



Contents List available at VOLKSON PRESS

## New Materials and Intelligent Manufacturing (NMIM)

DOI : <http://doi.org/10.26480/icnmim.01.2018.303.305>Journal Homepage: <https://topicsonchemeng.org.my/>

ISBN: 978-1-948012-12-6



# PREPARATION AND APPLICATION OF MOLECULARLY IMPRINTED FIBER-FILLED NEEDLE TRAP EXTRACTION DEVICE IN REAL SAMPLES

Xiaoyang Guo, Xiyue Wang, Bo zhu, Lili Lian, Hao Zhang, Wenxiu Gao, Yuanyuan Tian, Dawei Lou\*

Department of Analytical Chemistry, Jilin Institute of chemical Technology, 45 Chengde Street, Jilin 132022, PR China.

\*Corresponding author email: [dwlou@hotmail.com](mailto:dwlou@hotmail.com).

This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

### ARTICLE DETAILS

### ABSTRACT

#### Article History:

Received 26 June 2018

Accepted 2 July 2018

Available online 1 August 2018

In this study, a needle trap extraction device with a molecularly imprinted polymer coated on Dupont fibers was developed for extraction. A number of heat-resistant Dupont fibers were longitudinally filled into a glass capillary, followed by coating with a molecularly imprinted polymer as an extraction medium and were used to extract volatile organic compounds from environment. Subsequently, the extracted analytes were analyzed by gas chromatography. The linear detection range, recovery, limit of detection (LOD), limit of quantification (LOQ) was studied to evaluate the method. Calibration curves for benzene, toluene, ethylbenzene, and o-xylene were linear in the concentration range of 1–250 µg/L, and the corresponding correlation coefficients exceeded 9897. The LODs and LOQs of the analytes were in the ranges of 15–25 ng/L and 35–65 ng/L, respectively.

#### KEYWORDS

Benzene series, Needle trap extraction, Molecularly imprinted polymer.

### 1. INTRODUCTION

Benzene series products are from petroleum cracking or coal tar fractionation products, including benzene, toluene, ethylbenzene, o-xylene (BTEO) and other series of compounds. Inhaled by the body for a long time can cause chronic poisoning, anemia, neurasthenia and other diseases [1-3]. Benzene series has been identified as a strong carcinogen by the World Health Organization. However, the content of benzene series in newly-renovated room and laboratory can still pose a hazard to the human body [4]. Therefore, it is very important to accurately inspect the content of benzene in the air in the newly renovated experimental room before living.

In recent years, many micro sample preparation technologies and devices have been developed, such as solid-phase micro extraction technology (SPME) and so on [5,6]. Needle trap extraction (NTE) technology is a new type of sample preparation technology recently developed, especially with molecularly imprinted polymer (MIP) as an adsorption medium [7-10]. Technology can effectively concentrate VOCs in complex environments. MIP has the advantages of good selectivity and strong adsorption capacity. Combining these two technologies perfectly, we developed an advanced molecularly imprinted needle trap extraction device (NTD). This preparation of a NTD can be completed in a single step, without tedious post-processing steps such as grinding, screening, and filling [11].

The recently developed NTD that can be used with a gas chromatograph has limited needle diameter and length because of the need to match the inlet of a gas chromatograph. When the amount of polymer in the needle is large, the permeability is poor, the back pressure is high, and the thermal desorption at the gas chromatograph inlet is easy to fall off. This severely affects the service life of the extraction device. In this study, the pollutant of BTEO was selected as the target analyte, and the benzoic acid molecular imprinting with good permeability and reproducibility was prepared by controlling the amount and distribution of the polymer in the NTD by filling the fibers. Compared with non-fiber NTD, this new device has better performance. This method is simple, stable and suitable for the enrichment and trace analysis of benzene series in environmental

samples.

### 2. MATERIALS AND METHODS

#### 2.1 Materials

All reagents, solvents, and sample solutes were of analytical grade and were obtained commercially. 2,2'-Azobisisobutyronitrile was obtained from Tianjin Reagent Chemicals. Ethylene glycol dimethacrylate and a mixture of benzene, toluene, ethylbenzene, and o-xylene (BTEO) were purchased from Tokyo Chemical Industries (Tokyo, Japan). Benzoic acid was obtained from Dongxing Reagent Company (Shenyang, China). Dodecanol was obtained from Xinxi Reagent Company (Shenyang, China). 4-Vinylpyridine was obtained from Johnson Matthey and was distilled under vacuum. Dupont fibers, which was used as a heat-resistant fiber, was supplied by Dupont Company (Delaware, America). Water was purified by a Milli-Q system (Millipore, Bedford, MA, USA). The stainless needle was manufactured by the JingDing Company (Shenzhen, China).

#### 2.2 Preparation of the NTD

A glass capillary tube (inner diameter  $1.0 \pm 0.1$  mm) was packed with a bundle of high-temperature-resistant Dupont fibers. The polymer solution was injected with a syringe directly into the filled glass tube, which was then sealed. The polymer solution was prepared according to described before [9]. After a reaction at 60 °C for 24 h, the glass tube was clamped with tweezers and washed with a solution of ethanol/NaOH (4:1, v/v) to remove the template molecule, i.e., benzoic acid. Then, after being washed with ethanol to neutrality, the polymer fibers were blown with nitrogen to dryness. Next, the fibers were packed longitudinally into the stainless needle.

#### 2.3 Extraction and desorption

The NTD was connected to the gas bag. A sample of 50 mL of BTEO gas mixture with a certain concentration was extracted manually with a sampling pump. The process of extraction was shown in Figure 1. After extraction, the sampling pump and gas sampling bag were removed.

Subsequently, the NTD was connected to a common medical injector, in which 3.0 mL high-purity nitrogen was prepared as the desorption gas. Then, the NTD was inserted to the injection port of gas chromatograph and was thermal desorption by the port. The nitrogen was injected into the injection port after retained for 10 s.

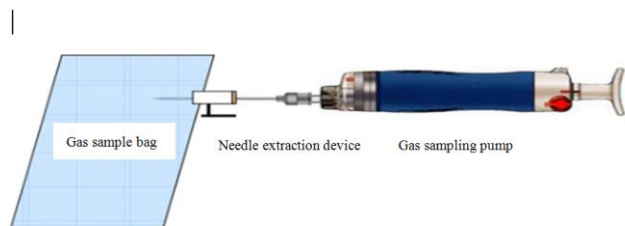


Figure 1: The process of extraction by NTD

### 3. RESULTS AND DISCUSSION

#### 3.1 The extraction influence of fiber species to NTD

In the experiment, molecularly imprinted polymers were prepared on the surfaces of Polyacrylonitrile fibers, Carbon fibers, and DuPont fibers respectively as the carrier of the adsorbent to prepare a molecularly-printed NTD. The comparison of the adsorption performance of three devices is shown in Figure 2. The results show that DuPont fiber is suitable carrier of the adsorbent.

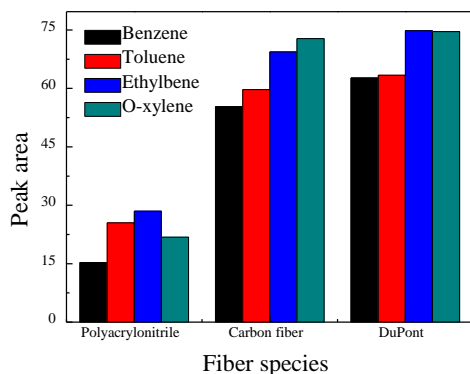


Figure 2: The extraction influence of fiber species to NTD

#### 3.2 Number of fibers used to pack the NTD

NTDs were prepared with 250, 300, 350, 400, 450 bundles of fibers, respectively, and the effect of different amounts of fibers on the enrichment performance of the device is shown in the Fig.3. In the range of 250-400 bundles, the peak area of the gas chromatogram obtained gradually increases with the increase of the number of fibers, and when 400 bundles of fibers are used, the peak area reaches a maximum value. So choose 400 bundles of fiber to preparation NTD.

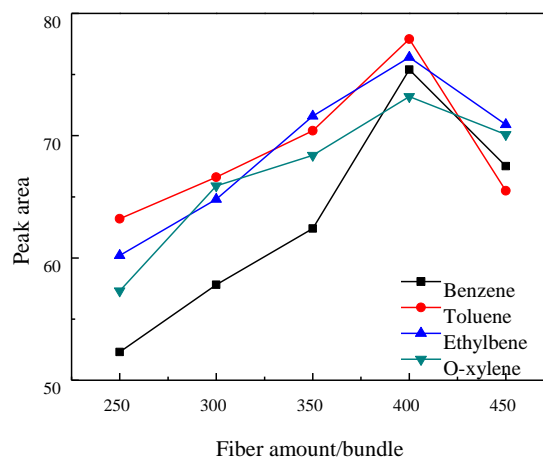


Figure 3: Performance of NTD for numbers of fibers bundles ranging from 250 to 450.

#### 3.3 Linear range, LOD, and LOQ of NTD coupled with gas chromatogram

Under the optimized conditions, the linearity of the response of the NTD-GC method was investigated using mixed standard samples of BTEO with concentrations of 1, 5, 10, 25, 50, 75, 100 and 250 µg/L. The resulting correlation coefficients, LOQ, LDQ, and linear equations by the NTD are shown in the Table 1. The results show that the NTD-GC method has excellent sensitivity and the NTD exhibits excellent enrichment of the samples.

Table 1: The method validation of NTD

Compound	Linear range (µg/L)	Linear calibration equations	r	LOD (ng/L)	LOQ (ng/L)
Benzene	1-250	y=7.46x+64.87	0.9897	25	65
Toluene	1-250	y=10.32x+41.92	0.9976	20	58
Ethylbenzene	1-250	y=26.3x+47.56	0.9988	15	42
o-Xylene	1-300	y=19.55x+43.65	0.9989	15	35

#### 3.4 Application of NTD for sampling of BTEO gas mixture from the environment

The prepared NTD was used to extract the BTEO in the actual sample. In this experiment, NTD was used to adsorb the gas in the parking lot, and gas chromatograph was used to analyzed the concentration of BTEO in the parking lot. The results showed that BTEO were detected in the parking lot. The concentration of BTEO was 3.55, 2.95, 0.77, 1.05 µg/L respectively.

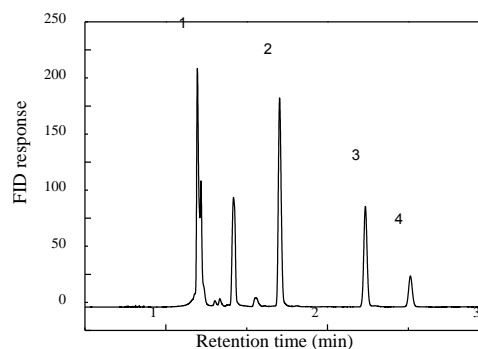


Figure 2: Gas chromatogram of BTEO after extraction by NTD in parking lot. The peak number correspond to the following: (1) benzene, (2) toluene, (3) ethylbenzene, and (4) o-xylene.

#### 4. CONCLUSION

In this study, a bundle of Dupont fibers with polymer coated on was used as the adsorbent in an NTD for extracting BTEO. The number of fibers was optimized. The linear detection range, LOD, LOQ, were used to evaluate the performance of the NTD. The results show it can be used as a sensitive low-cost device for the quantitative analysis of BTEO at low concentrations in air.

#### ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China [grant numbers 21375046, 2160505]; Science and Technology Development of Jilin Province (grant number 20140203013GX, 20130521024JH), and Research and Development for Industrial Technology of Jilin Province (grant number 2013C041). The financial support from the Key Laboratory of Fine Chemicals of Jilin Province is also acknowledged. The authors have declared no conflict of interest.

#### REFERENCE

[1] Cetin, E., Odabasi, M., Seyfioglu, R. 2003. Ambient volatile organic compound (voc) concentrations around a petrochemical complex and a petroleum refinery. *Science of the Total Environment*, 312 (1), 103-112.

[2] Shaikh, M.M., AlSuhaimi, A.O., Hanafiah, M.M. 2017. Leachable Volatile Organic Compounds from Polyethylene Plumbing Plastic Pipes: a case study of Medina Al Munawarah, Saudi Arabia. *Acta Chemica Malaysia*, 1(1), 01-03.

[3] Shirasu, M., Touhara, K. 2011. The scent of disease: volatile organic compounds of the human body related to disease and disorder. *Journal of Biochemistry*, 150 (3), 257.

[4] Urashima, K., Chang, J. 2000. Removal of volatile organic compounds

from air streams and industrial flue gases by non-thermal plasma technology. *IEEE Trans.dielect.elec.insula*, 7 (5), 602-614.

[5] Arthur, C.L., Pawliszyn, J. 1990. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, 62 (19), 2145-2148.

[6] Xu, C.H., Chen, G.S., Xiong, Z.H., Fan, Y.X., Wang, X.C., Liu, Y. 2016. Applications of solid-phase microextraction in food analysis. *Journal of Chromatography A*, 80 (1-2), 35-62.

[7] Wang, A., Fang, F., Pawliszyn, J. 2005. Sampling and determination of volatile organic compounds with needle trap devices. *Journal of Chromatography A*, 1072 (1), 127-35.

[8] Lou, D.W., Jun-Jie, O.U., Zhu, B., Wang, L., Wang, K., Wei-Yi, W.U. 2011. Preparation of formaldehyde molecularly imprinted polymer beads and its application in needle trap extraction coupled to gas chromatography. *Journal of Analytical Science*, 27 (6), 723-726.

[9] Lou, D., Chen, H., Wang, X., Lian, L., Zhu, B., & Yang, Q. 2016. Preparation and application of a coated-fiber needle extraction device. *Journal of Separation Science*, 39 (19), 3769-3774.

[10] Lou, D.W., Zhu, B., Sun, X.Y., Jun-Jie, O.U., Wang, L., Shen, P.G. 2011. Preparation of acetic acid molecularly imprinted polymer and its application on needle trap extraction technology. *Journal of Northeast Normal University*, 43 (4), 101-104.

[11] Zhang, W., He, X.W., Chen, Y., Li, W.Y., Zhang, Y.K. 2012. Molecularly imprinted polymer anchored on the surface of denatured bovine serum albumin modified CdTe quantum dots as fluorescent artificial receptor for recognition of target protein. *Biosensors and Bioelectronics*, 31 (1), 84-9.

