“Entry to the Stockholm Junior Water Prize 2025”

**Project Title:** New Sorbent-Enhanced Needle Trap Device for VOC Detection in Water

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## Abstract

Water is one of the most vital natural resources, and its quality is increasingly threatened by pollution from harmful substances. In particular, volatile organic compounds (VOCs) released into aquatic environments from industrial sources pose a serious environmental and public health concern, as even at low concentrations they can exhibit toxic and carcinogenic effects. This highlights the need for sensitive and reliable analytical methods. Existing analytical approaches often face limitations in availability, sensitivity, and environmental safety when effectively analyzing VOCs in water samples.

In this study, a new method for analyzing VOCs in water samples is proposed and tested, utilizing a Needle Trap Device (NTD) filled with a novel metal-organic framework (MOF), ZnMOF-74a, as the sorbent. The key outcome of this work is the demonstration of the high efficiency of ZnMOF-74a for detecting isoprene, acetone, benzene, and p-xylene in water samples. The method showed low limits of detection (ranging from 1.21 to 33.51 ng/L), high linearity with correlation coefficients (r² > 0.95), and excellent reproducibility (RSD < 8%). A comparative analysis with existing methods revealed the proposed approach's superior sensitivity (e.g., the LOD for acetone was four orders of magnitude lower than that of the SPME method).

Thus, the results contribute to the growing body of knowledge on the use of MOF-based sorbents in analytical chemistry, demonstrating their potential for developing more accurate and environmentally friendly pollutant monitoring methods. These findings may be valuable not only for analytical chemistry but also for water treatment, ecotoxicology, and public health risk assessment. In the future, the method could be adapted for VOC analysis in other media (air, soil) and for the development of portable sensors and automated environmental monitoring systems.

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Key words: microextraction, needle-trap device (NTD), metal-organic frameworks (MOFs), volatile organic compounds (VOCs)

Abbreviations and Acronyms: needle-trap device (NTD), metal-organic frameworks (MOFs), volatile organic compounds (VOCs), United Nations Environment Programme (UNEP), European Environment Agency (EEA), solid-phase microextraction (SPME), polycyclic aromatic hydrocarbons (PAHs), X-ray diffraction (XRD), Thermogravimetric analysis (TGA), hydrolyzed polyacrylonitriles (H-PAN), gas chromatograph (GC), Gas Chromatography – Mass Spectrometry (GC-MS), Mass Spectrometry (MS), selected ion monitoring (SIM), limit of detection (LOD), limit of quantification (LOQ), limit of blank (LOB).

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Biography

Participant 1: My name is Elina. I’m a high school student and a researcher, but above all, a passionate science enthusiast eager to make my own contribution to the scientific community. Driven by curiosity and commitment to make a change, I focus on topics that are not only relevant, but also allow me to apply my strengths and bring a meaningful impact.

Participant 2: My name is Adiskhan, and I am a rising senior from Kazakhstan, who is fascinated by the fields of organic chemistry and synthetic biology. My worldview is ‘scientific optimism’ — I believe that through collective research efforts, humanity will be able to overcome the current and future threats in the face of environmental and healthcare threats.

## Introduction

Volatile organic compounds (VOCs) are organic substances that easily evaporate into the environment due to their low boiling points. They pose a serious threat to aquatic ecosystems, entering water bodies through industrial discharges, atmospheric precipitation, and groundwater infiltration [[1]](#Ref_1). Due to their lipophilic properties, VOCs accumulate in bottom sediments, disrupting natural ecosystem cycles. This accumulation negatively affects water quality and worsens habitat conditions for aquatic organisms [[2]](#Ref_2). Importantly, VOC contamination in water bodies poses risks not only to the environment but also directly to human health. It has been established that even at low concentrations, chronic exposure to these compounds can lead to serious health risks, including liver damage, respiratory diseases, and cancer [[3](#Ref_3),[4,](#Ref_4)[5](#Ref_5),[6](#Ref_6)]. The threat posed by VOCs is supported by numerous studies. For example, a study by Kavcar et al. [[7](#Ref_7)] I n Turkey detected trihalomethanes, benzene, toluene, p-xylene, and naphthalene in drinking water. Although concentrations did not exceed regulatory limits, risk assessment indicated that bromodichloromethane and dibromochloromethane posed carcinogenic risks above the acceptable threshold (10⁻⁶) with long-term consumption. In another study, Zhang et al. [[8](#Ref_8)] identified 31 types of VOCs in 58 water bodies in the Yangtze River Delta (China), with toluene and styrene presenting high ecological risks, and 1,2-dichloroethane, bromodichloromethane, and 1,1,2-trichloroethane showing elevated carcinogenic risks to the population. Research by Im et al. (2021) revealed high concentrations of toluene in tributaries of the Han River Basin, which had toxic effects on aquatic life [[9](#Ref_9)]. These findings underscore the urgent need for comprehensive measures to monitor and reduce VOC emissions.

In response to this issue, the international community is strengthening environmental regulations. The United Nations Environment Programme (UNEP) and the European Environment Agency (EEA) are developing and implementing strict guidelines aimed at reducing VOC emissions and improving pollution monitoring systems. A key focus is the development of highly sensitive, selective, and environmentally friendly analytical methods for VOCs that ensure reliable detection in complex matrices and at low concentrations.

Traditional methods for VOC analysis, such as liquid-liquid extraction and solid-phase extraction, are widely used for water samples. However, these preparation techniques have notable disadvantages, including high cost, operational complexity, labor intensity, and the use of large volumes of organic solvents [10]. In recent years, modern microextraction techniques have gained increasing popularity, including stir bar sorptive extraction , solid-phase microextraction (SPME) [12], and Needle Trap Devices (NTD) [13]. A common advantage of these methods is the integration of sampling, extraction, and preconcentration into a single, compact, and user-friendly procedure. Comparative characteristics of various extraction methods are presented in Table 1.

**Table 1.** Comparison of extraction techniques

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Parameter** | **NTD** | **SPME** | **LLE** | **LPME** | | |
| **SDME** | **HF-LPME** | **DLLME** |
| **LOD range (ng/L)** | 0.01-10 | 5-50 | 100-500 | 5-50 | 45-75 | 5-100 |
| **Solvent volume (μL)** | None | None | >10000 | 1-5 | 1-5 | 100-1000 |
| **Sample volume (mL)** | 50-100 | <100 | >100 | 5-20 | 5-20 | 5-10 |
| **Extraction time (min)** | 5-50 | 15-50 | 15-50 | 10-30 | 10-60 | 5-45 |
| **Cost** | Moderate | Moderate | Moderate | Low | Low | Low |
| **Automation potential** | High | High | Low | Low | Moderate | Low |
| **Advantages** | Solvent-free, high variability, high mechanical stability | Solvent-free, great  efficiency in  preconcentration | Scalable | Independence  from a commercial  supplier | Independence  from a commercial  supplier, great  stability | High efficiency  Independence  from a commercial  supplier |
| **Disadvantages** | Dependence on commercial suppliers, clogging issues | Dependence on  commercial  suppliers, low  robustness | Low-selectivity, environmentally harmful | Poor stability of the organic phase; not suitable for dirty samples | Need for  membrane pre-conditioning,  possibility of  memory effects | Only suitable for liquid matrix sample; limitation in the choice of the proper solvent |

The sampling method using a Needle Trap Device (NTD) is based on the extraction of analytes by a sorbent packed inside a stainless steel needle (Figure 1) [14]. Unlike the widely used SPME, which relies on equilibrium between the sample matrix and the sorptive phase, the NTD method is based on the principle of exhaustive extraction. This is achieved by actively drawing the sample through the sorbent bed using a syringe or pump, allowing for more complete recovery of target compounds and significantly simplifying calibration procedures [15].

Additionally, the use of a stainless steel needle and fixed sorbent bed provides high mechanical stability and reproducibility, which is particularly important for field applications. Another key advantage of the NTD method is the broader range of compatible sorbent materials compared to other microextraction techniques, such as magnetic sorptive extraction or SPME, thereby expanding its applicability and enhancing selectivity [16].

Together, these features make the NTD method especially well-suited for VOC analysis in complex matrices, as well as in scenarios requiring automated sampling with minimal operator involvement and low solvent consumption.

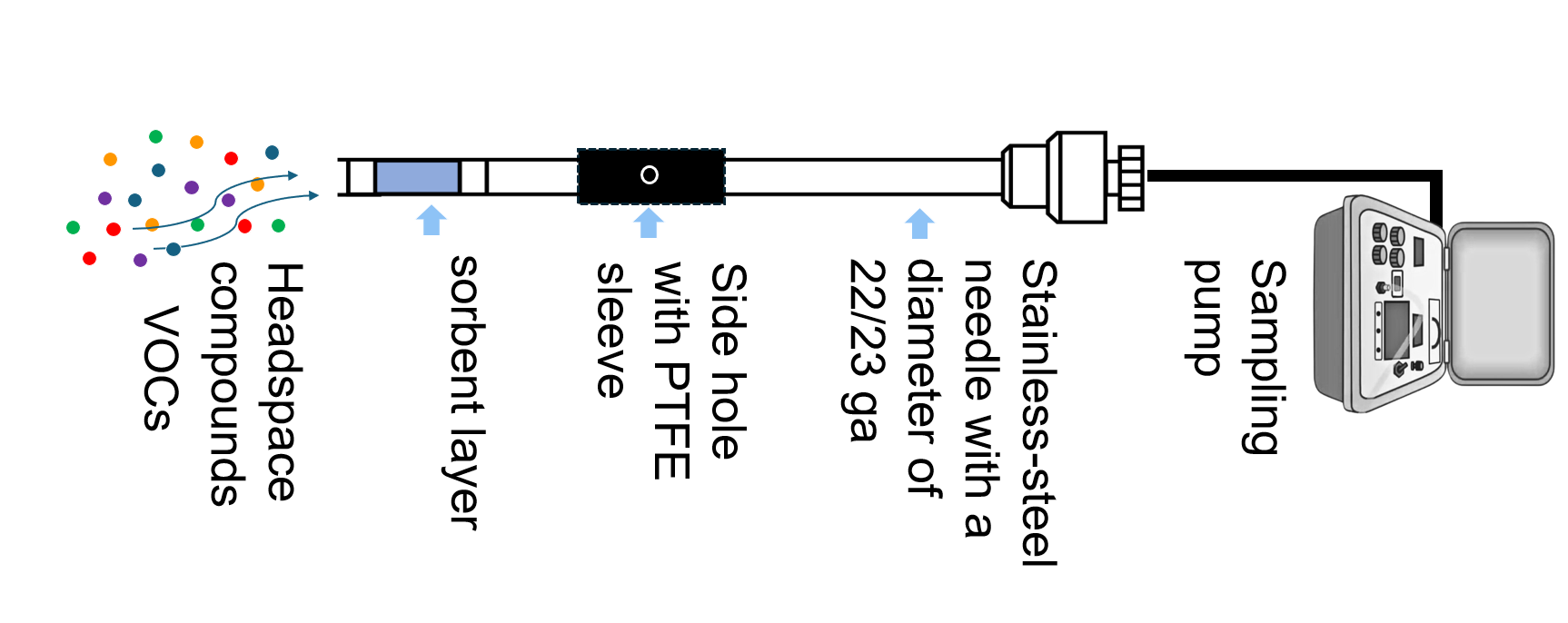


Figure 1. Needle Trap Device

The effectiveness of the NTD method largely depends on the properties of the sorbent used. Various types of sorbents have been studied to date, including commercial materials (such as Carboxen 1000 and Carbotrap B), carbon-based nanomaterials (nanotubes, graphene), polymeric sorbents, and MOFs. Among these, MOFs offer several significant advantages:

* A high specific surface area and porosity provide significantly greater sorption capacity, enabling the efficient adsorption of larger amounts of VOCs [17,18].
* The ability to control pore size and surface functionality of MOFs allows for high selectivity in adsorbing target analytes, which is critically important when analyzing samples with complex matrices [18,19].
* MOFs exhibit higher thermal stability compared to most polymeric sorbents, enabling efficient thermal desorption and minimizing sorbent degradation at the high temperatures used during analysis [19].
* Unlike carbon-based materials, MOFs are easier to functionalize due to their structural flexibility and are less prone to agglomeration, which improves their performance and simplifies the preparation of NTD devices [17,18]. This leads to increased reproducibility of results and reduced variability between different sorbent batches.

Studies confirm the effectiveness of MOFs in NTD for pollutant analysis. For example, Firoozichahak et al. demonstrated that MIL-125, a titanium-based MOF, exhibits high sorption capacity and sensitivity for extracting phenolic derivatives using NTD. This method achieved detection limits between 0.001 and 0.12 ng/mL, making it one of the most sensitive techniques for phenolic compound determination [20]. Soury et al. [21] investigated the use of Zn-MOF for sampling and analysis of polycyclic aromatic hydrocarbons (PAHs). Zn-MOF showed high efficiency as a sorbent for PAHs, reaching detection limits as low as 0.011 mg/m³ for naphthalene and 0.03 mg/m³ for benzo[a]pyrene. In studies by Alinaghi Langari et al. [19], an NTD based on UiO-66 was applied to extract aromatic amines such as aniline and o-toluidine. This sorbent demonstrated strong resistance to humidity and temperature, with detection limits ranging from 0.01 to 0.02 ng/mL.

An example is ZnMOF-74, which features a high specific surface area (up to 1570 m²/g) and significant pore volume (0.76 cm³/g), resulting in its high sorption capacity [22]. The presence of coordinatively unsaturated zinc ions in its framework creates active adsorption sites capable of selectively interacting with various adsorbate molecules. This material shows strong affinity for aromatic hydrocarbons; in particular, its sorption capacity for benzene is 7.06 mmol/g at room temperature, confirming its effectiveness in capturing VOCs [23].

Earlier research led to the development of a new modified structure—ZnMOF-74a [24]. Its overall framework is similar to the classic ZnMOF-74, but ZnMOF-74a features heart-shaped pores instead of the regular hexagonal pores found in ZnMOF-74. In classic ZnMOF-74, metal nodes are located at the junctions of three hexagonal pores and form infinite chains sharing edges. In contrast, in ZnMOF-74a, the metal nodes are positioned along the walls connecting two pores, with no metal present at the pore junctions.

|  |  |
| --- | --- |
| Изображение выглядит как диаграмма  Автоматически созданное описание | Изображение выглядит как искусство  Автоматически созданное описание с низким доверительным уровнем |
| а) | b) |

Figure 2 — Crystal structure of a) ZnMOF-74; b) ZnMOF-74a

It is assumed that, due to the structural similarity of ZnMOF-74a to the classic ZnMOF-74, this material will also be effective for sorption of VOCs. At the same time, the existing differences in pore geometry and the unique topology of coordinatively unsaturated active sites arrangement in ZnMOF-74a may influence the diffusion processes of molecules within the crystalline framework and the nature of their interaction with sorption centers. This, in turn, could potentially lead to changes in the selectivity and kinetics of sorption for different analytes.

To test this hypothesis, the present study investigates the application of ZnMOF-74a as a new sorbent for the NTD in the determination of VOCs in water samples. Additionally, a comparison of the analytical performance of the developed method with existing approaches for VOC analysis in water samples is conducted.

## Methods

### 2.1 Synthesis of ZnMOF-74a

For the synthesis of ZnMOF-74a, 1.317 g (6 mmol) of zinc acetate dihydrate (Zn(CH3COOH)×2H2O, Sigma-Aldrich, 98%) and 0.594 g (3 mmol) of 2,5-dihydroxyterephthalic acid (H2DOBDC, Sigma-Aldrich, 98%) were dissolved in 58.8 ml of tetrahydrofuran (THF, Honeywell, 99.9%). The resulting mixture was thoroughly stirred and transferred into a 100 ml glass-lined autoclave (Innovaster). The autoclave was maintained at 180 °C for 72 hours. The formed crystals were separated from the mother liquor by centrifugation, then washed three times with distilled water and three times with ethanol. Afterwards, the crystals were dried under vacuum at 110 °C for 12 hours.

Powder X-ray diffraction (XRD) analysis of the obtained samples was performed using a MiniFlex Benchtop powder XRD diffractometer (Rigaku) equipped with a copper X-ray source (λ\_CuKα1 = 1.54056 Å, λ\_CuKα2 = 1.54439 Å). Structural, compositional, and semi-quantitative analysis of the diffraction patterns was conducted using the GSAS-II software [25]. Thermogravimetric analysis (TGA) was carried out on an F3 STA-449 apparatus (Netzsch, Germany) coupled with a mass spectrometer QMS 403 D Aeolos (Netzsch, Germany) in an oxygen-argon atmosphere, heating at a rate of 5 °C/min up to 800 °C.

### 2.2 Preparation of NTD

For use in NTD devices, the obtained ZnMOF-74a particles were separated into fractions. To do this, 100 mg of MOF-74a was added to 10 ml of hexane in 15-milliliter vials. The mixture was homogenized using ultrasonic treatment at 60% power for 5 minutes at room temperature to ensure an even distribution of particles in the solvent. After homogenization, the resulting suspension was filtered through membrane filters with pore sizes ranging from 10 to 125 μm. The main fraction, constituting 70% of the filtrate, consisted of particles sized 50 μm. The obtained fractions were dried in a drying oven at 70 °C for 2 hours to remove residual solvent and obtain dry MOF-74a particles. The final product consisted of a 70% fraction with particle sizes of 50–75 μm.

For the fabrication of NTD devices, a layer of ZnMOF-74a sorbent (50–75 μm) measuring 2 cm in length and weighing approximately 1 mg was placed inside the needle. The sorbent was fixed using a steel wire with a diameter of 0.3 mm, which ensured uniform distribution of the material and prevented the formation of voids. To enhance the structural stability and prevent loss of sorbent particles, (hydrolyzed polyacrylonitriles) H-PAN filters were installed on both sides, which also allowed free gas flow through the device. The needle was sealed with Teflon caps to protect against contamination. The accuracy of the sorbent loading was controlled by weighing the needle before and after filling. At the final stage of device fabrication, permeability was checked by passing an inert gas through it. For sampling, NTD devices were used at a set flow rate of 3 ml/min.

### 2.3 Analyte solutions preparation

For the analysis of volatile organic compounds (VOCs), isoprene, acetone, benzene, and p-xylene were carefully prepared as concentrated stock solutions of each analyte, along with a blank solution containing no analytes. Analytical grade methanol (purity ≥99.9%) was used as the solvent. To provide the required volume of working solutions and account for the number of experiments and samplings, it was decided to prepare 100 ml of concentrated solutions with each VOC weighing 100 μg. The blank solution contained no analytes and consisted of pure solvent.

Each substance was accurately weighed on analytical balances and dissolved in 10 ml of methanol until completely dissolved. Then, the resulting concentrated solutions (and the blank solution) were transferred into 100 ml volumetric flasks, partially filled with deionized water, and diluted to the mark with water, creating working solutions with concentrations ranging from 0 to 500 ng/L.

All solution preparation procedures were carried out in a fume hood to minimize losses of volatile components, after which the solutions were thoroughly mixed by mechanical shaking or ultrasonic treatment to ensure homogeneity and prevent adsorption losses. The prepared working solutions were stored in tightly sealed borosilicate glass bottles at 4 °C and used within 7 days.

### 2.4 Sampling

For the extraction of volatile organic compounds (VOCs) from aqueous samples, a sampling setup (PAS Technology) was used. The setup included the following components: a mass flow controller with a range of 5–250 ml/min, calibrated for helium; a vacuum pump; a voltage regulator; a temperature controller; a heated purge tube housing; and a manual water delivery device. Sampling was performed by purging VOCs from aqueous solutions using an inert gas.

For the experiments, a fixed volume of water sample (10 ml) was introduced into a glass purge tube through a special port using a syringe. The solutions were purged with high-purity helium (>99.995%) at a flow rate of 40 ml/min for 10 minutes. During purging, the solutions were heated to 30 °C using a heating tube connected to a temperature controller. This promoted efficient transfer of VOCs into the gas phase. The gas mixture was directed to the NTD device, where compounds were captured by the ZnMOF-74a sorbent.

Due to the temperature difference between the sampling gas stream (30 °C) and the NTD needle (room temperature, ~25 °C), some water vapor present in the gas mixture condensed inside the needle. This condensation process is part of the operational mechanism of the NTD method.

### 2.5 Chromatographic analysis

The NTD needle containing the analyte was introduced into a hot injector (240 °C), where the condensed water instantly vaporized, creating high pressure inside the needle (approximately 50 bar). This pressure effectively transferred the trapped VOCs from the sorbent into the gas chromatograph (GC) column, ensuring their complete desorption for analysis.

Analyses were conducted using a 6890N/5973N GC-MS (Gas Chromatography – Mass Spectrometry) system (Agilent, USA) equipped with a split/splitless inlet and a Combi-PAL autosampler (CTC Analytics, Switzerland). VOC desorption from the NTD was performed in splitless mode at 240 °C using a 0.75 mm i.d. liner (Supelco, USA) for 1 minute. Analyte separation was carried out using a polar 30 m × 0.25 mm DB-WAXetr capillary column (Agilent, USA) with a 0.5 μm film thickness, at a constant carrier gas flow of 1.0 ml/min (helium, >99.995%, Orenburg-Techgas, Russia). The oven temperature program was as follows: initial hold for 6 minutes at 35 °C, ramp up to 170 °C at 30 °C/min, then hold at 170 °C for 2.5 minutes. The total GC run time per analysis was 13 minutes.

Temperatures of the mass spectrometer ion source, quadrupole, and interface were set to 240 °C. MS (Mass Spectrometry) detection was performed using electron impact ionization at 70 eV in either full scan mode (for qualitative analysis) or selected ion monitoring (SIM) mode (for quantitative analysis).

### 2.6 Calibration and determination of metrological features

Calibration of the instrument was performed using five standards containing the analytes (isoprene, acetone, benzene, and p-xylene) at concentrations of 5, 10, 50, 100, and 500 ng/L. Linearity of the calibration curve was evaluated by calculating the coefficient of determination (R²).

Calibration curve stability was controlled by a standard injection every 10 analyte samples. If the standard value deviated by more than 10% from the calibration curve, the analysis was halted and the instrument was recalibrated. Each measurement series also included at least one blank sample.

Qualitative determination of analytes was performed in full scan mode, while quantitative determination was carried out in SIM mode.

The limit of detection (LOD) is the minimum concentration of an analyte that can be reliably detected by an analytical system with a given probability (usually at 95%) [26,27]. The determination of LOD involves first establishing the limit of blank (LOB), followed by the calculation of LOD based on statistical processing of the results of multiple measurements of samples with low analyte concentrations.

(1)

where Sy,b – Standard deviation of the blank sygnals; b – slope of the calibration curve

The limit of quantification (LOQ) is the lowest concentration of analyte at which quantitative analysis with established accuracy and reproducibility characteristics is possible. The LOQ value is determined based on predefined acceptance criteria and metrological requirements specified by the developers of the analytical method. It should be noted that these criteria and requirements are not internationally adopted. In our case LOQ was calculated as follows:

(2)

Reproducibility assessment was performed using standard statistical methods by calculating the relative standard deviation ):

(3)

where σ – standard deviation and μ – mean value.

, where (4)

## 3 Results

### 3.1 Physicochemical investigation of ZnMOF-74a

The synthesis of ZnMOF-74a was carried out by a solvothermal method using anhydrous THF, according to the procedure described in [24]. The phase composition of the obtained product was analyzed by XRD. The diffractogram (Figure 1) shows a set of reflections characteristic of ZnMOF-74a CCDC (2382750). No additional unidentified peaks were detected on the diffractogram, indicating a high purity of the synthesized sample. The presence of a "halo" in the angular range of 5–15° 2θ is attributed to the instrumental contribution of the device.

|  |  |
| --- | --- |
|  |  |
| а) | b) |

**Figure 2 –** a) X-ray diffractogram of ZnMOF-74a; b) TGA curve of ZnMOF-74a showing mass loss events and thermal decomposition profiles.

To investigate the feasibility of using ZnMOF-74a for thermal desorption in GC-MS, TGA was employed. The mass loss curve revealed three main stages, reflecting sequential changes in the material (Figure 3).

The first stage of mass loss occurs at around 100 °C and is associated with the removal of surface water as well as partial release of water from the framework pores. This process corresponds to loosely bound moisture adsorbed on the surface and within the material. The second stage begins at approximately 270 °C and is related to the evaporation of residual solvents trapped within the porous MOF structure. The third stage, starting around 380 °C, corresponds to the decomposition of the organic ligand. As a result of this process, the framework structure breaks down and ZnO is formed. This stage represents the final phase of the material’s thermal degradation.

### 3.2 Chromatographic analysis

After conducting physicochemical studies, chromatographic analyses were performed on model systems containing isoprene, acetone, benzene, and p-xylene as typical volatile organic pollutants to demonstrate the functionality of the developed NTD devices. The chosen chromatographic parameters allowed effective separation of the target analytes with high selectivity, while the aqueous matrix did not affect the separation of the target compounds (Figure 5).

Figure 5 − Example of chromatographic separation of determined substances (full scan mode).

In order to examine the sensitivity of the system, ten blank samples (deionized water) were analyzed. Table 1 shows the limits of detection (LODs) and Quantification (LOQs) calculated using the equations (1) and (2). The water driven injection of the sample is clearly effective at producing sharp defined peaks and therefore low limits of detection (0.001–0.4 nM in 10 ml sample). The linearity of the method for a wide range of concentrations (from 5 to 500 mg/L) was sufficient to conduct quantitative evaluation.

**Table 1.** LODs, LOQs (n = 5) and correlation coefficients (r2) in the range of 5-500 ng/L.

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **LOD** | **LOQ** | **Linearity** |
| **ng/L** | **ng/L** | **R2** |
| Isoprene | 1.21 | 3.99 | 0.981 |
| Acetone | 2.26 | 7.46 | 0.974 |
| Benzene | 4.05 | 13.37 | 0.988 |
| P-Xylene | 33.51 | 110.58 | 0.952 |

The desorption efficiency study showed that the selected desorption temperature (240 °C) and time (1 min) effectively removed the studied VOCs from the NTD, with no carryover contamination observed. Reproducibility was investigated at concentrations of 100 and 250 ng/L, with RSD ranging from 1.94% to 7.86% (Table 2).

**Table 2.** Desorption efficiencies (%) and repeatabilities (RSD %) (n = 5) for concentrations of 100 and 250 ng/L.

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **Desorption efficiency** | **100 ng/L** | **250 ng/L** |
| **%** | **RSD, %** | **RSD, %** |
| Isoprene | > 99.76 | 4.96 | 1.94 |
| Acetone | > 99.55 | 4.80 | 2.95 |
| Benzene | > 99.19 | 4.56 | 3.59 |
| P-Xylene | > 93.30 | 7.86 | 5.35 |

For a comprehensive evaluation of the developed method’s effectiveness, the obtained analytical characteristics were compared with results from previous studies on VOC determination methods in water samples (Table 3).

**Table 3.** LODs and LOQs of four compounds for a range of detection methods

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **Method** | **LOD (ng/L)** | **LOQ (ng/L)** |
| Isoprene | Zn-MOF74a NTD | 1.21 | 3.99 |
| NTD with commercial sorbents | 1.57 | 5.23 |
| ZnO quantum dots | 10.00 | 33.00 |
| P-xylene | Zn-MOF74a NTD | 7.86 | 5.35 |
| NTD with commercial sorbents | 31.02 | 103.39 |
| Silver halide-coated fibres | 50 | 165.00 |
| Benzene | Zn-MOF74a NTD | 4.05 | 13.37 |
| NTD with commercial sorbents | 3.86 | 12.86 |
| Purge and trap GC | 7.30 | 24.33 |
| Acetone | Zn-MOF74a NTD | 2.26 | 7.46 |
| SPME | 12\*103 | 37\*103 |

## 4. Discussion

### 4.1 Analysis of Physicochemical Study Results

X-ray diffraction analysis confirmed the successful formation of the target crystalline phase ZnMOF-74a. The absence of extraneous reflections on the diffractogram indicates the phase purity of the synthesized material. The phase purity of ZnMOF-74a is a critically important factor for ensuring reproducibility of its sorption characteristics and minimizing the influence of secondary phases on analytical performance.

Thermogravimetric analysis revealed that ZnMOF-74a maintains structural integrity up to approximately 270 °C. This confirms that the material possesses sufficient thermal stability for use in NTD devices, where VOC desorption occurs at elevated temperatures (e.g., 240 °C). Thus, ZnMOF-74a can effectively release adsorbed analytes without the risk of degradation of its own structure or loss of sorption properties.

### 4.2 Method’s analytical characteristics evaluation

The developed NTD method using ZnMOF-74a sorbent demonstrated high efficiency in the separation and quantitative determination of isoprene, acetone, benzene, and p-xylene in water samples. The LODs ranged from 1.21 ng/L for isoprene to 33.51 ng/L for p-xylene. The best results were achieved for isoprene, which may be related to the specific interactions of this compound with the active sites of ZnMOF-74a. The higher LOD values for p-xylene are explained by its larger molecular size and weaker interaction with the sorbent.

The linearity of the calibration curves, with correlation coefficients above 0.95 for all studied compounds, confirms the suitability of the method for quantitative analysis over a wide concentration range (5–500 ng/L).

The reproducibility of the method, characterized by RSD values below 8%, indicates the stability of the sorption properties of ZnMOF-74a and the effectiveness of the thermal desorption procedure. The increase in RSD at lower concentrations is typical for microextraction methods and does not exceed acceptable limits.

## 4.3. Comparative Analysis and Prospects of the Method

The conducted comparative analysis of the analytical characteristics of the developed method with data reported in the literature for existing approaches to VOC determination in water samples [28] demonstrated its high competitiveness and, in some cases, superiority. The most significant advantage of the ZnMOF-74a NTD-based method was observed in the determination of acetone, where the limit of detection was four orders of magnitude lower than that of the SPME method. These results convincingly demonstrate the high sensitivity and efficiency of ZnMOF-74a as a sorbent for the analysis of VOCs in aqueous media.

Further work is planned to complete the validation of the developed method, including the determination of recovery, detailed reproducibility studies, and application of the method to real sample analysis. The range of target volatile organic compounds will also be expanded to confirm the universality and applicability of this approach to a broader spectrum of pollutants.

## Conclusion

In this study, a method for analyzing volatile organic compounds (VOCs) in water samples was developed based on the use of a Needle Trap Device (NTD) with a novel metal-organic framework ZnMOF-74a as the sorbent:

* The high efficiency of ZnMOF-74a as a sorbent for the determination of isoprene, acetone, benzene, and p-xylene in water samples was demonstrated, confirmed by desorption efficiency exceeding 93% for all studied compounds.
* High analytical performance was achieved: low limits of detection (ranging from 1.21 to 33.51 ng/L), strong linearity with correlation coefficients (r² > 0.95), and excellent reproducibility with relative standard deviations (RSD < 8%).
* Comparative analysis showed the superiority of the developed method in sensitivity compared to other approaches, including SPME, for several analytes; for example, the detection limit for acetone was four orders of magnitude lower than that of the SPME method.

The obtained results expand the knowledge on the application of MOF sorbents in analytical chemistry, demonstrating their potential for developing more precise and environmentally friendly methods for pollutant monitoring. These findings have broad practical significance and can be useful not only for analytical chemistry but also for water treatment, ecotoxicology, and public health risk assessment. In the future, the method can be adapted for VOC analysis in other matrices (air, soil), as well as for the development of portable sensors and automated environmental monitoring systems.

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