

REVIEW
of the official reviewer for dissertation work of
Ibragimova Olga on the theme “Development of simple and accurate methods for organic pollutants determination in the air based on
solid-phase microextraction”,
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 work was funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan under the grants AP05133158 (“Development of analytical methods, materials and equipment for cost-efficient “green” environmental monitoring”) and AP09058606 (“ Development of method for determination of organic pollutants time-weighted average concentrations for monitoring of ambient air of Almaty”).
2.	Importance for science	The work does not make makes a significant contribution to science, and its importance is not disclosed well disclosed	The work presents results covering several aspects of TWA-SPME: fundamental/theoretical & instrumental studies, development of methods and their application of to the determination of atmospheric organic pollutants. We believe that the work as whole provides both an advance on the knowledge of the technique and interesting data from its application, remarkably on the correlation between urban air quality and sanitary restrictions to human

			activity due to the recent COVID-19 pandemics.
3.	The principle of independence	Self-reliance level: 1) High; 2) Medium; 3) Low; 4) No independence	As far as it we could assess from the thesis and accessory documents, all experimental work described was performed essentially by the candidate - as well as the associate theoretical modelling, processing of data and interpretation of results. The relevance of the work is reflected on the papers resulting from it (appearing on indexed, peer-reviewed journals) as well as the registration of two patents.
4.	The principle of inner unity	4.1 Justification of the relevance of the thesis: 1) Justified; 2) Partially justified; 3) Not justified.	Works presenting devices and analytical protocols for time-weighted average determination of atmospheric constituents based on SPME - such as the present thesis - can be regarded as highly relevant and pertinent: although this is not exactly a novel approach, the combination of TWA + SPME has not been explored by the literature and there is opportunity and need for more improvement and applications.
		4.2 The content of the thesis reflects the topic of the thesis: 1) Reflects; 2) Partially reflects; 3) Does not reflect	After an introduction reviewing the current status of literature regarding the topics discussed on this thesis, the candidate organizes her experimental work and results on 5 sections - low-cost method for quantitation of air VOC using SPME; application to the assessment of seasonal / spatial VOC profiles in Almaty; study of the impact of covid-19 lockdown on air quality in Almaty; optimization of TWA-SPME air sampling by finite element analysis;

			and development of a TWA-SPME method for determination of air VOC modified using devices with alternate geometry. The abovementioned topics are consistent with the proposal of the thesis.
		4.3. The purpose and objectives correspond to the topic of the thesis: 1) <u>correspond</u>; 2) partially correspond; 3) do not correspond	The main objective of this work is the “development of simple and accurate methods based on solid-phase microextraction, which can improve the current methods, for the determination of single and time-weighted average concentrations of organic pollutants in the air”. The experimental work and results presented are fully covers this objective.
		4.4 All sections and provisions of the thesis are logically interconnected: 1) <u>completely interconnected</u>; 2) the interconnection is partial; 3) there is no interconnection	The sections as mentioned above in 4.2 are fully related one to another – although they describe independent work, their focus and aim are well correlated.
		4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: 1) <u>there is a critical analysis</u>; 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors	At the end of each section, the candidate discuss the material there presented and also ends her thesis with an overall, critical analysis of her work and results; also, she makes several recommendations related to the topic.
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? 1) completely new; 2) <u>partially new (25-75% are new)</u>; 3) not new (less than 25% are new)	As mentioned before, TWA-SPME is not a novel topic, but it has been seriously underappreciated and explored by people dealing with sample prep or air quality studies. Anyway, most of the findings and conclusions are new and as a whole the work is an welcome contribution to the area.
		5.2 Are the dissertation findings new?	See 5.1 above

		<p>1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)</p>	
		<p>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)</p>	See 5.1 above
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 presented conclusions are consistent and fully relatable to the results for each section of the thesis.
7.	The main provisions for the defense	<p>It is necessary to answer the following questions for each provision separately: <i>"1) The 65-μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber provides a better combination of detection limits (from 0.010 to 7 μg/m³) and relative standard deviations (RSDs) of slopes (<10% for 22 analytes) compared to 85-μm Carboxen (Car)/PDMS, 100-μm PDMS and 50/30-μm DVB/Car/PDMS for the determination of 25 volatile organic compounds in the air".</i></p> <p>7.1 Is the provision proven? 1) proven; 2) rather proven; 3) rather not proven; 4) not proven</p> <p>7.2 Is it trivial? 1) yes; 2) no</p> <p>7.3 Is it new? 1) yes; 2) no</p> <p>7.4 Application level: 1) narrow;</p>	The data presented clearly shows that PDMS/DVB fibers are the most suitable choice for the mentioned problem. Generally CAR/PDMS or DVB/CAR/PDMS are most suited to this task – although there are analytes and/or samples where this has been shown to occur. This is discussed and proven on the paper “Low-Cost Quantitation of Multiple Volatile Organic Compounds in Air Using Solid-Phase Microextraction” (<i>Separations</i> 2019 , 6, 51)

	<p>2) medium; 3) wide 7.5 Is it proven in the article? 1) yes; 2) no</p>	
	<p>"2) <i>The developed method based on SPME with a 65-μm PDMS/DVB coating provides spike recoveries in the range from 90 to 105% for 20 out of 25 studied analytes</i>".</p> <p>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</p>	<p>This is demonstrated and discussed in the same paper mentioned above (<i>Separations</i> 2019, 6, 51). These recoveries are adequate and a result of the successful optimization of the method, although they would be expectable considering the overall sensitivity/detectability of the hardware and devices employed.</p>
	<p>"3) <i>The seasonal variations of 9 out of 19 studied VOCs were significant ($p < 0.01$) with maximum concentrations on winter sampling days in Almaty in 2020</i>".</p> <p>7.1 Is the provision proven? 1) proven; 2) rather proven;</p>	<p>The results and associated discussion on the paper "Seasonal and Spatial Variation of Volatile Organic Compounds in Ambient Air of Almaty City, Kazakhstan" (<i>Atmosphere</i> 2021, 12, 1592) support fully this provision.</p>

	<p>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</p>	
	<p><i>"4) Decreasing diameter of the diffusion path from 0.75 to 0.34 mm allows achieving better accuracy of the determination of TWA concentrations of 9 out of 13 VOCs using Car/PDMS SPME fiber exposed in a glass liner".</i></p> <p>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;</p>	<p>This was proved satisfactorily and discussed on the paper "Optimization of Time-Weighted Average Air Sampling by Solid-Phase Microextraction Fibers Using Finite Element Analysis Software" (<i>Molecules</i> 2018, <i>23</i>, 2736) – both through numerical / theoretical analysis and experimental observations.</p>

		3) wide 7.5 Is it proven in the article? 1) yes; 2) no	
8.	The principle of reliability Reliability of sources and information provided	8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) yes; 2) no	The methodological approach used on the experimental work follows in general that adopted in most similar developments in the area, and is clearly presented and described.
		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	Specially the experiments and results described on Section #5 of the thesis – which is heavily based on numerical and computational work – the processing of data is carried out using adequate computational tools. Also, state-of-art GC equipment has been used through the work.
		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	The correlation between the results observed and conclusions are consistent and are consistent with the current theory and previous literature observations.
		8.4 Important statements are confirmed / partially confirmed / not confirmed by references to current and reliable scientific literature	Results and conclusions are coherent with those usually expected on similar works on the literature.
		8.5 Used literature sources are sufficient / not sufficient for a literature review	The thesis cites 161 works, most of them recent papers on the pertinent areas, from indexed // peer reviewed journals. The thesis subject is well covered and comprehensively reviewed.
9	Practical value principle	9.1 The thesis has theoretical value: 1) yes; 2) no	Specially the numerical modelling of TWA-SPME has a significant relevance


			to the theoretical background of the techniques.
		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 methods for TWA-SPME quantitation of air VOC presented here are fully applicable to related samples and analytical problems.
		9.3 Are the practice suggestions new? 1) completely new; 2) partially new (25-75% are new); 3) not new (less than 25% are new)	As mentioned in other sections, TWA-SPME is not a unknown approach but there is a significant amount of novel data and methodologies.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) average; 3) below average; 4) low.	The thesis is overall well-written, organized and clearly structured.

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

1) 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.

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