ANNOTATION

of the thesis for the degree of Doctor of Philosophy (PhD)
on educational program «8D05301 – Chemistry».

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Modeling the processes of solid-phase microextraction of organic compounds from environmental objects

Characterization of the work. This study is aimed at the improvement of the efficiency of the development of analytical methods for environmental objects based on solid-phase microextraction using computer modeling.

Relevance of the research topic. Environmental pollution caused by toxic chemicals has significant adverse effects on both human health and the economy. Environmental monitoring serves as the foundation for estimating and identifying sources of risk, as well as for making decisions regarding environmental pollution. Establishing a proper system of environmental monitoring is a highly complex task that demands substantial financial and human resources, particularly in developing countries like Kazakhstan.

Environmental regulations in Kazakhstan mandate the use of certified analytical methods, many of which are outdated and involve costly and labor-intensive sample preparations, especially for organic pollutants. The current high cost of analysis can be mitigated by developing cost-effective methods. Traditional environmental analyses are expensive primarily due to time-consuming sample preparations. However, modern equipment allows for continuous and fully automated sample analysis without significant cost escalation.

Headspace (HS) solid-phase microextraction (SPME) is considered one of the most promising sample preparation methods for identifying organic pollutants in environmental samples due to its simplicity, environmental friendliness, automation, and ability to achieve low detection limits at a minimal cost of analysis. Nonetheless, optimizing SPME parameters demands extensive experimental efforts and expenses. Achieving a proper balance between detection limits and accuracies requires thorough optimization of approximately ten extraction parameters (such as fiber coating type, coating dimensions, extraction temperature, extraction time, pH, amount of salt added to a sample, sample/headspace ratio, agitation/stirring rate, and pressure in a vial) and desorption parameters (desorption temperature and time). This process can be time consuming, costly, and complex. Optimization proceeds step by step, during which it is impossible to explore all parameter combinations. Method developers often prioritize maximizing analyte responses over accuracy during optimization due to its complexity. Consequently, SPME-based methods for various analytes and sample types are not yet widely available.

Simulation of the SPME process is an effective tool for developing and optimizing analytical methods. However, models to simulate the effects of many important extraction parameters (such as extraction temperature, pressure, ionic strength of water samples, and

soil moisture) are still unavailable, and method optimization still requires significant experimental work and expense from method developers. By incorporating 8 of the effects of these parameters into a computational model, there is great potential to replace experimental optimization.

The objective of the work is to establish theoretical and computational basis for developing SPME models to enhance the optimization process and predicting the optimal parameters of SPME for various analytes and samples without conducting elaborative experimental optimization. This goal was achieved during the development of new computational models for simulation of SPME of VOCs from air, water and soil.

The following tasks were set to accomplish the objective of the work:

1) to develop mathematical and physical models of processes taking place during SPME of VOCs from air, water and soi;

2) to determine diffusion coefficients and distribution constants of analytes in different matrices;

3) to evaluate the accuracy of different prediction methods for calculating the diffusion coefficients of VOCs in air, water and soil using experimental and empirical data;

4) to develop a computational model of SPME of BTEX from air for optimization of an extraction time of analytes at different temperatures, pressures, sample volumes and geometries at constant or changing conditions;

5) to develop a computational model of SPME of BTEX from water for optimization of stirring speed, fiber insertion depth, pressure, sample volume and the concentration of added salt;

6) to develop a computational model of SPME of BTEX from soil for optimization of sample mass, location of the fiber, extraction time and pressure.

Objects of the research: computational models of processes occurring during solid phase microextraction of volatile organic compounds from air, water, soil.

Subject of the research: the optimization of SPME of VOCs from air, water, soil using COMSOL Multiphysics®.

The methods of the research. The scientific method was used to disclose knowledge gaps, formulate research questions and hypotheses, design experiments in this study. Computational program COMSOL Multiphysics ® was used for construction of SPME models and SPME optimization. Gas chromatography–mass spectrometry (GC-MS) was used for signal measurement during the optimization and development of analytical methods.

The scientific novelty of the research:

1) Diffusion coefficients of BTEX in the PDMS fiber using capillary inverse gas chromatography were established for the first time.

2) The effect of diffusion in PDMS coating, distribution constants, and extraction temperature of SPME of BTEX from air were evaluated and established for the first time using finite element analysis.

3) The effect of stirring rate, fiber insertion depth, sample volume, concentration of added salt and pressure conditions on the performance of SPME of BTEX by Car/PDMS

coating from water using finite element analysis were evaluated and established for the first time.

4) The effect of sample mass, pressure in the system, distribution constant on SPME of benzene by Car/PDMS coating from soil using finite element analysis were established for the first time.

Validity and reliability of the results obtained. The results obtained are valid and reliable because all experiments were conducted with one or two independent variables while the other variables were held constant. The dependent variables depicted the main parameters of the methods such as precision, recovery, analyte responses, limits of detection and quantification, and reproducibility. All measurements were performed in two to four repetitions. Gas chromatography with mass spectrometric detection was used to achieve sensitive and selective identification and separation of VOCs.

The theoretical and practical importance of the dissertation. This research improved the theory of solid-phase microextraction behind the optimization parameters of the method by using computer simulation. Computational models of solid-phase microextraction of volatile organic compounds from environmental objects were developed. The developed models make it possible to optimize the SPME parameters to increase the extraction efficiency and reduce the analysis time. The models can be used to generate complete extraction profiles at various temperatures, pressures, sample volumes and geometries under constant or varying conditions. Almost all input data can be found in scientific literature and databases or can be predicted using the proposed computational methods. In addition, estimation methods were performed to generate the predicted values of diffusion coefficient of VOC in air, distribution coefficient in air and soil. The only experimental step that the end users of the developed model must perform is the determination of the diffusion coefficients in the fiber using reversed gas chromatography (if not available in the literature). Training material and simulation videos have been developed to enable end users to model themselves and extract extraction profiles by incorporating data from their subjects. All developed computer models were validated experimentally and compared with the results of other studies and experiments.

The main statements to be defended:

1) The computational optimization of temperature and time of solid-phase microextraction of VOCs from air can be achieved using prediction techniques of Fuller method for diffusion coefficients in air, LTPRI indices and van't Hoff equation for estimation of distribution constants between headspace and fiber, and inverse gas chromatography for diffusion in PDMS with RMSDs in the range between 4.5% to 13.3% compared to obtained experimental extraction profiles at 298K.

2) At coating-air distribution constant equal to 10000 at T = 298K, the decrease of the diffusion coefficient of benzene in PDMS from $2 \cdot 10^{-9}$ to $1 \cdot 10^{-10}$ $m^2 s^{-1}$ results in 43% increase of extraction time (from 46 to 66 seconds) for extraction of 80% of equilibrium amount of analyte on fiber.

3) Southworth approach allows obtaining simulated HSSPME profiles of BTEX from water by Car/PDMS coating, which are closest to experimental profiles compared to other approaches with RMSD in the range 8.8-10%.

4) Computational models, using vacuum and increasing stirring speed from 500 to 1000 and 2000 RPM allows to decrease equilibration time ($t_{0.95}$) of SPME of benzene from water using 85 μm Car/PDMS fiber by 2.5 (48%) and 3.8 min (71%), respectively.

5) Equilibrium in the system of SPME of benzene from soil with Vac-HSSPME (0.0313 atm) can be reached 42-43 times faster compared to HSSSPME at all studied distribution constants and sample masses of benzene extraction by Car/PDMS coating.

The main results of the study:

1) The computational optimization of temperature and time of solid-phase microextraction of VOCs from air can be achieved using prediction techniques of Fuller method for diffusion coefficients in air, LTPRI indices and van't Hoff equation for estimation of distribution constants between headspace and fiber, and IGC for diffusion in PDMS with RMSDs in the range between 4.5% to 13.3% compared to obtained experimental extraction profiles of BTEX at 25°C and 40°C. Diffusion in the coating is a limiting stage in the extraction process at lower distribution constant between coating and air. When coating-air distribution constant equals to 10^3 the decrease of diffusion in the PDMS coating from $2 \cdot 10^{-9}$ m^2 s^{-1} to 10^{-10} m^2 s^{-1}, results the increase of the equilibration time from 6.5 to 32.6 seconds for extracting 80% of benzene at 25°C. At coating-air distribution constant equals to 10^5 similar decrease diffusion in the PDMS coating results increase from 46 to 66 seconds of equilibration time of benzene.

2) Vac-HSSPME provides faster equilibration compared to HSSPME for all (with any K_{fh} and HLC) VOCs from water at 298K under ideal stirring conditions by Car/PDMS coating. Increase of stirring speed from 500 to 1000 and 2000 RPM allows to decrease equilibration time ($t_{0.95}$) of benzene extraction from water by 2.5 (48%) and 3.8 min (71%), respectively under vacuum conditions. Southworth approach for estimating mass transfer coefficients at water-headspace boundary allows computational optimization of extraction time of SPME from water with RMSDs in the range 8.8-10% compared to experimental extraction profiles.

3) Equilibration time of benzene extraction by Car/PDMS coating from dry soil at Vac HSSPME (0.0313 atm) can be reached faster at 2.3 min compared to traditional HSSSPME, where equilibrium under atmospheric pressure (1 atm) is reached at 97 min Equilibration time ($t_{0.95}$) depends on both sample mass and soil-headspace distribution constant of the analyte. For the small sample masses less than 5 g, and soil-headspace distribution constants less than 100, equilibrium in the system can be achieved less than after 1 min of benzene extraction at K_{fh}=150 000 and less than 0.1 min at K_{fh}=8300 by Car/PDMS porous coating at 298K under vacuum conditions. For soil-headspace distribution constants more than 10^5 equilibration at the same time can be achieved for the sample mass of 10 g.

The accordance of the dissertation theme to a plan of the research work and various State programs. The dissertation theme complies with the plan of the research work. The research work was conducted under the projects funded by the Ministry of Education and Science of Kazakhstan: "Efficient development of environmental and

analytical methods based on headspace solid-phase microextraction using computer simulation" (No. AP08052684, 2020-2022).

Presentation of the practical results. The main results of the work were presented at the following international conference:

- 1st European Sample Preparation Conference (Online event, 11-12 March, 2021)

Publications. The results of this research were published in 4 scientific papers, including:

- one article in the international scientific journal indexed in Scopus and Web of Science (Thomson Reuters/Clarivate Analytics) databases with impact-factor 6.911;
- two articles in journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan;
- one abstract of international scientific conference (online event)

The author's contribution to the research consists of preparation and analysis of literature review, planning and performing the experiments, interpreting the obtained data, and integrating them into the final results and analytical methods.

Description of contribution of the PhD student to each publication

1) Kapar A. et al. Modeling the effect of temperature on solid-phase microextraction of volatile organic compounds from air by polydimethylsiloxane coating using finite element analysis // Analytica Chimica Acta., 2022. Vol. 1195. P. 339431. https://doi.org/10.1016/j.aca.2022.339431 (Validation, formal analysis, investigation, writing original draft, writing review and editing.)

2) Muratuly A., Kapar A., Kenessov B. Modeling headspace solid-phase microextraction of volatile organic compounds from water samples with porous coatings using finite element analysis // Advances in Sample Preparation, 2022. Vol. 3. https://doi.org/10.1016/j.sampre.2022.100030 . (Validation, writing original draft, writing review)

3) Kenessov B., Kapar A. Optimization of headspace solid-phase microextraction of volatile organic compounds from dry soil samples by porous coatings using COMSOL Multiphysics // Chemical Bulletin of Kazakh National University. Center of Physical Chemical Methods of Research and Analysis, 2022. № 4. P. 4–12. https://doi.org/10.15328/cb1300 (Validation, writing review and editing)

The structure of the dissertation. The dissertation is presented in 90 pages and contains 15 tables, 21 figures and 157 references. The dissertation consists of an introduction, four chapters, conclusion and list of references.