Environmental Health Engineering and Management Journal. 2025;12:1546
http://ehemj.com
doi 10.34172/EHEM.1546

Environmental Health Engineering and Management Journal

Review Article

Environmental Health Engineering and Management

Open Access Publish Free

Sampling of air pollutants by MOFs, COFs, and POFs in needle traps: A systematic review

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Abstract

Background: Air pollution poses significant risks to human health. Advanced sorbents such as metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and porous organic frameworks (POFs) offer high sampling efficiency for airborne pollutants. Integrating these materials into needle trap devices (NTDs) provides a solvent-free approach to air monitoring.

Methods: A systematic review was conducted using PubMed, Scopus, and Web of Science to identify studies employing MOFs, COFs, and POFs in NTDs for air sampling. Key analytical parameters, including sampling efficiency, desorption conditions, and validation against standard methods (e.g., NIOSH), were assessed.

Results: MOF-, COF-, and POF-based NTDs exhibited exceptional pollutant capture efficiency, with detection limits as low as 0.000016 µg/mL (MOFs), 0.0051 µg/mL (PAF-6), and 0.013 µg/mL (COFs) for PAHs, VOCs, and pesticides, respectively. Optimization via response surface methodology (RSM) enhanced sensitivity by 20–40% and reduced relative standard deviations (RSD) to < 10%, ensuring high reproducibility. These sorbents demonstrated long-term stability, retaining > 95% of analytes over 60 days of storage, and showed strong agreement ($R^2 = 0.97–0.99$) with standard methods (e.g., NIOSH 5515, 5600). Notably, MOF-based NTDs achieved a broad linear dynamic range (LDR) of 0.00073–12 µg/mL, outperforming traditional sorbents in trace-level detection.

Conclusion: MOF-, COF-, and POF-packed NTDs provide an efficient, cost-effective, and eco-friendly solution for air monitoring. Their high sampling capacity and compatibility with analytical methods highlight their potential for broader applications in occupational and environmental health. Further research should enhance sorbent selectivity and regeneration for improved air quality assessments.

Keywords: Air monitoring, Adsorption, Metal-organic frameworks, Covalent organic frameworks, Porous organic frameworks

Citation: Golbaghi A, Pourbabaki R, Faghihi Zarandi A, Sadeghian M, Damiri Z. Sampling of air pollutants by MOFs, COFs, and POFs in needle traps: A systematic review. Environmental Health Engineering and Management Journal. 2025;12:1546. doi: 10.34172/EHEM.1546.

Article History:
Received: 4 February 2025
Revised: 18 May 2025
Accepted: 1 June 2025
ePublished: 2 August 2025

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Introduction

Air pollution remains a critical global challenge, significantly impacting public health and environmental sustainability. Over 90% of populations in low- and middle-income countries are exposed to hazardous air quality levels, underscoring the urgent need for efficient air monitoring solutions. At present, air contamination is linked to an astonishing one in three deaths caused by strokes, lung cancer, and ongoing respiratory illnesses. Additionally, the World Health Organization (WHO) indicates that almost 90% of individuals residing in low- and middle-income countries do not have access to clean air (1). Air pollutants can be divided into two primary categories: gases and solid materials, commonly known as particulate matter (PM) (2). The WHO projects that air contamination, stemming from particles in the air (PM), polycyclic aromatic hydrocarbons (PAHs), VOCs, sulfur dioxide (SO_2), ozone (O_3), and nitrogen oxides (NOx), leads to more than two million premature fatalities each year. This concerning statistic underscores the effects of air pollution, affecting not just outdoor city settings but also indoor spaces, especially those impacted by burning solid fuels (3).

Porous materials, such as Metal-Organic Frameworks (MOFs), Covalent Organic Frameworks (COFs), and Porous Organic Frameworks (POFs), are renowned for their high surface area, tunable porosity, and exceptional adsorption capacity, making them ideal for air pollutant

capture (4).

Adsorption technology, particularly utilizing MOFs, activated carbons (ACs), hyper cross linked polymeric resins (HPRs), and zeolites, has demonstrated effectiveness in mitigating VOCs through mechanisms involving electrostatic attraction, polar and non-polar interactions, and partitioning, with adsorption capacity influenced by surface area, pore volume, pore size, and surface functional groups (5).

A novel approach has been introduced for gathering and isolating PAHs from our surrounding atmosphere. It employs needle trap devices (NTDs) that are packed with an imine-based covalent-organic framework (COF) to effectively capture and concentrate these substances. The unique properties of COFs, including their expansive surface area, customizable pore dimensions, and strong affinity for PAHs, make them ideal for sampling tasks in this scenario. Additionally, the lightweight construction and ease of use associated with COF-filled NTDs offer an invaluable tool for tracking PAHs in various environmental settings, thereby improving our comprehension of environmental health (6).

Recently a growing interest has been seen in POFs due to their remarkable characteristics, impressive efficiency, and wide-ranging uses. With a notably high surface area, unique crystalline arrangement, and the ability to be tailored for specific needs, POFs stand out as excellent options for applications such as gas capture and separation, catalysis, super capacitors, chemo sensing, and various medical uses (7). Furthermore, POFs, which consist of organic components connected by robust chemical bonds, have shown remarkable capabilities in trapping and isolating light hydrocarbons. This has generated significant enthusiasm regarding their potential application as adsorbents in various separation techniques (4).

In the field of air monitorig and analysis, microextraction techniques such as NTD have been extensively investigated. SPME involves the use of a coated fiber to efficiently extract analytes, offering advantages such as high sensitivity, reusability, and rapid analysis (8,9). On the other hand, NTD simplifies the sampling process, reduces analysis time, and provides a solvent-free approach by incorporating a sorbent within a small needle. These techniques not only contribute to cost reduction but also promote environmental sustainability (10-13). Microextraction techniques such as NTD have shown promise in overcoming some limitations of traditional methods (14). Numerous studies have investigated the impact of temperature and time on analyte adsorption in Microextraction techniques, specifically NTD. Desorption conditions for various MOF-packed NTDs have been optimized in prior studies. For instance, the optimal desorption conditions for PAH analysis using Zn-MOF in NTDs were found to be 379°C for 9 minutes (15). The highest peak area was achieved with NTDs filled with a hydroxyapatite/polyaniline nanocomposite (NTD-HAP/PA) at 250°C with a 3-minute desorption time (16).

NTDs are recognized as a unique sorbent-based technique among various methods employed for analytical extractions. These instruments utilize syringe needles, akin to those found in gas chromatography (17) injections, which are partially filled with appropriate sorbents. This configuration allows for the collection and trapping of volatile organic compounds, which are then transferred to a GC instrument through thermal desorption. While NTDs possess several characteristics and benefits similar to solid-phase microextraction (SPME), the larger size of their sorbent bed enhances their durability and permits more comprehensive extraction processes (18).

This research investigated the use of MOFs, COFs, and POFs as materials for capturing airborne pollutants in needle traps. The main goal is to evaluate how effective, specific, and practical these innovative porous materials are at trapping various air contaminants in both work environments and wider ecological settings. Through a thorough examination of existing literature, this study aimed to compare MOFs, COFs, and POFs in terms of their ability to adsorb pollutants, their longevity, and their recyclability. Additionally, it seeks to pinpoint the strengths, weaknesses, and prospects linked to these adsorbents, highlighting their critical role in improving the precision and dependability of air quality assessments and monitoring occupational exposure.

Materials and Methods

This systematic review protocol was designed following the JBI manual and the theoretical framework proposed by Arskey and O'Malley (19), updated by Levac, Colquhoun, and O'Brien and Peters et al (20,21). In addition, the Preferred Reporting Items for Systematic Reviews and Meta-Analyses Extension for Scoping Reviews (PRISMA-ScR) guided its development (22). The study protocol was preregistered in the Open Science Framework (OSF) on January 16th, 2025 (registration code: osf.io/usmhk)

Search strategy

PubMed, Scopus, Web of Science, and grey literature, such as Google Scholar were queried for studies published up to March 2025. Keywords adapted for each database were Metal organic framework, covalent organic framework, porous organic framework, porous aromatic framework and microextraction. Detailed search strategies are described in Supplementary Materials Table S1. No date-related restrictions or study design were considered in the initial search. Then, according to exclusion criteria, some studies were excluded. The process was independently performed by two investigators. The selection details for peer-reviewed and grey literature should be presented as a flowchart, following PRISMA-ScR guidelines (22). At

this stage, the reviewers will perform a new search across all databases to check for further studies for possible inclusion.

Study selection strategy

Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) was used to identify the full set of articles included in the databases and to illustrate the flow of the review process (23). Our search strategy incorporated controlled vocabulary terms and/or keywords designed to retrieve literature relevant to the terms 'MOF, 'COF, 'PAF', and 'Microextraction'. The detailed search strategy, including all of the terms, is listed in Supplementary Materials Table S1. A total of 1,843 articles were identified in the databases (Figure 1). After reviewing the titles and abstracts of the papers, review articles, non-occupational studies, letters to the editor, conference abstracts, review studies, and non-English language articles were excluded. Also, studies not relevant to the present review objectives were excluded. The full text of the remaining articles was read, and those investigating microextraction methods (MOFs, COFs, and POFs) in air were considered eligible. The reference lists of the eligible studies were also explored. A total of 12 articles were identified.

Data extraction procedure

Descriptive data were extracted using a predefined checklist, which consisted of the author's name, study location (country and workplace), year of publication, type of adsorbent, analyte, analytical methods, and characteristics of adsorbent. Quantitative variables include LOD, LOQ, LDR, Repeatability (%), Reproducibility (%), desorption time, desorption temperature, and R^2.

Results

Figure 2 outlines the key stages involved in developing a new sampling technique. It begins with the selection of an appropriate adsorbent material, such as MOFs, COFs, or POFs. The selected adsorbent is then synthesized and characterized using techniques such as X-ray Diffraction (XRD), Brunauer-Emmett-Teller (3), surface area analysis, Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR), and Dynamic Light Scattering (DLS) to assess its structural and physicochemical properties. After characterization, the adsorbent is packed into an NTD for sampling.

Sampling parameters were subsequently optimized using software tools, including Design Expert. This step involves identifying the optimal conditions for sample collection, including analyte concentration, flow rate, and relative humidity. Following this, the desorption parameters were optimized to ensure efficient recovery of the analyte from the adsorbent. Subsequently, analytical parameters, including Relative Standard Deviation (RSD), Limit of Quantification (LOQ), Limit of Detection (LOD), Linear Dynamic Range (LDR), precision, and accuracy, were determined to evaluate the performance of the sampling method. Finally, the developed sampler was validated by comparing its performance with established standard sampling methods.

This sequential approach ensures the development of a robust and reliable sampling technique suitable for various applications. Figure 2 illustrates the sequential design and development for the NTD sampler. Additionally, Table 1 presents information related to the 12 eligible studies.

Step 1: Design of the setup

In studies evaluating the performance of NTDs for air

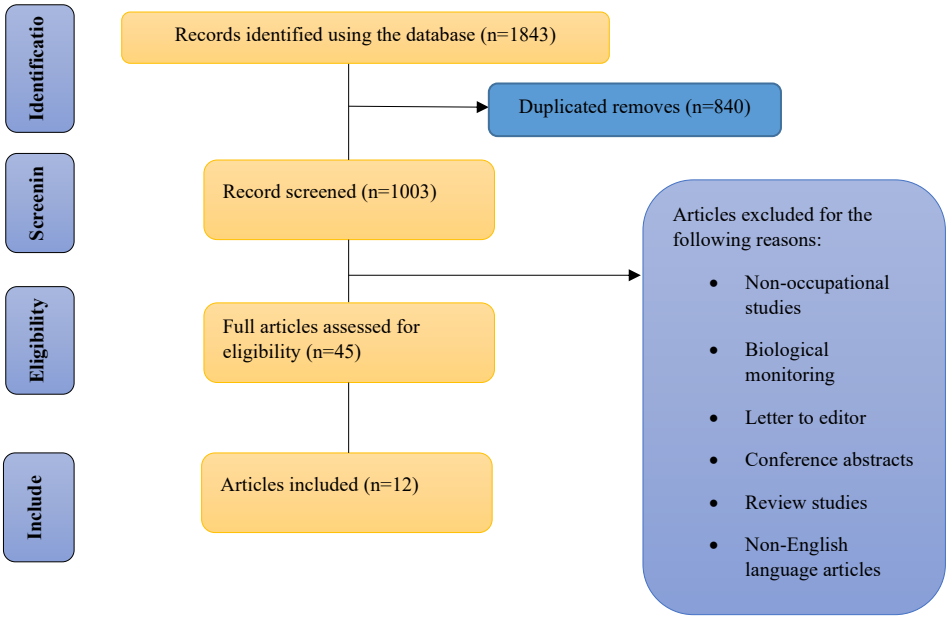

Figure 1. Flow diagram of the study selection process

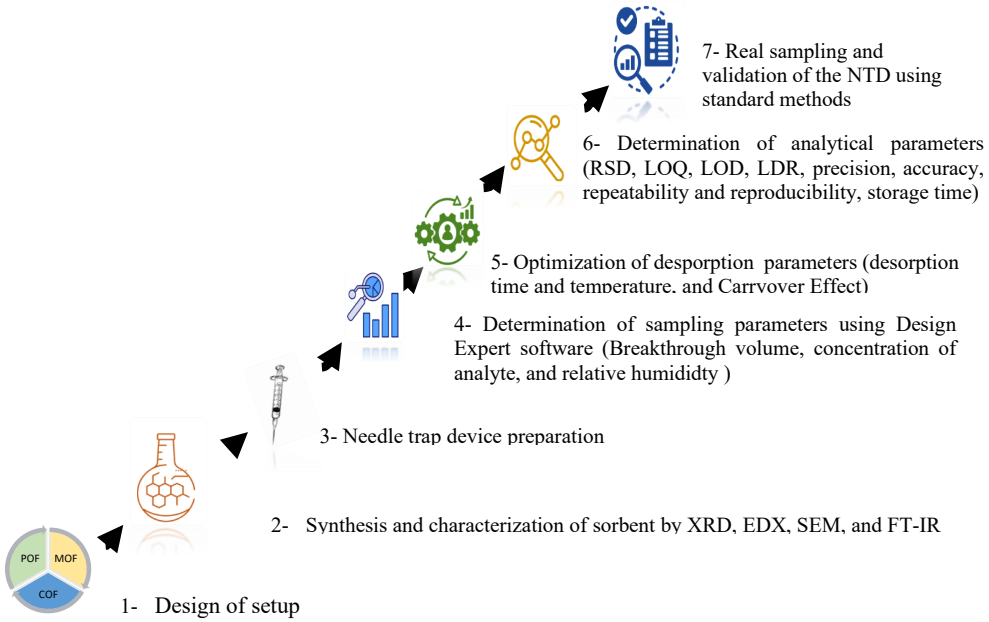

Figure 2. The sequence of design and development for the NTD sampler

pollutant sampling, two setups have been employed. Among them, the setup in Figure 3 is specifically designed for the sampling of PAHs, including aromatic polycyclic compounds (17,24,25) under controlled conditions to enhance the accuracy of pollutant concentration measurements and improve the efficacy of the sampling method. This setup was designed to evaluate the performance of NTDs packed with POF, COF, or MOF materials and consists of the following components:

1. Standard Sampling Chamber: A modified glass Erlenmeyer flask serves as the sampling chamber, equipped with three outlets:
- One connected to the MOF, PAF, and COF-packed NTD (TMC-BD-COF).
- Another connected to a sorbent tube for comparison with standard methods.
- An air inlet to maintain airflow within the chamber.
2. PAHs Vapor Generation: PAHs are heated using a stirring heater set to 140°C, generating PAH vapors inside the chamber.
3. Sampling Devices:
- The PAF, MOF, and COF NTD are utilized to trap and analyze the PAH vapors.
- The standard sorbent tube operates with the NTD for parallel sampling, serving as a reference for comparison.
4. Sampling Pumps:
- Two low-flow sampling pumps (SKC, USA) are connected to both the NTD and the standard sorbent tube, each operating at a flow rate of 1 ml/min to ensure controlled and precise sampling conditions.

The controlled generation of PAH vapors and simultaneous sampling using both the NTD and the standard sorbent tube were enabled by this configuration, facilitating a comparative analysis of sampling efficiencies.

The setup in Figure 4 is specifically designed for the sampling of aromatic amines and VOCs, including benzene, toluene, ethylbenzene, and xylene, as well as airborne organochlorine pesticides in air matrices (26-30). This system incorporates several components to ensure controlled sampling conditions and accurate analysis. A high-volume vacuum pump maintains a steady airflow through the system, while a digital thermo-hygrometer monitors temperature and relative humidity. Two low-flow sampling pumps are integrated: One designated for NTD sampling and another for activated charcoal sampling, following the NIOSH 1003 method.

The primary sampling space is a standard glass chamber, where the temperature is regulated at 30°C by Heater A to optimize conditions. A syringe pump injects target analytes into the airflow, creating controlled concentrations. Additionally, a thermostat and a thermostatic preheating chamber regulate the temperature and humidity of the incoming air, respectively. Heater B warms an Erlenmeyer flask containing distilled water, generating water vapor to adjust the relative humidity within the system.

This integrated setup enables the efficient and precise collection of volatile and semi-volatile compounds, facilitating their analysis and quantification under controlled conditions. The system allows for precise analyte generation and environmental control, enabling simultaneous sampling and analysis using both NTD and charcoal-based methods.

Step 2: Synthesis and characterization of sorbent by XRD, SEM, EDX, and FT-IR

Synthesis and characterization of the PAF-6

The synthesis of the PAF-6 adsorbent was streamlined

Table 1. Characteristics of the included studies.

N	Sorbent		Sorbent amount	Analyte		LOD	LOQ	LDR	Repeatability (%)	Reproducibility (%)	R^2	Desoption time (min)	Desoption temperature (C)	Ref
1	COF	MC-BD-COF@ SiO_2	20 mm	Halogenated hydrocarbons (HHCs)	CCL4	0.013 (µg/L)	0.041 (µg/L)	0.04-15 (µg/L)	6.39	6.41	0.97			
					PCE	0.077 (µg/L)	0.21 (µg/L)	0.2-100 (µg/L)	5.3	4.7	0.97	5	260	(31)
					PHCL	0.059 (µg/L)	0.16 (µg/L)	0.16-30 (µg/L)	5.41	6.89	0.95			
2	COF	imine-based 2D COF	15 mm	Polycyclic aromatic hydrocarbons(Naphthalene (Nap) Anthracene (Ant), Pyrene (Pyr), Phenanthrene (Phe), Benzo(a)pyrene (BaP), Ethanol (EtOH), Ethyl acetate (EtOAc) and Acetone)	Naphthalene	5-200 (µg/L)	0.027 (µg/L)	0.091 (µg/L)	6.38	9.5	0.982			
					Phenanthrene (Phe)	0.05-2 (µg/L)	0.0218 ($\mu g.L^{-1}$)	0.072 ($\mu g.L^{-1}$)	5.57	10.34	0.995			
					Anthracene (Ant)	0.05-2 (µg/L)	0.0219 (µg/L)	0.069 (µg/L)	5.36	9.59	0.978	2-10	280-310	(24)
					Pyrene (Pyr)	0.05-0.8 (µg/L)	0.0213 (µg/L)	0.065 (µg/L)	4.02	8.51	0.978			
					Benzo(a)pyrene (BaP)	0.05-1 (µg/L)	0.022 (µg/L)	0.067 (µg/L)	4.81	9.52	0.972			
3	PAF-6	PAF-6-MNPs	5 mm	Polycyclic aromatic compounds(anthracene, naphthalene, and pyrene)	Naphthalene	0.0051 (µg/L)	0.051 (µg/L)	0.000015–205 (µg/L)	19.2	2	0.96			
					Naphthalene	0.0034 (µg/L)	0.0104 (µg/L)	0.00001–1.18 (µg/L)	20.5	21.8	0.98	7-8	350	(32)
					Pyrene	0.0041 (µg/L)	0.0124 (µg/L)	0.00012–1.34 (µg/L)	17.8	22.9	0.97			
4	MOFs	Zn-MOF	15 mm	Aromatic Hydrocarbons		0.01-0.02 ng/ml	0.03-0.07 ng/ml	0.01-262 ng/ml	-	1.1-1.4		9	379	(25)
5	MOFs	HKUST-1	1.5 mg	Benzene, toluene, ethylbenzene, as well as mxylene, o-xylene, and p-xylene (BTEX)	Benzene	0.16 mg/m^3	0.52 mg/m^3	0.2-2.2 mg/m^3						
					Toluene	0.38 mg/m^3	1.1 mg/m^3	0.4–380 mg/m^3						
					Ethylbenzene,	0.5 mg/m^3	1.4 mg/m^3	0.5-435 mg/m^3	5.5–13.2	5.3–12.3 %		6	275	(26)
					m-, p-Xylene	0.4 mg/m^3	1.32 mg/m^3	0.3–2200 mg/m^3						
					o-Xylene mg/m^3	0.4 mg/m^3	0.2 mg/m^3	0.4–2200 mg/m^3						
6	MIP@ MOF	MIL-101(Fe)	1 mg	Pesticides	Diazinon pesticide	0.02 ng/ml	0.1 ng/ml		3.9–5.1	5.1–6.4	0.9781	4.5	262	(27)
7	MOFs	MIL-100(Fe)	-	Airborne organochlorine pesticides	Hexachlorobenzene	0.13 $\mu g/m^3$	0.55 $\mu g/m^3$	0.55–12000 $\mu g/m^3$	9.5	9.2				
					Aldrin	0.11 $\mu g/m^3$	0.61 $\mu g/m^3$	0.61–12000 $\mu g/m^3$	8.4	8.2				
					α-Chlordane	0.04 $\mu g/m^3$	0.21 $\mu g/m^3$	0.21–12000 $\mu g/m^3$	8.9	8.3	0.9882	5	280	(28)
					Dieldrin	0.016 $\mu g/m^3$	0.73 $\mu g/m^3$	0.73–12000 $\mu g/m^3$	9.1	9.1				
					o,p'-DDT	0.22 $\mu g/m^3$	1.03 $\mu g/m^3$	1.03–12000 $\mu g/m^3$	9.1	11.1				
					p,p'-DDT	0.41 $\mu g/m^3$	1.82 $\mu g/m^3$	1.82–12000 $\mu g/m^3$	8.3	10.3				
8	MOF	UIO-66-NH_2	1.5 cm	Halogenated volatile organic compounds (HVOCs)	Chloroform	0.02 ng/mL	0.03 ng/mL	0.01-200 ng/mL			0.98			
					Carbon tetrachloride	0.01 ng/mL	0.02 ng/mL	0.01-201 ng/mL	2.3-9.1		0.98	4	280	(29)
					Perchloroethylene	0.03 ng/mL	0.05 ng/mL	0.01-202 ng/mL			0.99			
9	MOFs	Zn^3 (BTC)2	1.5 mg		Benzo[a]pyren	0.01 mg/m^3	0.03 mg/m^3	0.01-0.5 mg/m^3	5.7-8.7	7.3-17		9	379	(33)
10	MOFs	Zirconium based metal–organic framework (UIO-66)	1.5 cm	Aromatic amines	Aniline	0.02 ng/mL	0.03 ng/mL	0.01–100 ng/mL			0.99			
					N,N-Dimethylaniline	0.02 ng/mL	0.03 ng/mL	0.01–100 ng/mL	1.3–6.8%	6.9-9.7	0.97	3	270	(30)
					o-Toluidine	0.01 ng/mL	0.05 ng/mL	0.01–100 ng/mL			0.98			

Table 1. Continued.

N	Sorbent		Sorbent amount	Analyte		LOD	LOQ	LDR	Repeatability (%)	Reproducibility (%)	R^2	Desoption time (min)	Desoption temperature (C)	Ref
11	MOFs	MIL-125	1 Mg	Phenolic derivatives	Chlorophenol	0.12 ng/mL	0.62 ng/mL	0.62–150 ng/mL	5.3-9.1	8.6-10.3	0.99	4.6	270	(34)
					o-Cresol	0.001 ng/mL	0.003 ng/mL	0.001–150 ng/mL	4.9-8.9	7.8-13.4	0.98	4		
					p-Cresol	0.002 ng/mL	0.005 ng/mL	0.001–150 ng/mL	3.4-7.5	7.4-11.8	0.98	4		
					Phenol	0.001 ng/mL	0.004 ng/mL	0.001–150 ng/mL	5.5-8.2	7.8-12.1	0.98	4.8		
12	MOFs	Zn-MOF	1.5 mg	Polycyclic aromatic hydrocarbons	Naphthalene	0.011 mg m·3	0.04 mg m^{-3}	0.01–262 mg m^{-3}	8.6-9.2	5.3-11.4	0.98-0.99	7	331	(15)
					Phenanthrene	0.021 mg/m^3	0.07 mg/m^3	0.021-1 mg m^{-3}	5.2-7	5.9-14		7	331	
					Phenanthrene	0.01 mg/m^3	0.03 mg/m^3	0.01–1 mg/m^3	7.8-9.5	8.7-12.4		8	378	
					Pyrene	0.015 mg/m^3	0.05 mg/m^3	0.015-1 mg/m^3	3.6-6.2	10.9-24.1		9	374	
					Benzo[a]Pyrene	0.01 mg/m^3	0.03 mg/m^3	0.01-0.5 mg/m^3	5.7-8.7	7.3-17		9	379	

into two primary steps. In the first step, cyanuric chloride and dimethylethanolamine were mixed in dioxane at 0°C. Piperazine was subsequently added dropwise to the mixture, which was maintained at 0°C for 4 hours. Following this, the mixture underwent ultrasonication for 30 minutes and was dried under nitrogen gas at 50°C. The resultant solid was further dried in an oven at 95°C for 24 hours, and washed with various solvents before final drying. In the second step, iron bisulfate was dissolved in a water-hydrazine solution and ultrasonicated until a green color developed. PAF-6 was then introduced, and the pH was adjusted to 11 using ammonia. The solution was subsequently refluxed for 2 hours, after which the adsorbent was magnetically separated and dried (32).

Figure S1 provides a comprehensive characterization of the PAF-6 MNPs sorbent using various analytical techniques. The characterization of PAF-6-MNPs demonstrated their porous microstructure and irregular agglomerates with an approximate diameter of 50 nm. FTIR analysis revealed peaks at 560 (Fe–O bond), 1492, and 1165 cm^{-1} (triazine rings), confirming the incorporation of PAF-6 into the magnetic nanoparticles. A peak near 1000 cm^{-1} indicated Si–O–Si stretching, signifying the successful coating of SiO_2 on the Fe_3O_4 surface. The magnetic particles exhibited strong magnetic separation capability, allowing for rapid collection with a magnet. EDS analysis confirmed the composition, with the primary elements being carbon, nitrogen, oxygen, and iron, thereby verifying the Fe_3O_4 coating with the PAF layer (32).

Synthesis and characterization of the COF

The COF was synthesized by first dissolving 1060 mg (4 mmol) of TMC in 30 mL of EtOAc in a 100 mL round-bottom volumetric flask. A solution of BD (740 mg, 4 mmol) in 30 mL of EtOAc was then added dropwise to the flask over 1 hour while stirring at 0°C. The temperature was maintained at 30°C using a constant-temperature magnetic stirring water bath. The reaction was allowed to proceed for 24 hours to facilitate the formation of the adsorbent. The resulting COF was sequentially filtered with double-distilled water, EtOH, and acetone. The yellowish-green COF was then covered with aluminum foil and placed in an oven at 70°C overnight to ensure complete drying. After characterization, which included assessments of specific surface area and thermal stability, the dried COF was ground in a mortar and sieved through a 40-mesh screen (24). The results obtained from the characterization of the COF are shown in Figure S2. Characterization results reveal several key properties of the synthesized COF. FTIR analysis confirms the successful formation of the COF by the absence of the C–O stretching band of TMC and the appearance of new bands corresponding to amide and carboxylic acid groups. XRD analysis demonstrates the good crystallinity of the COF with a prominent peak indicating the presence of TMC-p-phenylenediamine crystals. The COF exhibits excellent thermal stability, maintaining its mass up to approximately 500°C, making it suitable for thermal desorption in GC analysis. Also, Figure S3 shows the FE-SEM imaging reveals a porous, spherical columnar morphology, suggesting a high potential for contaminant capture. EDS analysis confirms the elemental composition of the COF, with carbon, nitrogen, and oxygen as the primary constituents, along with the presence of silica from sample preparation (24).

Another COF studied is TMC-BD-COF@SiO_2, a composite material created by incorporating a Covalent Organic Framework (COF) into silica (SiO_2) nanoparticles. This composite is specifically designed to enhance the COF's properties and its interactions with target compounds, making it suitable for applications such as sampling, microextraction, and environmental analysis. The synthesis of COF@SiO_2 involved a multi-step process. First, SiO_2 nanoparticles were activated with HCl. Next, APTES was utilized to introduce amine groups

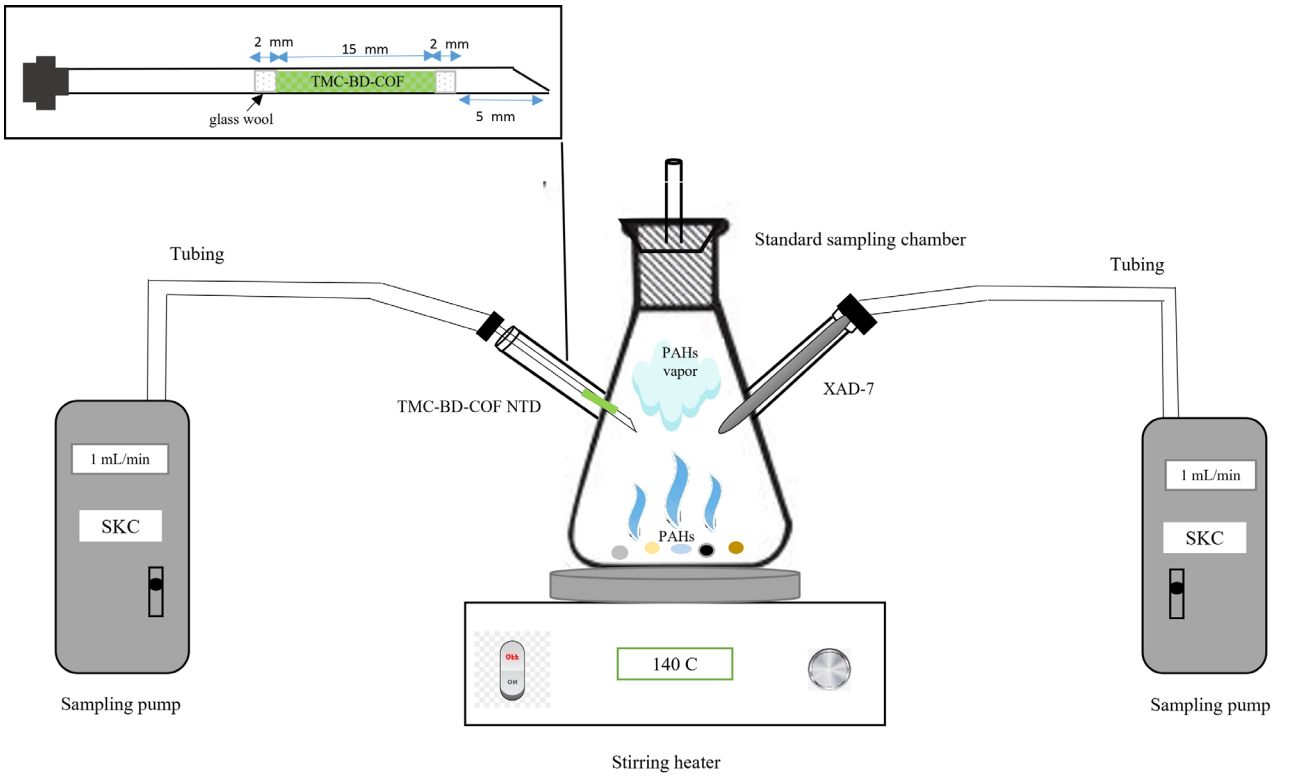

Figure 3. Schematic of standard sampling chamber; pumps, heater, and other components for optimization of the sorbent-packed NTD (24)

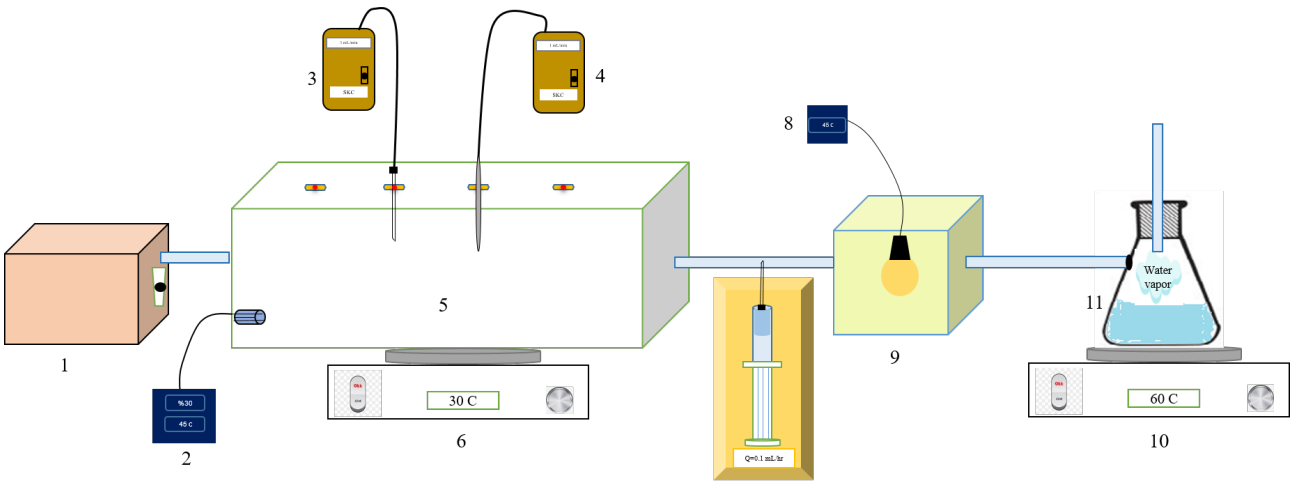

Figure 4. Schematic representation of the standard sampling chamber. 1: High-volume vacuum pump, 2: Digital thermo-hygrometer, 3: Low-flow sampling pump (SKC 222–3) for NTD sampling, 4: Low-flow sampling pump (SKC 222–3) for sampling by standard sorbent tube, 5: Standard glass chamber, 6: Heater A, 7: Syringe pump, 8: Thermostat, 9: Thermostatic preheating chamber, 10: Heater B, and 11: Erlenmeyer flask (31)

onto the SiO_2 surface. The amine-functionalized SiO_2 was then reacted with TMC and BD in EtOAc to form the COF@SiO_2 composite. Characterization through FTIR confirmed the successful formation of the COF, as evidenced by the appearance of characteristic peaks for amide and carboxylic acid groups. According to the PXRD analysis, the COF@SiO_2 exhibits an amorphous nature. The FE-SEM images revealed a porous, spherical columnar morphology, while TEM confirmed this structure, although some particle agglomeration was noted (31).

Synthesis and characterization of the MOFs

Based on the findings of various studies on MOFs, including Zn-MOF (33), HKUST-1 (26), Zn3(BTC)2 (25), MIL-100(Fe) (28), MIL-125 (34), UiO-66 (30), and UiO-66-NH_2 (29), these materials have been effectively utilized as sorbents in needle traps for pollutant sampling. The synthesis of MOFs is summarized below.

Synthesis of MIL-100 (Fe)

The synthesis of MIL-100(Fe) involved the use of iron

powder, trimesic acid (H3BTC), hydrofluoric acid (HF), and nitric acid (HNO_3). The precursor solution was transferred to an autoclave and heated at 150°C for 12 hours. The product was purified by refluxing in distilled water and ethanol. The purified MIL-100(Fe) was then centrifuged, dried, and activated at 80°C for 24 hours (28).

The structural and morphological characteristics of MIL-100(Fe) were analyzed and are illustrated in Figure S4. The FT-IR analysis of the MIL-100(Fe) metal-organic framework (MOF) confirmed the presence of carboxylate groups, as indicated by the disappearance of broad peaks in the range of 3087–2554 cm^{-1} and the absence of a free carbonyl group peak at 1720 cm^{-1}. This observation suggests the successful incorporation of trimesic acid (H3BTC) into the structure. The shifting of vibration peaks in the spectrum further indicates coordination between H3BTC and Fe^{3+} ions. The powder X-ray diffraction (PXRD) pattern demonstrated the high crystallinity and purity of the MIL-100(Fe) MOF, with diffraction peaks aligning with previously reported studies. Energy-dispersive X-ray spectroscopy (EDX) and elemental mapping analyses confirmed the presence of iron (Fe), carbon (C), and oxygen (O) within the MOF structure, showing a uniform distribution of these elements. Field emission scanning electron microscopy (FE-SEM) images revealed polyhedral microstructures with face sizes ranging from 5 to 10 μm, which is consistent with earlier reports (28).

Synthesis of UiO-66 and UiO-66-NH_2

UiO-66 was synthesized by initially combining zirconium chloride, hydrochloric acid (HCl), and dimethylformamide (DMF), followed by 20 minutes of sonication. Terephthalic acid and additional DMF were subsequently added to the mixture, which was then sonicated again. The solution was placed in an oven at 80°C for 12 hours, followed by 6 hours at 120°C under hydrothermal conditions. After the reaction, the upper phase was removed, and ethanol was added to the lower phase, which was heated at 60°C for 48 hours. Finally, the solution was heated to 150°C for 2 hours, resulting in crystalline UiO-66-NH_2 with a synthesis yield of 68% (30).

Synthesis of the Zn-MOF

Zn-MOF thin films were synthesized in a two-electrode electrochemical cell. Zinc nitrate and sodium nitrate were dissolved in deionized water, while trimesic acid was dissolved in ethanol. Following mixing, the precursor solution was aged at PH 2.1 before electrochemical deposition. The resulting thin film was allowed to age at room temperature and subsequently activated by heating at 150°C and 200°C in a vacuum oven before use (25,33).

Synthesis of the MIP@MOF

MIP@MOF refers to composites that integrate molecularly imprinted polymers for selective adsorption. The MIP@MOF core-shell nanocomposite was synthesized by combining 126 mg of diazinon as a template with 20 mg of MIL-101(Fe), 142 mg of methacrylic acid (the functional monomer), methanol, and acetonitrile, which was stirred for 60 minutes. Subsequently, 1.88 mL of EGDMA and 20 mg of AIBN were added, and the mixture was sonicated for an additional 60 minutes. Polymerization was carried out in an oil bath at 60°C for 24 hours under a nitrogen atmosphere. Following polymerization, the diazinon template was removed via Soxhlet extraction using a methanol-acetic acid mixture, and the MIP@MOF nanocomposite was dried in a vacuum oven at 65°C for 10 hours (27). Figure S5 presents FE-SEM images of MIL-101(Fe) and the MIP@MOF nanocomposite, illustrating the surface morphology of the synthesized crystals. MIL-101(Fe) exhibits uniform polyhedral structures with sizes ranging from 370 to 420 nm. In contrast, the MIP@MOF nanocomposite demonstrates that the MIL-101(Fe) cores are enveloped by MIP shells, confirming the successful formation of a core-shell structure. Figure S6 presents HR-TEM images that further corroborate this observation, revealing MIL-101(Fe) crystals as uniform square-shaped thin films measuring 200-300 nm, while the MIP@MOF nanocomposite displays thicker, amorphous MIP layers surrounding the MIL-101(Fe) cores. FTIR analysis identifies characteristic functional groups, with peaks at 1580.84 and 1654.55 cm^{-1}, indicating C=O bonds in carboxylates, and peaks at 1381.87 and 1418.79 cm^{-1} associated with C=C vibrations (27).

The comparison of synthesis methods, activation, purification, and synthesis times of the four MOFs highlights significant differences in their approaches and efficiencies. Electrochemical methods, employed for Cu-MOF and Zn-MOF, are notably faster, facilitating thin-film formation with relatively rapid activation processes (3 hours for Cu-MOF and 24 hours for Zn-MOF). In contrast, hydrothermal synthesis, utilized for MIL-100(Fe) and UiO-66, requires longer reaction times, with MIL-100(Fe) necessitating a 12-hour autoclave treatment, followed by extensive purification and activation steps. The purification process for MIL-100(Fe) is more complex, involving refluxing and centrifugation, while the other MOFs utilize simpler washing and filtration methods. Overall, electrochemical synthesis provides a more time-efficient approach, whereas hydrothermal methods produce high-quality crystalline structures, albeit with a greater time investment.

Activation processes for all MOFs involve heating, but the temperatures and durations vary. Cu-MOF and Zn-MOF are activated in vacuum ovens at 423 K and 200°C, respectively, while MIL-100(Fe) is activated at 80°C, and UiO-66-NH_2 undergoes a final heating step at 150°C.

Step 3- Needle trap device preparation

The preparation of the NTD in these studies involved a

structured and methodical process to ensure efficient packing, airflow regulation, and optimal desorption of analytes. The main body of the NTD typically consisted of a gauge-22 spinal needle, serving as the housing for the adsorbent material. To secure the adsorbent and prevent clogging, layers of glass wool, measuring between 2 and 3 mm, were placed at both ends of the packed sorbent. Additionally, a small gap was left at the needle tip to avoid direct contact with the gas chromatography (17) injection port and to prevent the adsorbent from spilling. The adsorbent materials varied across studies and included COFs, MOFs, and mixed sorbents combined with glass powder. The inclusion of glass particles served a dual purpose: it prevented blockage and ensured stability during sampling. The absorbent amount in PAF is 5 mm. COFs are typically packed in longer lengths of 15-20 mm due to their high surface area and stability (24). In contrast, MOFs, which are known for their exceptional sampling properties, usually require smaller amounts—between 1 and 1.5 mg or lengths of about 1.5 cm for optimal performance (Figure S7) (16,27,29,30). The variation in adsorbent amounts, ranging from 1 mg to 20 mm packed lengths, reflects the diverse properties and applications of these materials. Selecting the appropriate sorbent and its quantity is crucial for efficient analyte sampling and concentration. This underscores the need to carefully consider factors such as adsorbent type, surface area, pore size, and target analytes during the design and optimization of NTD.

Airflow through the packed NTD was a critical factor, typically measured using a soap bubble flow meter. Optimal sampling flow rates ranged from 0.8 to 3.0 ml/min, depending on the specific study (26,28-30). Flow rates exceeding 3.0 ml/min reduced repeatability, while lower flow rates decreased analyte concentration (26). Before each experiment, the NTDs underwent conditioning or aging at elevated temperatures until a stable GC baseline was achieved. Sampling was conducted using calibrated pumps, and analytes were desorbed using inert carrier gases such as nitrogen, delivered via medical syringes. Optimal desorption times and conditions were determined to maximize analyte recovery, often through surface response methodologies. In summary, the preparation of NTDs involves meticulous packing, securing, and conditioning steps to ensure stability, proper flow regulation, and effective analyte desorption. The combination of adsorbents with glass particles, glass wool anchoring, and optimized flow rates (2–3 ml/min) is essential for achieving high performance and repeatability. Careful selection of desorption parameters, including temperature, carrier gas flow, and time, further enhances the efficiency of analyte transfer into the GC column (26,28-30).

Step 4: Determination of sampling parameters using Design Expert software (Breakthrough volume, concentration of analyte, and relative humidity)

To optimize the sampling conditions for the NTD, key parameters including breakthrough volume, analyte concentration, and relative humidity were investigated using Design Expert software and the Response Surface Methodology (RSM). The breakthrough volume (BTV) serves as a pivotal indicator, specifying the maximum air volume that can pass through the NTD before the sorbent reaches saturation. Notably, Zn-MOF-based NTDs have demonstrated a BTV of approximately 2500 mL for Benzo[a]pyrene at a 0.5 mg/m^3 concentration (33). Similarly, MIL-100(Fe)-based NTDs exhibited a BTV ranging from 500 to 2500 ml for organochlorine pesticides (28), while the UiO-66-based NTD designed for aromatic amines performed optimally at an air sample volume of 1000–2000 ml (30). In this study, the analyte concentrations were controlled by generating a standard atmosphere in a glass chamber under regulated temperature and humidity. Specifically, PAHs were tested at 0.1–0.5 mg/m^3 (33), diazinon pesticide at 0.02–0.1 mg/m^3 (27), and VOCs at 0.01–262 ng/ml (26). Humidity significantly influences the adsorption efficiency of MOF-based NTDs. Under high humidity conditions, water molecules may compete with the analytes for sampling sites, thereby reducing the trapping efficiency. In the optimized setups, humidity levels of 20–45% were found suitable for phenolic derivatives (34), 25% for pesticides (27), and 30–70% for VOCs (29).

Step 5: Optimization of desorption parameters (desorption time, temperature, and carryover effect)

Optimizing thermal desorption is critical for ensuring complete analyte release from MOF-based NTDs while preventing thermal degradation. Therefore, the desorption temperature and desorption time were systematically optimized for each sorbent to maximize efficiency. Additionally, the carryover effect was assessed to confirm the reusability of the sorbents and eliminate the risk of cross-contamination between consecutive samples.

The optimal desorption temperature varied based on the MOF structure and the target analytes, ensuring complete analyte recovery while preventing degradation. For Zn-MOF, an optimal temperature of 379°C was identified for PAHs (e.g., Benzo[a]pyrene). At temperatures above 380°C, partial thermal degradation occurred, while temperatures below 370°C led to incomplete desorption, reducing overall efficiency (33). In the case of MIL-100(Fe), 280°C provided the best conditions for desorbing organophosphate pesticides (OCPs), facilitating efficient analyte release without compromising the integrity of the sorbent. Higher temperatures posed a risk of pesticide degradation, while lower temperatures resulted

in incomplete elution from the MOF's pores (28). Similarly, for UiO-66-NH_2, a desorption temperature of 280°C enabled rapid release of halogenated VOCs while maintaining structural stability. However, exceeding 300°C increased the risk of analyte breakdown (29). Lastly, MIP@MOF exhibited optimal desorption for diazinon pesticide at 262°C, ensuring complete analyte transfer into the gas phase while minimizing thermal decomposition (27). These findings underscore the importance of tailoring desorption conditions to each MOF's thermal and structural properties for maximum extraction efficiency.

The optimal desorption time was carefully determined to maximize analyte release efficiency while minimizing peak broadening and sample loss. For Zn-MOF, a 9-minute desorption time was required to achieve complete release of PAHs, ensuring full recovery and preventing peak tailing (33). In the case of MIL-100(Fe), 5 minutes was sufficient for organophosphate pesticides (OCPs), as extending the desorption time further did not enhance analyte recovery and instead increased baseline noise (28). For UiO-66-NH_2, a 4-minute desorption was adequate for halogenated VOCs, given their higher volatility and fast elution behavior (29). Similarly, MIP@MOF exhibited optimal desorption for diazinon pesticide at 4.5 minutes, ensuring nearly complete analyte transfer while preventing excessive heat exposure that could lead to pesticide degradation (27). These optimized desorption times were tailored to each MOF-based NTD, balancing efficient analyte recovery, stability, and reproducibility across different target compounds.

To evaluate the carryover effect, a blank injection was conducted immediately after each desorption cycle to determine whether residual analytes remained in the sorbent. The results showed that all tested MOF-based NTDs, including Zn-MOF, MIL-100(Fe), UiO-66-NH_2, and MIP@MOF, exhibited no significant carryover, confirming that the optimized desorption conditions effectively cleared the sorbent bed. This finding highlights the high reliability and reusability of these MOFs for consecutive sampling, making them well-suited for high-throughput environmental and occupational air monitoring without the risk of cross-contamination.

The optimization of desorption parameters, including temperature, time, and carryover assessment, ensures highly efficient and reliable performance of MOF-based NTDs for air pollutant sampling. Complete analyte recovery is achieved by precisely tuning temperature and time, preventing analyte degradation while maximizing extraction efficiency. Additionally, the preservation of sorbent integrity is crucial, particularly for thermally sensitive compounds, ensuring the long-term usability of the MOF-based NTDs. The high reusability and throughput of these sorbents are further confirmed by the negligible carryover effect, which allows for consecutive sampling without the risk of cross-contamination. By employing response surface methodology (RSM) and iterative experimental design, these MOF-based NTDs provide a solvent-free, efficient, and cost-effective solution for air pollutant monitoring, offering high sensitivity, reproducibility, and applicability across various airborne contaminants (27-29,33).

Step 6: Determination of analytical parameters (RSD, LOQ, LOD, LDR, precision, accuracy, repeatability, reproducibility, and storage time)

The analytical performance of different NTDs was evaluated using relative standard deviation (RSD), limit of quantification (LOQ), limit of detection (LOD), linear dynamic range (LDR), precision, accuracy, repeatability, and reproducibility. A summary of analytical parameters for various MOF-based NTDs is presented in Table 2.

Over 60 days at 4°C, Zn-MOF-based NTDs showed no notable decrease in analyte concentrations (15), and MIL-125-based NTDs similarly preserved phenolic derivatives for up to 60 days (34). By comparison, diazinon pesticide samples exhibited only minimal degradation when stored for 7 days (27).

Step 7 - Real sampling and validation of the NTD using standard methods

To validate the efficiency of the MOF-based NTDs, real sampling was performed in field conditions and compared with NIOSH standard methods. The results are summarized in Table 3.

The Zn-MOF NTD has been successfully employed for the quantification of PAHs in diesel exhaust, showing strong correlation with NIOSH 5515 (15). In industrial settings, NTD-UiO-66 effectively monitored aromatic amines with results closely matching NIOSH 2002 (30). Furthermore, in agricultural environments, MIL-100(Fe)-NTD demonstrated high accuracy for organochlorine pesticides, aligning well with NIOSH 5600 (28).

Table 4 presents a comprehensive comparison of the analytical performance of three sorbents, COF, PAF, and MOFs, employed in the needle trap technique. Key parameters assessed include sensitivity (LOD and LOQ), linear dynamic range (LDR), precision (repeatability and reproducibility), linearity (R^2), and desorption conditions (time and temperature).

Discussion

The integration of advanced porous materials such as MOFs, COFs, and POFs into NTDs represents a significant advancement in air pollutant monitoring. These materials exhibit exceptional sampling capacities due to their high surface areas, tunable pore architectures, and chemical functionalities tailored for specific analytes. However, to fully appreciate their potential and limitations, it is critical to contextualize these findings within the broader

Table 2. Analytical performance of different NTDs

Sorbent Type	Analyte	LOD (ng/mL)	LOQ (ng/mL)	LDR (ng/mL)	Repeatability (%)	Reproducibility (%)	Reference
Zn-MOF	PAHs	0.01 - 0.02	0.03 - 0.07	0.01 - 262	1.1 - 1.4	5.3 - 24.1	(26)
MIL-100(Fe)	Organochlorine Pesticides	0.13	0.55	0.55 - 12000	9.5	9.2	(28)
MIP@MOF	Diazinon pesticide	0.02	0.1	-	3.9 - 5.1	5.1 - 6.4	(27)
UiO-66-NH_2	Halogenated VOCs	0.01 - 0.03	0.02 - 0.05	-	2.3 - 9.1	-	(29)

Table 3. Validation of the efficiency of the MOF-based NTDs

Analyte	NTD Method (R^2 Value)	NIOSH Method (R^2 Value)	Reference
PAHs	0.99	NIOSH 5515	(33)
Organochlorine Pesticides	0.9882	NIOSH 5600	(28)
Aromatic Amines	0.98 - 0.99	NIOSH 2002	(30)

Table 4. Comparison of analytical performance in sorbents

Sorbent	Sorbent amount	LOD (µg/ml)	LOQ (µg/ml)	LDR (µg/ml)	Repeatability (%)	Reproducibility (%)	R^2	Desorption time (min)	Desorption temperature (°C)
COF	15 mm	0.013	0.021	0.04-15	4.02- 6.39	4.7-10.34	0.97-0.995	2-10	260-310
PAF-6	5 mm	0.0051	0.051	0.000015–205	17.8–20.5	20–22.9	0.96-0.98	7-8	350
MOFs	15 mm or 1.5 mg	0.000016	0.00073	0.00073–12	1.3–13.2	1.1-12.4	0.97-0.99	3-9	262-380

literature and address key challenges and opportunities for future applications.

The high sampling efficiency of MOF-, COF-, and POF-based NTDs, as demonstrated in this review, aligns with numerous studies highlighting the superiority of these materials over traditional sorbents, such as activated carbons (ACs) and zeolites. For instance, Li et al emphasized that MOFs outperform ACs in capturing VOCs due to their ordered porosity and customizable surface chemistry, which enhance both sampling kinetics and selectivity (5). Similarly, COFs have shown remarkable affinity for PAHs owing to their π-π interactions and hydrophobic pore environments (6). These properties are particularly advantageous for NTDs, where rapid analyte capture and minimal interference from humidity or competing molecules are critical (7).

Despite their advantages, the practical deployment of MOFs and COFs in field applications faces challenges related to environmental stability. For example, He et al noted that certain MOFs, such as HKUST-1, exhibit reduced structural integrity under high humidity due to water molecule intrusion into their metal-ligand frameworks (35). This limitation was observed in MIL-100(Fe)-based NTDs, where sampling efficiency for organochlorine pesticides decreased at relative humidity levels above 70% (28). To mitigate such issues, recent studies have explored the hydrophobic functionalization of MOFs. Chambers et al demonstrated that amine-modified MIL-125-NH_2 retained its adsorption capacity for formaldehyde even at 80% humidity, suggesting that post-synthetic modifications could enhance the robustness of MOF-based sorbents in real-world conditions (36).

The development of composite sorbents, such as MIP@MOF and COF@SiO_2, highlights a promising direction for improving both selectivity and stability (6,27). By integrating molecularly imprinted polymers (MIPs) with MOFs, Rahimpoor et al achieved selective sampling of diazinon pesticide, even in complex matrices containing structurally similar compounds (27). Similarly, silica-supported COFs (COF@SiO_2) exhibited enhanced mechanical stability and resistance to agglomeration, addressing a common limitation of pure COFs in flow-through systems (31). These innovations underscore the potential of hybrid materials to overcome the limitations of individual frameworks.

While laboratory-scale studies have demonstrated the efficacy of MOF- and COF-based NTDs, scalability remains a concern. The synthesis of many MOFs involves costly ligands and energy-intensive processes, such as hydrothermal or solvothermal methods. However, electrochemical synthesis routes, as employed for Zn-MOF, offer a faster and more cost-effective alternative. Furthermore, the reusability of these sorbents—validated by negligible carryover effects in this review—reduces long-term operational costs. For instance, Zn-MOF-based NTDs maintained consistent performance over 60 days of storage, suggesting durability suitable for large-scale environmental monitoring programs (15).

The strong correlation between MOF-based NTDs and NIOSH standard methods (e.g., NIOSH 5515 for PAHs and NIOSH 5600 for pesticides) reinforces their reliability. These findings are consistent with the findings of Duan et al who reported that NTDs packed with $Zn_3(BTC)_2$ achieved detection limits for PAHs comparable to those of conventional solid-phase microextraction (SPME) fibers, but with superior reproducibility (< 10% RSD)

(17). Field applications in industrial and agricultural settings further validate their practicality. For example, UiO-66-NH_2 NTDs effectively monitored halogenated VOCs in manufacturing facilities, with results matching those of activated charcoal tubes (29). Such performance highlights the potential of NTDs to replace solvent-intensive methods in occupational health assessments.

In terms of sensitivity, MOFs demonstrate superior performance with the lowest LOD (0.000016 μg/ml) and LOQ (0.00073 μg/ml), making them highly suitable for trace-level detection. PAF ranks second, while COF exhibits the least sensitivity among the three. Regarding linear dynamic range, PAF shows a significant advantage, providing a broad range from 0.000015 to 205 μg/ml, which is optimal for detecting a wide variety of analyte concentrations. MOFs and COF have narrower LDRs. In the comparison of precision, COF achieves the best results with the lowest repeatability (4.02–6.39%) and reproducibility (4.7–10.34%), indicating high consistency and reliability in repeated analyses. PAF-6 exhibits the highest variability, while MOFs demonstrate moderate precision.

All three sorbents show strong linearity, with R^2 values close to or exceeding 0.97. Concerning desorption conditions, COF is advantageous due to a short desorption time (2–10 minutes) and moderate temperature (260–310°C), enhancing efficiency and energy conservation. PAF-6 necessitates the highest temperature (350°C) for desorption, which may be a limitation. MOFs provide balanced performance with a desorption time of 3–9 minutes and a broad temperature range (262–380°C). In conclusion, MOFs represent the optimal choice when high sensitivity and balanced overall performance are required. PAF is more suitable when a wide linear range is critical, although it compromises precision and necessitates harsher desorption conditions. COF is ideal for applications that prioritize precision, stability, and moderate operational requirements. The optimal selection ultimately depends on the analytical objectives, whether sensitivity, range, or reproducibility is prioritized.

Current research on the application of sorbents in the needle trap method has primarily been conducted under controlled laboratory conditions with specific analytes. This approach presents a significant limitation, as it does not consider the competitive adsorption phenomena of various pollutants present in real-world samples. In practical scenarios, the simultaneous presence of multiple pollutants with distinct properties can affect the functionalized sorbent's ability to selectively adsorb the target analyte, leading to decreased efficiency, accuracy, and sensitivity of the method. Therefore, to achieve a more precise and applicable assessment of this method in real-world contexts, future studies must investigate the performance of sorbents in the presence of complex mixtures of pollutants and analyze the effects of competitive adsorption. The inherent limitation of a small sorbent bed in NTD restricts their use for continuous sampling or in environments with high analyte concentrations. This limitation leads to rapid breakthrough, which can significantly affect the reliability of the results. While NTDs are useful in specific applications, they face constraints when sampling air analytes at elevated concentrations and over prolonged occupational exposure periods. As a result, the limited capacity of NTDs prevents them from serving as the sole sampling method for an entire work shift, as they quickly become saturated, leading to breakthrough and potential sampling inaccuracies. The manual packing of sorbent in a needle trap results in significant inconsistencies in density, amount, and particle distribution within the needle. These inconsistencies can lead to variable airflow, breakthrough volumes, and poor reproducibility, ultimately compromising the reliability of analytical results. Implementing automated filling systems would mitigate these limitations by ensuring precise and uniform packing, enhancing throughput, reducing contamination, and improving overall quality control. Consequently, this would render needle trap microextraction a more robust and efficient technique. Considering that the needle trap sampling process operates at low concentrations and low air flow rates, a primary challenge in this field is the generation of dynamic and well-defined concentrations within the air stream. As a result, concentration generation during the dynamic phase frequently experiences substantial fluctuations in air flow.

In conclusion, the findings of this study establish a robust foundation for implementing novel sorbent materials as media in the NTD method for extracting and monitoring VOCs and other pollutants in workplace environments. Several research pathways have been identified for further exploration. One proposed study aimed to investigate the application of NTD and other microextraction techniques to assess exposure levels to various analytes in workplace settings, as recommended by ACGIH guidelines. Additionally, it is suggested that PAFs and COFs may serve as innovative adsorbents in other microextraction methods, such as SPME, for the extraction of analytes relevant to occupational health. The development of hybrid sorbent materials is also proposed, with the goal of enhancing extraction and sampling methodologies, as well as their application in workplace sampling. Furthermore, as part of a separate study, a comparative analysis of all new sorbents (MOFs, COFs, and PAFs) is being conducted to identify the most effective sorbent for the extraction and sampling of the same analyte under consistent conditions.

To enhance the reliability of the results obtained through the needle trap method, a thorough examination of the selectivity of the employed adsorbents is essential. Consequently, it is recommended that future research

prioritize the investigation of competitive adsorption involving various pollutants on the adsorbent. This is imperative, as real samples often contain multiple pollutants that simultaneously compete for binding sites on the adsorbent, potentially diminishing the efficiency and accuracy of target compound extraction. Gaining insights into this competitive interaction is crucial for developing improved adsorbents and more reliable extraction methodologies. To improve selectivity in the needle trap sampling method, the implementation of functionalized sorbents is proposed as a novel and effective strategy. These materials, characterized by their large porous structures and the capability to modify their chemical properties via functionalization, can establish specific interactions with target analytes. This enhances selective adsorption and substantially minimizes the presence of interfering substances in complex samples, ultimately resulting in increased accuracy, sensitivity, and reliability of needle trap analyses. Finally, an important area of investigation is the comparative evaluation of MOFs, COFs, and PAFs for the extraction of emerging biomarkers in biological monitoring. As a final point, the comparative evaluation of MOFs, COFs, and PAFs for the extraction of emerging biomarkers in biological monitoring is a significant area of research.

Conclusion

Integrating advanced adsorbents such as MOFs, COFs, and POFs into NTDs has proven highly effective for monitoring various airborne pollutants. These sorbents' high surface area, tunable pore size, and strong adsorptive affinity enable precise capture of contaminants ranging from PAHs and VOCs to pesticides and aromatic amines. Moreover, by leveraging software-driven optimization (e.g., Design Expert with response surface methodology), key sampling parameters including breakthrough volume, analyte concentration, relative humidity, and desorption conditions can be fine-tuned to achieve maximum efficiency and reproducibility. Despite these advancements, challenges like ligand costs and humidity sensitivity require targeted research. Electrochemical synthesis and hybrid frameworks represent promising paths to scalable, robust sorbents. Collaborative efforts between material scientists and industrial hygienists will be critical to translate lab-scale innovations into field-ready solutions.

Studies have consistently demonstrated minimal analyte degradation over storage periods, particularly for Zn-MOF- and MIL-125-based NTDs, and strong correlation with established reference methods (e.g., NIOSH 5515, 5600, and 2002). These findings reinforce the reliability of MOF- and COF-packed NTDs as solvent-free, cost-effective, and environmentally friendly alternatives for both laboratory and field applications. Looking ahead, further research into diverse framework structures and functionalized sorbents will likely expand the applicability of NTDs, optimizing the capture and detection of an even broader range of airborne contaminants in occupational and environmental settings.

Acknowledgments

We are grateful for the invaluable support provided by Ahvaz University of Medical Sciences throughout the research process.

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Competing interests

The authors declare no competing interests related to this study. All research was conducted independently without any financial or personal relationships that could have influenced the work reported in this paper.

Ethical issues

This study was approved by the Ethics Committee of the Student Research Committee at Ahvaz University of Medical Sciences (IR.AJUMS.REC.1404.237).

Funding

This project was approved in the Student Research Committee at Ahvaz University of Medical Sciences.

Supplementary files

Supplementary file 1 contains Tables S1 and Figures S1-S7.

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