

# Synthesis and Characterization of Zn<sub>3</sub> (BTC)<sub>2</sub> Nanoporous Sorbent for Sampling from Benzo[a]pyren using Needle Trap in the Air

Shiva Soury<sup>1</sup>, Abdulrahman Bahrami<sup>2\*</sup>, Saber Alizadeh<sup>2</sup>, Farshid Ghorbani Shahna<sup>1</sup>, Davood Nematollahi<sup>2</sup>

<sup>1</sup> Center of Excellence for Occupational Health, Occupational Health and Safety Research Center, School of Public Health, Hamadan University of Medical Sciences, Hamadan, Iran

<sup>2</sup> Faculty of Chemistry, Bu-Ali-Sina University, Hamedan 65174-38683, Iran

## Abstract

**Introduction:** In this study, Zn<sub>3</sub>(Btc)<sub>2</sub> (metal organic framework) sorbent was introduced for sampling of Benzo[a]pyren from the air. The purpose of this study was to develop the sampling and analysis method by needle trap, with no sample preparation step.

**Material and method:** Zn<sub>3</sub>(Btc)<sub>2</sub> sorbent was electrochemically synthesized and its properties were specified by FTIR, FE-SEM, and PXRD techniques. A glass chamber with a temperature of 120°C was used to make the certain concentration of Benzo[a]pyren. Factors affecting the efficiency of needle trap were evaluated and optimized using a response surface method considering a specific operating interval to achieve the highest efficiency. The performance of the proposed method was also investigated using the real samples.

**Results:** The highest desorption efficiency of Benzo[a]pyren was obtained when using the needle trap containing Zn<sub>3</sub> (Btc)<sub>2</sub> sorbent at 379°C and 9 min retention time. No significant reduction was observed in the analyte concentration by maintaining the sampler for 60 days. The limit of detection and limit of quantification of Benzo[a]pyren were obtained 0.01 and 0.03 mg/m<sup>3</sup>, respectively. The percentage of standard deviation of the measured values of Benzo[a]pyren in diesel exhaust was calculated 4.1%.

**Conclusion:** The highest desorption efficiency of Benzo[a]pyren was obtained when using the needle trap containing Zn<sub>3</sub> (Btc)<sub>2</sub> sorbent at 379°C and 9 min retention time. No significant reduction was observed in the analyte concentration by maintaining the sampler for 60 days. The limit of detection and limit of quantification of Benzo[a]pyren were obtained 0.01 and 0.03 mg/m<sup>3</sup>, respectively. The percentage of standard deviation of the measured values of Benzo[a]pyren in diesel exhaust was calculated 4.1%.

**Keywords:** Air Monitoring; Electrochemical Synthesized; Needle Trap Device; Polycyclic Aromatic Hydrocarbons; Zn<sub>3</sub>(BTC)<sub>2</sub> Metal-organic Framework.

\*Corresponding Author: Abdulrahman Bahrami

Email Address: bahrami@umsha.ac.ir

## 1. Introduction

In recent years, the development of the needle trap method as a one-step solvent-free method for sampling from analytes has attracted much attention [1-3]. The type of sorbent used in needle trap is very effective on its performance. Metal-Organic Frameworks (MOFs) are among the sorbents that can be used in needle trap. Zn<sub>3</sub>(BTC)<sub>2</sub> sorbent has not been used in any matrix for sampling from polycyclic aromatic hydrocarbons so far. Therefore, in the present study, spinal needle filled with this (NTD: Zn<sub>3</sub>(BTC)<sub>2</sub>) sorbent were examined for sampling from Benzo[a]pyren in the air.

## 2. Material and Methods

In this study, electrochemical cell was used to synthesize a thin film from Zn<sub>3</sub>(BTC)<sub>2</sub>. The carbon electrode (3\*10\*20) was used as the active electrode and the neutral electrode from stainless steel. The sorbent properties were determined by FTIR, FE-SEM and PXRD devices. Spinal needles with gage 22 (O.D. 0.71mm, I.D. 0.39mm) were used to make the needle trap. First, mix 1.5 mg of sorbent with 1 mg of broken glass and then the needle was filled with a metal piston and the sorbent sides were blocked with 3 mm glass wool. A glass chamber with a temperature of 120°C was used to make the certain concentration of Benzo[a]pyren. Factors affecting the efficiency of the needle trap, such as temperature and desorption time, breakthrough volume were evaluated and optimized using a response surface method considering a specific operating interval to achieve the highest efficiency. In this study, the relationship between variables of temperature of injection section of GC device (at five levels: 220, 250, 300, 350, 380°C) and desorption time (at five levels: 1.5, 3, 5.5, 8, 9.5 min) on the efficiency of needle trap was investigated. In analyzing the breakthrough volume, the percentage of analyte removed from the first needle trap and penetrated to the second trap was considered as response using RMS method. The breakthrough volume was investigated in the concentration range of 0.1 to 0.5 mg/m<sup>3</sup> and volume of 500 to 2500 ml. In addition, repeatability and reproducibility, limit

of quantification and limit of detection of method were determined. Finally, the proposed sampler was tested in the real environment after determining the factors affecting performance and the amount of Benzo[a]pyren from diesel exhaust was determined and the results were compared with NIOSH 5515 standard method.

## 3. Results and Discussion

The highest desorption efficiency of Benzo[a]pyren was obtained from needle trap containing Zn<sub>3</sub>(BTC)<sub>2</sub> sorbent at 379°C and 9 min retention time (Fig. 1). The second-degree model was chosen as the best model because of the lower standard deviation of Std.Dev., high values of R-Squared and low value of PRESS. The significance and results of each parameter and their interactions using the squared model in the form of variance analysis have been shown in Table 1. According to the high molecular weight of Benzo[a]pyren and its relatively low volatility, more temperature and time of adsorption are needed for separation from the sorbent surface. The results of the present study are consistent with the studies conducted with solid-phase microextraction on PAHs [4, 5].

If the concentration of Benzo[a]pyren is 0.5 mg/m<sup>3</sup> and the volume of sampling air is more than 2500 ml, the needle trap is saturated and the analyte passes through the sorbent bed. The model coefficients for predicting the breakthrough volume are presented in Formula 1. The breakthrough volume is lower compared to other sampling devices (6) due to the limited amount of sorbent inside the needle trap (1.5 mg).

### Formula 1:

$$Y = 3.18 - 2.82 \times 10^{-3} X_1 - 9.1 X_2 + 0.01 X_1 X_2 + 3.82 \times 10^{-7} X_1^2 + 0.8 X_2^2$$

Y: The peak area of Benzo[a]pyren

X<sub>1</sub>: Volume of air sampled (mL)

X<sub>2</sub>: Analyte concentration (mg / m<sup>3</sup>)

The results showed that no significant reduction was observed in the sample by maintaining sampler for 60 days at ambient temperature. However, the sample should be protected from heat and

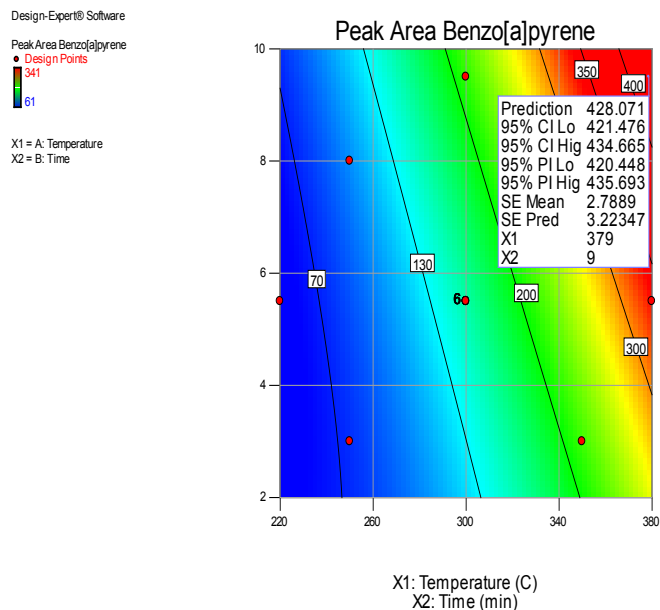


Fig. 1. Impact of temperature and time variables on the desorption of Benzo[a]pyren from needle trap

Table 1. Results of variance analysis of selecting optimization model of Benzo[a]pyren desorption process from sorbent

Source	Sum of squares (seq. SS)	Degree of freedom (D.F)	Mean squares (adj. MS)	F-value	p-Value Prob > F
<b>Square</b>	80996	1	728.64	6199.98	< 0.0001
Temperature	69475.4	5	16199.20	26590.59	< 0.0001
Time	7875.4	1	69475.44	3014.20	< 0.0001
Temperature* Time	1024	1	7875.44	391.92	< 0.0001
Temperature <sup>2</sup>	2613.2	1	1024.00	1000.16	< 0.0001
Time <sup>2</sup>	147.37	1	2613.19	56.40	0.0001
<b>Residual Error</b>	18.29	1	147.37		
Lack-of-Fit	1.62	7	2.61	0.13	0.9374
Pure Error	16.67	3	0.54		
Cor Total	81742.9	4			

R<sup>2</sup> = 0.9998

R<sup>2</sup> -pred = 0.9994

R<sup>2</sup> -adjusted = 0.9996

ultraviolet radiation according to the NIOSH 5515 method and the retention time of the samples was not mentioned [7]. The samples can be maintained for 7 days by protecting from heat and ultraviolet radiation at 4°C in EPA TO-13A method [8]. The results of investigating the method validation are shown in Table 2. The percentage of standard deviation of the measured values of the Benzo[a]pyren in diesel exhaust was calculated 4.1%.

#### 4. Conclusion

According to the results of the present study, the developed method has acceptable repeatability and reproducibility and it can be used as a method for sampling from Benzo[a]pyren with high collection efficiency at low concentrations.

#### 5. Acknowledgment

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**Table 2.** Values of repeatability, reproducibility, LOD and LOQ of the needle trap method

Analyte	Repeatability		Reproducibility		LOD mg/m <sup>3</sup>	LOQ mg/m <sup>3</sup>	LDR mg/m <sup>3</sup>
	RSD % N=6 Injections		RSD% N=6 injections				
	Three Concentrations - One NTD		Three NTDs				
Benzo[a]Pyrene	0.02	8.7	NTD1	11.9	0.01	0.03	0.01-0.5
	0.1 mg/m <sup>3</sup>	5.7	NTD2	7.3			
	0.5	6.8	NTD3	17			

## 6. References

- [1] 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. *Microchemical Journal*. 2019;148:346-54.
- [2] Negar Motakef-Kazemi N. A Novel Sorbent Based on Metal–Organic Framework for Mercury Separation from Human Serum Samples by Ultrasound Assisted- Ionic Liquid-Solid Phase Microextraction. *Analytical Methods in Environmental Chemistry Journal*. 2019, 2(3): 67-78.
- [3] Warren JM, Parkinson DR, Pawliszyn J. Assessment of thiol compounds from garlic by automated headspace derivatized in-needle-NTD-GC-MS and derivatized in-fiber-SPME-GC-MS. *Journal of Agricultural and Food Chemistry*. 2013;61(3):492-500.
- [4] Wang X, Wang Y, Qin Y, Ding L, Chen Y, Xie F. Sensitive and selective determination of polycyclic aromatic hydrocarbons in mainstream cigarette smoke using a graphene-coated solid-phase microextraction fiber prior to GC/MS. *Talanta*. 2015;140:102-8.
- [5] Koziel JA, Odziemkowski M, Pawliszyn J. Sampling and analysis of airborne particulate matter and aerosols using in-needle trap and SPME fiber devices. *Analytical chemistry*. 2001;73(1):47-54.
- [6] 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. *Journal of Chromatography A*. 2017;1527:33-42.
- [7] National Institute for Occupational Safety and Health (NIOSH). Polynuclear Aromatic Hydrocarbons By Gc: Method 5515. Fourth ed 15 August 1994. p. 2-7.
- [8] U.S. Environmental Protection Agency (EPA). Determination of Polycyclic Aromatic Hydrocarbons (PAHs) in Ambient Air Using Gas Chromatography/Mass Spectrometry (GC/MS). Method TO-13A. 1999;EPA/625/R-96/010b.