ABSTRACT

of the thesis for the degree of Doctor of Philosophy (Ph.D.) on specialty «6D072100 – Chemical technology of organic compounds»

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Improvement of the technologies for *in situ* growth of solid-phase microextraction coatings based of metal-organic frameworks

Characterization of the work.

This study is aimed at the development of the technologies for *in situ* growth of solid-phase microextraction coatings based of metal-organic frameworks.

The relevance of the work.

Classical sample preparation methods used for extracting organic pollutants require the use of toxic reagents and specialized equipment, making the process laborious and potentially leading to analyte degradation and loss. One alternative sample preparation method is solid-phase microextraction (SPME). SPME is a simpler and more economical method of sample preparation that does not use solvents, and requires less sample volume for analysis. The SPME procedure is based on the extraction of analytes directly from the sample or from the gas phase above the sample onto a sorptive coating, followed by desorption of the analytes into the injector of a gas chromatograph or into a high-performance liquid chromatography (HPLC) system. Commercially available fibers used in SPME have diameters ranging from 7 to 100 μm and most of themare hydrophobic, which limits their use for quantitative determination of hydrophilic analytes. Additionally, commercial fibers have low selectivity, which is an important factor in determining pollutants in complex matrices. Another limitation of commercial fibers is their low sorption capacity, which leads to decreasing accuracy of analysis results due to competition between target analytes and other compounds in the matrix. The existing drawbacks of commercial fibers have led to the need for the development of new and highly efficient SPME coatings. In recent years, various materials have been studied for the development of more effective coatings for SPME, such as carbon nanotubes, conductive polymers, graphene oxide, molecularly imprinted polymers, metal or metal oxide nanoparticles, ionic liquids, and metal-organic frameworks (MOFs).

MOFs are crystalline three-dimensional coordination polymers consisting of metal centers connected by organic linkers through coordination bonds. This material is characterized by homogeneously structured nanoscale pores, high surface area (up to 7000 m^2/g), thermal stability and high resistance to organic solvents. The ability to control pore size, a wide range of metal centers and organic linkers allows the synthesis of SPME coatings based on MOFs with high selectivity and adsorption effectiveness, as well as control over the hydrophilic/hydrophobic properties of the fiber.

MOF-199 is a promising material for developing fiber-based SPME due to its high surface area (Brunauer-Emmett-Teller, BET) of 1500-2100 m^2/g. Coatings based on MOF-199 in combination with gas chromatography (GC) have been successfully used for quantitative determination of volatile (VOCs) and semi-volatile organic compounds (SVOCs) in air, water, soil, and food products.

In this work, the *in situ* solvothermal method was chosen for the synthesis of MOF-199-based SPME fibers due to its simple procedure. In the *in situ* method, a pre-prepared substrate was immersed in a solution of metal salt and ligand, followed by synthesis using a stainless-steel hydrothermal autoclave under heating. This method does not require the use of adhesive, which can reduce surface area, and allows for control of particle size and thickness by varying process parameters. However, the *in situ* solvothermal method proposed by the Cui group (2009) for the preparation of MOF-199 fiber has some drawbacks, such as low mechanical stability of the coating and lack of automation. Additionally, the number of studies that have optimized the *in situ* synthesis parameters for the preparation of MOF-199 coatings is limited. Therefore, improving the technology for *in situ* growth of coatings for solid-phase microextraction based on metal-organic framework structures is currently relevant.

The aim of the study: improving the *in situ* growth technology of coatings for solid-phase microextraction based on metal-organic framework structures has been the aim of this work. The following tasks were set accordingly:

1. To optimize the technology for obtaining mechanically stable and homogeneous fiber coatings based on MOF-199.
2. To study the physicochemical properties of the obtained fibers.
3. To compare the developed MOF-199 fiber coatings with commercial solid-phase microextraction fibers.
4. To establish the distribution constants and possible period of use of the new fibers.
5. To develop a methodology for the quantitative determination of volatile organic compounds in the air using the new solid-phase microextraction fibers.

Objects of the study: improvement of the *in situ* growth technology for metal-organic framework-based solid-phase microextraction coatings.

The subjects of the research: selection of optimal parameters for *in situ* growth of coatings for solid phase microextraction based on metal-organic framework structures.

The methods of the research

The dissertation work employed both scientific and engineering methods. *In situ* synthesis in solvothermal conditions was used to synthesize the SPME coatings. The structure of MOF-199 was characterized using the Brunauer-Emmett-Teller method, X-ray diffraction analysis, and thermogravimetric analysis. Scanning electron microscopy was used to determine the thickness and morphology of the SPME fibers. Gas chromatography with mass spectrometric detection was utilized to study the distribution constants, possible periods of use, compare with commercial fibers, and validate the newly developed fibers on real samples.

The main research results

1. The optimal conditions for obtaining MOF-199 based SPME fiber with a thickness of 22±3 μm were determined to be 96.5% ethanol and a synthesis duration of 16 hours.

2. MOF-199 coatings with a thickness of 22 ±3 μm at 25 VOCs showed responses at 16 VOCs that were 1.3-82.3 times higher than for the commercial Polydimethylsiloxane/Divinylbenzene fiber.

3. The possible number of reuse cycles for the MOF-199 based coating (22±3 μm) is at least 35 extraction and desorption cycles.

4. The distribution constants for 9 VOCs between air and MOF-199 coating were $9x10^4$ -$127x10^4$. For methylene chloride, benzene and toluene, distribution constants were 1.2-2.3 times higher than between commercial Carboxen/Polydimethylsiloxane fiber and air.

5. The optimal conditions for obtaining a MOF-199 based SPME fiber with a thickness of 21±5 μm were determined to be butanol, addition of acetic acid and $Cu(NO_3)_2 \times 3H_2O$.

6. The possible number of reuse cycles for theMOF-199 based coating (21±5 μm) is at least 50 extraction and desorption cycles.

7. Using theSPME fiber based on MOF-199 (21±5 μm) provides low detection limits (0.03-0.09 $\mu g/m^3$) and high accuracy (73-108%) for quantitative determination of benzene, toluene, ethylbenzene and xylenes in the air.

The scientific novelty of the research

The novelty lies in defining the optimal conditions for obtaining SPME coatings based on MOF-199 and developing two methods for their preparation. In addition, MOF-199 fibers were first tested for the determination of 25 VOCs in the air. Of the 8 VOCs, the distribution constants between the MOF-199 coating and air were determined for the first time for 5 VOCs. The developed methodology has detection limits that are 141-277 and 74-227 times lower than those of existing methods based on MOF-199 fibers and Carboxen/Polydimethylsiloxane, respectively.

The theoretical significance of the thesis

For the first time, the optimization of the technology for obtaining SPME fibers based on MOF-199 has been carried out. Additionally, the distribution constants of VOCs between the MOF-199 coating and gas phase at 40°C have been established for the first time, and the effect of solvent on the extraction efficiency of the MOF-199 fiber has been determined.

The practical significance of the thesis

Under the research, technologies for obtaining SPME fibers based on MOF-199 were developed, and a methodology for the quantitative determination of volatile organic compounds in air samples was developed. This method is characterized by high accuracy and reproducibility, as well as low detection limits. Such an improvement of the methodology will make it more accessible for laboratories in Kazakhstan and expand its application in air quality monitoring.

The validity and reliability of the results the obtained data were confirmed using selective, accurate, and modern analysis methods, as well as the scientific method. To ensure reliability and reproducibility, all experiments were conducted in several parallels.

Relation of the thesis with research and government programs

The work was carried out within the framework of the projects of the Ministry of Education and Science of the Republic of Kazakhstan: "Development of analysis methods, materials and equipment for economically efficient "green" environmental monitoring" for 2017-2019 (AP05133158) and " Development of method for determination of organic pollutants time-weighted average concentrations for monitoring of ambient air of Almaty" for 2021-2023 (AP09058606).

The main provisions to be defended.

1. The *in situ* solvothermal method using $Cu(NO_3)_2·3H_2O$, benzene-1,3,5-tricarboxylic acid, a temperature of 120°C, a concentration of 96.5% ethanol, and a synthesis time of 16 hours allows obtaining of a MOF-199 coating for solid-phase microextraction with a thickness of 22±3 μm on a stainless steel substrate.

2. The distribution constants of benzene, toluene, and dichloromethane between the MOF-199 coating with a thickness of 22±3 μm, obtained by the *in situ* solvothermal synthesis using 96.5% ethanol for 16 hours, and air at a temperature of 40°C are 2.3, 2.1, and 1.2 times higher, respectively, than the known distribution constants between a Carboxen/Polydimethylsiloxane fiber with a thickness of 85 μm and air.

3. The use of $Cu(NO_3)_2·3H_2O$ in the *in situ* solvothermal method at a temperature of 120°C for 16 hours utilizing benzene-1,3,5-tricarboxylic acid allows the production of MOF-199 coating for solid-phase microextraction on a stainless steel substrate surface.

4. By using a MOF-199 fiber synthesized by the 16-hour *in situ* solvothermal method using $Cu(NO_3)_2·3H_2O$, benzene-1,3,5-tricarboxylic acid, butanol, and acetic acid at a temperature of 120°C, low detection limits (0.03-0.09 $\mu g/m^3$) and high accuracy (73-108%) for the determination of benzene, toluene, ethylbenzene, and xylenes in 20 mL air samples by solid-phase microextraction combined with gas chromatography and mass spectrometric detection are achieved.

Approval of practical results of the work. The main results of the work were presented at the following international conferences, seminars, and forums: International Conference " FARABI ALEMI" (Almaty, April 8-9, 2019); International Conference " FARABI ALEMI" (Almaty, April 6-8, 2021); International Chemical Engineering Symposia (Osaka, Japan, March 15-17, 2020); 23rd International Symposium on Advances in Extraction Technologies (Alicante, Spain, June 29 - July 2, 2021); and European Research Course on Atmospheres (Grenoble, January 15 - February 4, 2023).

Publications

The results of the research work are reflected in 8 scientific papers, including 1 article in the international journal Mesoporous and Microporous Materials (Q1, Impact factor 5.876, Percentile 86%), 2 articles in the international journal Microchemical Journal (Q1, Impact factor 5.304, Percentile 80%), 1 utility model patent, and abstracts of 4 presentations at international scientific conferences and symposia.

The personal contribution of the Ph.D. candidate to the preparation of each article was as follows:

In the articles "New *in situ* solvothermally synthesized metal-organic framework MOF-199 coating for solid-phase microextraction of volatile organic compounds from air samples" (Microporous and Mesoporous Materials, 2021, Vol. 328, P. 111493, Q1 WoS) and " MOF-199-based coatings as SPME fiber for measurement of volatile organic compounds in air samples: Optimization of *in situ* deposition parameters" (Microchemical Journal, 185, Q1 WoS), Omarova A.S. is the first author. The Ph.D. candidate participated in conducting all the experiments and interpreting the results and prepared the initial drafts of the articles with descriptions of the introduction, methodology, results, conclusion, and graphics. Additionally, Omarova A.S. participated in formatting the articles according to the journal's requirements and improving the articles after each stage of peer review.

In the article " A review on preparation methods and applications of metal–organic framework-based solid-phase microextraction coatings" (Microchemical Journal, 2022, Vol. 175, P. 107147), Omarova A.S. is the first author and corresponding author. The Ph.D. candidate participated in data collection and analysis, wrote initial drafts of the second and fourth chapters, actively participated in writing the first chapter of the book, and improved and revised the third chapter. Additionally, Omarova A.S. participated in formatting the article according to the journal's requirements, submitting the article to the journal, and improving the article after each stage of peer review.