REVIEW

of the official reviewer for dissertation work of

Kapar Anel on the theme "Modeling the processes of solid-phase microextraction of organic compounds from environmental objects", submitted for the degree of Doctor of Philosophy (PhD) in the Educational Program "8D05301 - Chemistry"

№	Criteria	Eligibility (one of the options must be checked)	Justification of the position of the official reviewer
1.	The topic of the thesis (as of the date of its approval) corresponds to the directions of development of science and/or state programs	1.1 Compliance with priority areas of science development or government programs:	
		1) The thesis was completed within the framework of a project or target program financed from the state budget (indicate the name and number of the project or program) 2) The thesis was completed within the framework of another state program (indicate the name of the program) 3) The dissertation corresponds to the priority direction of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate the direction)	This research work was conducted within the framework of project funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan: Grant No. AP08052684, "Efficient development of environmental and analytical methods based on headspace solid-phase microextraction using computer simulation".
2.	Importance for science	The work **makes**/does not make a significant contribution to science, and its importance is **well disclosed**/not disclosed	This research enhances the understanding of the theory of solid-phase microextraction (SPME) by employing computer simulations of optimization of SPME parameters. Computational models were developed to simulate the SPME process for volatile organic compounds in environmental samples. These models enable the optimization of SPME conditions, improving extraction efficiency and significantly reducing analysis time, thus contributing to the advancement of analytical methodologies in environmental science.
3.	The principle of independence	Self-reliance level: 1) **High;** 2) Medium; 3) Low;	Based on publications and our assessment of the results presented in the thesis, the PhD candidate has conducted the experiments, analyses of data, verification of hypotheses, and preparation of thesis independently. The main results have been

		4) No independence	published in high-impact scientific journals. Based on these results, the level of independence in the self-reliance level would be evaluated as high.
4.	The principle of inner unity	4.1 Justification of the relevance of the thesis: 1) **Justified;** 2) Partially justified; 3) Not justified.	The dissertation topic is of high importance and relevance in the field of green sample preparation and analysis. Optimizing parameters of analytical methods requires extensive experimental effort and expense. In SPME-based analysis, achieving the right balance between detection limits and accuracy involves thorough optimization numerous extraction parameters such as fiber coating type, extraction temperature, time, pH, sample/headspace ratio, agitation rate, desorption temperature and time. Simulation of the SPME process is a valuable tool for developing and optimizing analytical methods.
		4.2 The content of the thesis reflects the topic of the thesis: 1) **Reflects;** 2) Partially reflects; 3) Does not reflect	The content of the thesis reflects the topic of the thesis. The thesis content includes chapters on development of computational models for simulating SPME of organic compounds from air, water, and soil. Thus, the content of the thesis reflects the topic of the thesis. Experimental design allows to evaluate the hypotheses presented in the study.
		4.3. The purpose and objectives correspond to the topic of the thesis: 1) **correspond;** 2) partially correspond; 3) do not correspond	The purpose of the study: "to establish theoretical and computational basis for developing SPME models to enhance the optimization process and predicting the optimal parameters of SPME for VOCs and air, water, soil samples without conducting elaborative experimental optimization." Experiments and results fully correspond to the objectives and the topic of the thesis.
		4.4 All sections and provisions of the thesis are logically interconnected: 1) **completely interconnected;** 2) the interconnection is partial; 3) there is no interconnection	Sections and provisions of the thesis are logically interconnected. Each model and study are being built upon the previous with more complicated processes involved in the simulations.

		4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: 1) **there is a critical analysis;** 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors	The author of the thesis provides critical analysis of the findings and results in the separate conclusions for each chapter, as well as in the general conclusion of the thesis.
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? 1) completely new; 2) **partially new (25-75% are new);** 3) not new (less than 25% are new)	The concepts presented as the scientific results of the research were original and validated through experiments and simulations. While the models are partially built on existing theory, these methods and simulations were applied for SPE for the first time.
		5.2 Are the dissertation findings new? 1) completely new; 2) **partially new (25-75% are new);** 3) not new (less than 25% are new)	The dissertation findings are new and are supported by experimental results.
		5.3 Technical, technological, economic or management decisions are new and reasonable: 1) completely new; **2) partially new (25-75% are new);** 3) not new (less than 25% are new)	The decision protocols for the technical and economic managements used for the thesis are reasonable and acceptable.
6.	The validity of the main findings	All main conclusions **are**/are not based on scientifically significant evidence or well-grounded (for qualitative research and areas of training in the arts and humanities)	The main findings of the thesis were validated in the experimental and theoretical studies. The adequate research methods applied to solve the tasks allowed to validate the conclusions reasonably, reliably and argumentatively.
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: *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*	This provision was fully proven in the second chapter of the thesis. The model developed for SPME of BTEX from air is consistent with experimental results. The provision is discussed in paper "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

		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. 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) **no** 7.3 Is it new? 1) **yes;** 2) no 7.4 Application level: 1) narrow; 2) **medium**; 3) wide 7.5 Is it proven in the article? 1) **yes;** 2) no	
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: 2) *Increasing the coating-air distribution constant from 1000 to 10000 at constant temperature and diffusion coefficient in PDMS coating equal to 10^{-11} m^2s^{-1} results in 43% increase of equilibration time.* 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather not proven;	This provision is fully proven. The effect of diffusion coefficients in the PDMS coating at different coating-air distribution constants is studied in computational models and is also discussed in paper "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.

		4) not proven 7.2 Is it trivial? 1) yes; 2) **no** 7.3 Is it new? 1) **yes;** 2) no 7.4 Application level: 1) narrow; 2) **medium**; 3) wide 7.5 Is it proven in the article? 1) **yes;** 2) no	
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: 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%.* 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) **no** 7.3 Is it new? 1) **yes;** 2) no	This provision was validated by experimentally obtained results and was proven and discussed in "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.

		7.4 Application level: 1) narrow; 2) **medium**; 3) wide 7.5 Is it proven in the article? 1) **yes;** 2) no	
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: 4) *Using vacuum and increasing stirring speed from 500 to 1000 and 2000 RPM allows to decrease equilibration time ($t_{95\%}$) of benzene using 85 μm Car/PDMS fiber by 2.5 (48%) and 3.8 min (71%), respectively.* 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) **no** 7.3 Is it new? 1) **yes;** 2) no 7.4 Application level: 1) narrow; 2) **medium**; 3) wide 7.5 Is it proven in the article? 1) **yes;** 2) no	The provision was proven and is discussed in the paper in "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.,

7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: 5) *Equilibrium in the system 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.* 7.1 Is the provision proven? 1) **proven;** 2) rather proven; 3) rather not proven; 4) not proven 7.2 Is it trivial? 1) yes; 2) **no** 7.3 Is it new? 1) **yes;** 2) no 7.4 Application level: 1) narrow; 2) **medium**; 3) wide 7.5 Is it proven in the article? 1) **yes;** 2) no	The provision was proven and was discussed in paper "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, provision is well clarified and proven.
8.	The principle of reliability Reliability of sources and	8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) **yes;** 2) no	The methodologies employed in the dissertation were thoroughly described and presented with comprehensive detail. Each step was clearly outlined, allowing a complete understanding of the processes, and the provided explanations provide insights into the rationale behind their application.

	information provided	8.2 The results of the thesis were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) **yes;** 2) no	Computer simulations were obtained using COMSOL Multiphysics® Software, which is a reliable and acknowledged instrument for modeling and optimization of various processes and is widely used in research. Gas chromatography mass spectrometry (GC-MS) instrument was utilized for analysis. GC-MS systems are acknowledged for their reliability, sensitivity, selectivity and robustness. Thus, in this work, modern and reliable methods were selected for conducting the research.
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research (for areas of training in pedagogical sciences, the results have been proven on the basis of a pedagogical experiment): 1) **yes;** 2) no	Results and conclusions were adequately validated and proven.
		8.4 Important statements are **confirmed** / partially confirmed / not confirmed by references to current and reliable scientific literature	When possible, the results and conclusions were confirmed and compared with the references in scientific literature.
		8.5 Used literature sources are **sufficient**/not sufficient for a literature review	The literature sources are sufficient and provide a comprehensive review for the dissertation.
9	Practical value principle	9.1 The thesis has theoretical value: 1) **yes;** 2) no	The thesis aimed at deeper understanding the mechanisms and processes taking place during SPME of various compounds from air, water, and soil. The models discussed and employed in simulations together with experimental validation are of great theoretical value.
		9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice: 1) **yes;** 2) no	The developed models have practical value for environmental chemistry. These models can be used for optimization of extraction parameters of SPME, for a better understanding of an extraction process, disclosing and solving various problems related with, e.g., poor accuracy and precision of the analysis.
		9.3 Are the practice suggestions new? 1) completely new;	Computational models together with experimental data validate the reliability of findings and offer some practical suggestions

		2) **partially new (25-75% are new);** 3) not new (less than 25% are new)	for SPME-based method development that have substantial degree of novelty.
10.	The quality of writing and design	Academic writing quality: 1) **high**; 2) average; 3) below average; 4) low.	The thesis is well-written and organized, presenting the information in a clear and coherent manner. However, it would benefit from several revisions, including the addition and removal of certain content to improve clarity and focus. Additionally, some minor errors need to be corrected to enhance the overall quality and precision of the work.
11.	Notes on a thesis		Despite numerous advantages the remarks as follows: 1. In Chapter 2, the effect of humidity on extraction process was not discussed. The humidity also was not described in modeling parameters. 2. In Chapter 4, the simulated extraction profiles were not compared with experimental data, as in previous chapters and samples. 3. For experimental data in Chapter 3, there are no error bars.
12.	Scientific level of the doctoral student's articles on the topic of research (in case of defense of the dissertation in the form of a series of articles, the official reviewers comment on the scientific level of each article of the doctoral student on the topic of research)		All articles are scientifically robust and well-structured. Here's an analysis of its scientific level: **Alignment with Core Topic**: The study develops a computational models to predict the behavior of VOCs during SPME using PDMS, Car/PDMS coating. This directly pertains to the research focus on modeling solid-phase microextraction processes. The emphasis on **modeling extraction processes** under varying temperatures, pressures, fiber insertion depth, distribution constants aligns closely with objective of understanding and simulating SPME dynamics. **Methodological Framework**: The article establishes a foundation for estimating critical parameters such as diffusion coefficients and fiber-air distribution constants, essential for accurate SPME modeling.

			These methodologies can serve as blueprint research, especially if work involves optimizing SPME for other organic compounds or complex matrices in the future. These articles are **highly relevant** to the research topic because it not only develops a novel computational model for SPME but also addresses key challenges in extracting and analyzing organic compounds from environmental matrices. Its focus on VOCs and temperature effects makes a strong contribution to understanding and improving SPME processes, which is central to the research objectives.
13.	Decision of the official reviewer (pursuant to paragraph 28 of the present Model Regulations)		This thesis on the topic "**Modeling the processes of solid-phase microextraction of organic compounds from environmental objects** " submitted for the degree of Doctor of Philosophy is a complete study with reliable discussed scientific results. The work meets the requirements of the Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan for dissertations for the degree of Doctor of Philosophy (PhD) in the specialty "8D05301-Chemistry" and can be awarded the degree PhD.

In reviews, official reviewers indicate one of the following solutions:

1) to award the degree of Doctor of Philosophy (PhD) or Doctor of Specialization.

2) send the thesis for revision (except for cases of thesis defense in the form of a series of articles);

3) refuse to award the degree of Doctor of Philosophy (PhD) or Doctor of Specialization.

Copies of the reviews of the official reviewers are handed over to the doctoral student no later than 5 (five) working days before the defense of the thesis.

Official Reviewer:
Chief Researcher of the Laboratory of Engineering Profile
"Physical and Chemical Methods of Analysis" of
Korkyt Ata Kyzylorda University, PhD, Associate Professor _____ Nurgali Akylbekov



