NIOSH has recommended that the samples must be stored at 263 K in a container.

### 3.6.5. In-field measurements

In order to validate this technique, the occupational exposure to air pollutants in the real field was assessed using the NTD. After optimization of the developed method, the efficiency of the NTD: Cu-MOF method was assessed by measuring the BTEX concentrations in fuelling stations with six NTDs packed with Cu-MOF. Table 8 presents the comparison results of the proposed NTD and the standard method (NIOSH 1501). According to the results, there was no significant difference between the developed method and standard method for the field sampling of the analytes of interest. These results indicated that the developed NTD can be used as a novel, solventless and fast method for sampling and analysis of such compounds in workplaces.

**Table 8.** The BTEX concentrations in ambient air of fuelling stations

Analyte	Mean ( $N = 6$ ), mg/m <sup>3</sup>		$p$ -Value
	NIOSH 1501	NTD: Cu-MOF	
Benzene	35.8	39.6	0.07
Toluene	54	55	0.095
Ethylbenzene	36	39	0.084
<i>m</i> -, <i>p</i> -Xylene	83	87	0.054
<i>o</i> -Xylene	91	92	0.093

## 4. Conclusions

In this study, NTD-(HKUST-1) was used for the first time to measure the concentrations of BTEX compounds in air. HKUST-1 with suitable pore sizes and open metal sites (Lewis acid sites) showed an excellent capacity for adsorbing BTEX. NTD-(HKUST-1) method was optimized by focusing on different aspects of the sampling (such as temperature and humidity) and desorption conditions (such as temperature and time). Then, the developed method was used for the field sampling of BTEX and compared with NIOSH method 1501. The measurement results for both methods were in a good agreement. The results indicated that the NTD-HKUST-1 is a reusable, inexpensive, solventless and fast technique. The NTD- HKUST-1 with a high sensitivity could be coupled with GC as a powerful method for monitoring of BTEX in air.

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## References

- [1] Durmusoglu, E.; Taspinar, F.; Karademir, A. Health Risk Assessment of BTEX Emissions in the Landfill Environment. *J. Hazard. Mater.* **2010**, *176*, 870-877. <https://doi.org/10.1016/j.jhazmat.2009.11.117>
- [2] IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, v. 100F; International Agency for Research on Cancer: Lyon, 2012.
- [3] Riboni, N.; Trzcinski, J.W.; Bianchi, F.; Massera, C.; Pinalli, R.; Sidisky, L.; Dalcanale, E.; Careri, M. Conformationally Blocked Quinoxaline Cavitand as Solid-Phase Microextraction Coating for the Selective Detection of BTEX in Air. *Anal. Chim. Acta* **2016**, *905*, 79-84. <https://doi.org/10.1016/j.aca.2015.12.005>
- [4] Ma J-Q., Liu L., Wang X.; Chen, L.-Z.; Lin, J.-M.; Zhao, R.-S. Development of Dispersive Solid-Phase Extraction with Polyphenylene Conjugated Microporous Polymers for Sensitive Determination of Phenoxycarboxylic Acids in Environmental Water Samples. *J. Hazard. Mater.* **2019**, *371*, 433-439. <https://doi.org/10.1016/j.jhazmat.2019.03.033>
- [5] Wang, R.; Ma, X.; Zhang, X.; Li, X.; Li, D.; Dang, Y. C8-Modified Magnetic Graphene Oxide Based Solid-Phase Extraction Coupled with Dispersive Liquid-Liquid Microextraction for Detection of Trace Phthalate Acid Esters in Water Samples. *Ecotox. Environ. Safe.* **2019**, *170*, 789-795. <https://doi.org/10.1016/j.ecoenv.2018.12.051>
- [6] Lendor, S.; Hassani, S.-A.; Boyaci, E.; Singh, V.; Womelsdorf, T.; Pawliszyn, J. Solid Phase Microextraction-Based Miniaturized Probe and Protocol for Extraction of Neurotransmitters from Brains in Vivo. *Anal. Chem.* **2019**, *91*, 4896-4905. <https://doi.org/10.1021/acs.analchem.9b00995>
- [7] Ghavidel, F.; Shahtaheri, S.J.; Jazani, R.K.; Torabbeigi, M.; Froushani, A.R.; Khadem, M. Optimization of Solid Phase Microextraction Procedure Followed by Gas Chromatography with Electron Capture Detector for Pesticides Butachlor and Chlorpyrifos. *Am. J. Anal. Chem.* **2014**, *5*, 535-546. <https://doi.org/10.4236/ajac.2014.59061>
- [8] Koziel, J.A.; Odziemkowski, M.; Pawliszyn, J. Sampling and Analysis of Airborne Particulate Matter and Aerosols Using In-Needle Trap and SPME Fiber Devices. *Anal. Chem.* **2001**, *73*, 47-54. <https://doi.org/10.1021/ac000835s>
- [9] Chen, J.; Zhang, B.; Zheng, D.; Dang, X.; Ai, Y.; Chen, H. A Novel Needle Trap Device Coupled with Gas Chromatography for Determination of Five Fatty Alcohols in Tea Samples. *Anal. Methods* **2018**, *10*, 5783-5789. <https://doi.org/10.1039/C8AY01894D>
- [10] Kleebblatt, J.; Schubert, J.K.; Zimmermann, R. Detection of Gaseous Compounds by Needle Trap Sampling and Direct Thermal-Desorption Photoionization Mass Spectrometry: Concept and Demonstrative Application to Breath Gas Analysis. *Anal. Chem.* **2015**, *87*, 1773-1781. <https://doi.org/10.1021/ac5039829>
- [11] Mesarchaki, E.; Yassaa, N.; Hein, D.; Lutterbeck, H.E.; Zindler, C.; Williams, J. A Novel Method for the Measurement of VOCs in Seawater Using Needle Trap Devices and GC-MS. *Marine Chem.* **2014**, *159*, 1-8. <https://doi.org/10.1016/j.marchem.2013.12.001>
- [12] Reyes-Garcés, N.; Gómez-Ríos, G.A.; Souza Silva, É.A.; Pawliszyn, J. Coupling Needle Trap Devices with Gas Chromatography-Ion Mobility Spectrometry Detection as a Simple Approach for On-Site Quantitative Analysis. *J. Chromatogr. A* **2013**, *1300*, 193-198. <https://doi.org/10.1016/j.chroma.2013.05.042>
- [13] Warren, J.M.; Parkinson, D.-R.; Pawliszyn, J. Assessment of Thiol Compounds from Garlic by Automated Headspace Derivatized In-Needle-NTD-GC-MS and Derivatized In-Fiber-SPME-GC-MS. *J. Agricult. Food Chem.* **2013**, *61*, 492-500. <https://doi.org/10.1021/jf303508m>
- [14] Eom, I.-Y.; Risticovic, S.; Pawliszyn, J. Simultaneous Sampling and Analysis of Indoor Air Infested with Cimex Lectularius L. (Hemiptera: Cimicidae) by Solid Phase Microextraction, Thin Film Microextraction and Needle Trap Device. *Anal. Chim. Acta* **2012**, *716*, 2-10. <https://doi.org/10.1016/j.aca.2011.06.010>
- [15] Vallecillos, L.; Borrull, F.; Sanchez, J.M.; Pocurrull, E. Sorbent-Packed Needle Microextraction Trap for Synthetic Musks Determination in Wastewater Samples. *Talanta* **2015**, *132*, 548-556. <https://doi.org/10.1016/j.talanta.2014.08.016>
- [16] Eom, I.-Y.; Jung, M.-J. Identification of Coffee Fragrances Using Needle Trap Device-Gas Chromatograph/Mass Spectrometry (NTD-GC/MS). *Bull. Korean Chem. Soc.* **2013**, *34*, 1703-1707. <https://doi.org/10.5012/bkcs.2013.34.6.1703>
- [17] Trefz, P.; Kischkel, S.; Hein, D.; James, E.S.; Schubert, J.K.; Miekisch, W. Needle Trap Micro-Extraction for VOC Analysis:

Effects of Packing Materials and Desorption Parameters. *J. Chromatogr. A* **2012**, *1219*, 29-38.

<https://doi.org/10.1016/j.chroma.2011.10.077>

[18] Alizadeh, S.; Nematollahi, D. Electrochemically Assisted Self-Assembly Technique for the Fabrication of Mesoporous Metal-Organic Framework Thin Films: Composition of 3D Hexagonally Packed Crystals with 2D Honeycomb-like Mesopores. *J. Am. Chem. Soc.* **2017**, *139*, 4753-4761. <https://doi.org/10.1021/jacs.6b12564>

[19] Alizadeh, S.; Nematollahi, D. Convergent and Divergent Paired Electrodeposition of Metal-Organic Framework Thin Films. *Sci. Rep.* **2019**, *9*, 14325.

<https://doi.org/10.1038/s41598-019-50390-y>

[20] Liu, C.; Yu, L.-Q.; Zhao, Y.-T.; Lv, Y.-K. Recent Advances in Metal-Organic Frameworks for Adsorption of Common Aromatic Pollutants. *Microchim. Acta* **2018**, *185*, 342.

<https://doi.org/10.1007/s00604-018-2879-2>

[21] Li, J.-R.; Sculley, J.; Zhou, H.-C. Metal-Organic Frameworks for Separations. *Chem. Rev.* **2012**, *112*, 869-932.

<https://doi.org/10.1021/cr200190s>

[22] Lin, K.-S.; Adhikari, A.K.; Ku, C.-N.; Chiang, C.-L.; Kuo, H. Synthesis and Characterization of Porous HKUST-1 Metal Organic Frameworks for Hydrogen Storage. *Int. J. Hydrogen Energ.* **2012**, *37*, 13865-13871.

<https://doi.org/10.1016/j.ijhydene.2012.04.105>

[23] Chui, S.S.-Y.; Lo, S.M.-F.; Charmant, J.P.H.; Orpen, A.G.; Williams, I.D. A Chemically Functionalizable Nanoporous Material  $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$ . *Science* **1999**, *283*, 1148-1150.

<https://doi.org/10.1126/science.283.5405.1148>

[24] Bentley, J.; Foo, G.S.; Rungta, M.; Sangar, N.; Sievers, C.; Sholl, D.S.; Nair, S. Effects of Open Metal Site Availability on Adsorption Capacity and Olefin/Paraffin Selectivity in the Metal-Organic Framework  $\text{Cu}_3(\text{BTC})_2$ . *Ind. Eng. Chem. Res.* **2016**, *55*, 5043-5053. <https://doi.org/10.1021/acs.iecr.6b00774>

[25] *NIOSH Manual of Analytical Methods*; Eller, P., Cassinelli, M., Eds.; Diane Publ., 1994.

[26] Poormohammadi, A.; Bahrami, A.; Farhadian, M.; Ghorbani-Shahna, F.; Ghiasvand, A. Development of Carbotrap B-Packed Needle Trap Device for Determination of Volatile Organic Compounds in Air. *J. Chromatogr. A* **2017**, *1527*, 33-42.

<https://doi.org/10.1016/j.chroma.2017.10.062>

[27] Witek-Krowiak, A.; Chojnacka, K.; Podstawczyk, D.; Dawiec, A.; Pokomeda, K. Application of Response Surface Methodology and Artificial Neural Network Methods in Modelling and optimization of Biosorption Process. *Biores. Technol.* **2014**, *160*, 150-160. <https://doi.org/10.1016/j.biortech.2014.01.021>

[28] Soury, S.; Bahrami, A.; Alizadeh, S.; Ghorbani-Shahna, F.; Nematollahi, D. Development of a Needle Trap Device Packed with Zinc Based Metal-Organic Framework Sorbent for the Sampling and Analysis of Polycyclic Aromatic Hydrocarbons in the Air. *Microchem. J.* **2019**, *148*, 346-354.

<https://doi.org/10.1016/j.microc.2019.05.019>

[29] Thompson, M.; Ellison, S.L.R.; Wood, R. Harmonized Guidelines for Single-Laboratory Validation of Methods of Analysis (IUPAC Technical Report). *Pure Appl. Chem.* **2002**, *74*, 835-855. <https://doi.org/10.1351/pac200274050835>

[30] Zali, S.; Jalali, F.; Es-haghi, A.; Shamsipur, M. New Nanostructure of Polydimethylsiloxane Coating as a Solid-Phase Microextraction Fiber: Application to Analysis of BTEX in Aquatic Environmental Samples. *J. Chromatogr. B* **2016**, *1033*, 287-295. <https://doi.org/10.1016/j.jchromb.2016.08.045>

[31] Orazbayeva, D.; Kenessov, B.; Koziel, J.A.; Nassyrova, D.; Lyabukhova, N.V. Quantification of BTEX in Soil by Headspace SPME-GC-MS Using Combined Standard Addition and Internal Standard Calibration. *Chromatographia* **2017**, *80*, 1249-1256. <https://doi.org/10.1007/s10337-017-3340-0>

[32] Zhao, Z.; Wang, S.; Yang, Y.; Li, X.; Li, J.; Li, Z. Competitive Adsorption and Selectivity of Benzene and Water Vapor on the Microporous Metal Organic Frameworks (HKUST-1). *Chem. Eng. J.* **2015**, *259*, 79-89.

<https://doi.org/10.1016/j.cej.2014.08.012>

[33] Wang, A.; Fang, F.; Pawliszyn, J. Sampling and Determination of Volatile Organic Compounds with Needle Trap Devices. *J. Chromatogr. A* **2005**, *1072*, 127-135.

<https://doi.org/10.1016/j.chroma.2004.12.064>

[34] Zevedegani, S.K.; Bahrami, A.; Rismanchian, M.; Shahna, F.G. Analysis of Xylene in Aqueous Media Using Needle-Trap Microextraction with a Carbon Nanotube Sorbent. *J. Sep. Sci.* **2014**, *37*, 1850-1855. <https://doi.org/10.1002/jssc.201400262>

[35] Warren, J.M.; Pawliszyn, J. Development and Evaluation of Needle Trap Device Geometry and Packing Methods for Automated and Manual Analysis. *J. Chromatogr. A* **2011**, *1218*, 8982-8988. <https://doi.org/10.1016/j.chroma.2011.10.017>

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## РОЗРОБЛЕННЯ ПРИСТРОЮ ДЛЯ УТРИМУВАННЯ ГОЛКИ З СОРБЕНТОМ HKUST-1 ДЛЯ ВІДБОРУ ПРОБ І АНАЛІЗУ BTEX В ПОВІТРІ

**Анотація.** Вперше розроблений пристрій для утримання голки (NTD) з сорбентом HKUST-1 (металоорганічний каркас на основі Cu), який призначений для відбору проб та аналізу бензену, толуену, етилбензену та ксилену (BTEX) в атмосферному повітрі. Синтезований за допомогою електрохімічного процесу адсорбент HKUST-1 розташований у голці 22 розміру. Для забезпечення різних концентрацій BTEX шприцева помпа підключена до скляної камери для впорскування сполук BTEX з певною швидкістю. Для оптимізації аналітичних параметрів, а саме об'єму проскоку, умов десорбції та умов відбору проб використано програмне забезпечення Design-expert (версія 7). Визначено, що оптимальні умови десорбції досягаються за 548 K протягом 6 хв, а найкращі умови відбору проб – за 309 K та 20% вологості. Визначено, що показники LOQ та LOD розробленого пристрою знаходяться в межах 0,52–1,41 та 0,16–0,5 мг/м<sup>3</sup>, відповідно, а повторюваність та відтворюваність методу становлять 5,5–13,2 та 5,3–12,3 %, відповідно. Встановлено, що NTD, які зберігаються в холодильнику (> 277 K), і за кімнатної температури (298 K), зберігають проби BTEX щонайменше протягом 10 та 6 днів відповідно. Показано, що NTD з сорбентом HKUST-1 може бути використаний як надійний та корисний метод для визначення BTEX у повітрі.

**Ключові слова:** повітря, HKUST-1, металоорганічний каркас, електрохімія, пристрій для утримання голки, леткі органічні сполуки.