REVIEW
of the official reviewer for dissertation work
Yerkanat Syrgabek on the theme «Development of methods for the determination of pesticides in grapes using solid-phase microextraction» presented for the degree of Doctor of Philosophy (PhD) in the specialty «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)	The study was conducted within the framework of: - grant funding for scientific and/or scientific-technical projects for 2020-2022 under the topic “Improvement and development of highly sensitive methods to ensure food safety in Kazakhstan” project IRN AP08857501; - grant funding for scientific and/or scientific-technical projects for 2023-2025 under the topic “Development of a biological product to increase the yield of grapes” project IRN AP19680563; - grant funding for research by young scientists under the “Zhas Galym” project for 2024-2026 on the topic “Development of highly sensitive "green" methods for the analysis of residual amounts of pesticides in

			grapes" project IRN AP22685606.
2.	Importance for science	The work makes/does not make a significant contribution to science, and its importance is well disclosed/not disclosed	The work represents a significant contribution to the sciences and to society. This study advances the understanding of vacuum and miniaturized headspace solid-phase microextraction (Vac-HSSPME) for detecting pesticides in grapes. Optimal extraction parameters were identified, improving sensitivity and efficiency. The method was adapted for semi-volatile pesticides and evaluated using green analytical chemistry tools (GAPI, AGREEprep, BAGI), proving its sustainability and practicality. The optimized methods were implemented in a grape quality control laboratory, leading to a certified measurement procedure that enables fast, eco-friendly pesticide analysis and supports food safety and quality standards.
3.	The principle of independence	Self-reliance level: **1) High;** 2) Medium; 3) Low; 4) No independence	The self-reliance of the authors is clear. The self-reliance level the author consists in the literature data, carrying out the experiment and analyzing of pesticides in the samples using GC-MS after the sample preparation by vacuum and miniaturized SPME, evaluation and interpretation of obtaining results, including deep validation of

			greenness and practicality.
4.	The principle of inner unity	4.1 Justification of the relevance of the thesis: **1) Justified;** 2) Partially justified; 3) Not justified.	The relevance of the thesis is well **justified** in the literature review, the research conducted is not doubt important for science.
		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.
		4.3. The purpose and objectives correspond to the topic of the thesis: **1) correspond;** 2) partially correspond; 3) do not correspond	The purpose and objectives fully **correspond** to 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	All sections and provisions of the thesis are **completely interconnected.**
		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 solutions proposed by the author are substantiated and confirmed by research using modern methods of physical-chemical, spectral, experimental and statistical analysis. At each stage of the work, the author makes evidence-based and experimentally confirmed conclusions.
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? **1) completely new;** 2) partially new (25-75% are new);	This is the first time that Vac-HSSPME/GC-MS methodology is optimized for detecting six pesticides

		3) not new (less than 25% are new)	(metribuzin, oxyfluorfen, fluroxypyr, epoxiconazole, boscalid, and quizalofop-methyl) in grapes, defining key analytical characteristics. This is also the first time that Mini-HSSPME–GC-MS si proposed for the analysis of ten pesticides (including atrazine, simazine, tebuconazole, and others), including a fully parameters optimization as well as a complete analytical performance evaluation. The environmental sustainability of both optimized methods and existing approaches was assessed using GAPI, AGREEprep, and BAGI, resulting in a unified greenness metric for pesticide analysis in grapes. It is also the first study of these characteristics.
		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)	
		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)	
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 reliability of the experimental data was ensured through controlled testing conditions. Analytical performance indicators such as detection limits, recovery, linearity, accuracy, and reproducibility were conveniently evaluated. Measurements were performed in parallel experiments to guarantee

			statistical reliability. Pesticide identification and quantification were carried out using a highly sensitive gas chromatography–mass spectrometry (GC-MS) system, providing excellent selectivity and accuracy. All the conclusions are correctly stablished.
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: 7.1 Is the provition 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	1. Optimization of Vac-HSSPME parameters for GC-MS analysis of pesticides in grapes. The optimal conditions for vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) of metribuzin, oxyfluorfen, fluroxypyr, epoxiconazole, boscalid, and quizalofop-methyl in grape samples were established as: extraction temperature 70 °C, extraction time 40 min, PEG fiber, sample volume 1 mL, vacuum time 60 s (pumping rate 170 L/min), and pH 10. Using the Vac-SPME Arrow setup, the limits of detection (LOD) ranged from 0.02-1.3 ng/mL and limits of quantification (LOQ) from 0.1-4.4 ng/mL. 2. Optimization of Mini-HSSPME parameters for GC-MS analysis of

			pesticides in grapes The optimal parameters for miniaturized headspace solid-phase microextraction (Mini-HSSPME) of atrazine, simazine, prometryn, cyanazine, tebuconazole, metribuzin, fluroxypyr-methyl, epoxiconazole, boscalid, and quizalofop-methyl were: extraction temperature 90 °C, extraction time 30 min, pre-incubation time 10 min, PDMS (100 ⌈m) fiber, sample volume 200 ⌈L with salt addition, and pH 6.The method achieved LOD values of 0.05-3.0 ng/mL and LOQ values of 0.2-10.1 ng/mL 3. Assessment of Method Greenness and Analytical Performance The Vac-HSSPME method scored 0.67 (AGREEprep) and 60.0 points (BAGI), while the Mini-HSSPME method achieved higher scores of 0.79 (AGREEprep) and 67.5 points (BAGI), demonstrating improved greenness and analytical sustainability.

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	Yes, the methodology is described in sufficient detail
		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	Yes, modern and innovative methods are proposed and used as vacuum SPME, mini-SPME, GC-MS as well as innovative metric tools as AGREEprep, BAGI and GAPI.
		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 developed methods have been confirmed and applied in official laboratory.
		8.4 **Important statements are confirmed** / partially confirmed / not confirmed by references to current and reliable scientific literature	Yes, Important statements are confirmed
		8.5 Used literature sources are sufficient/not sufficient for a literature review	The literature research is very complete. In fact, 2 review articles are included in this thesis, both in Q1 high impact journals
9	Practical value principle	9.1 The thesis has theoretical value: **1) yes;** 2) no	This study enhances the understanding and application of Vac-HSSPME for quantitative pesticide analysis in grapes. Critical parameters including fiber type, temperature, extraction and desorption times, pre-incubation, salt effect, pH, vacuum duration, and

			sample volume were systematically optimized, improving sensitivity and analytical efficiency. The method was successfully adapted for semi-volatile pesticides, extending its applicability without increasing resource consumption. Additionally, the greenness and practical feasibility of the developed methods were rigorously evaluated using GAPI, AGREEprep, and BAGI, supporting sustainable, transferable, and potentially automated analytical approaches for complex food matrices.
		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	Practically, the optimized methods were implemented in a grape quality control laboratory at the Kazakh Scientific Research Institute of Fruit and Vegetable Growing, leading to an implementation act and a draft measurement procedure for certification. These methods enable rapid, eco-friendly pesticide determination, support compliance with modern standards, and strengthen food safety and national quality control systems.
		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)	Yes, the methods are completely new as well as the application of the metric tools in this area.

10.	The quality of writing and design	Academic writing quality: **1) high;** 2) average; 3) below average; 4) low.	The quality of academic writing as well as design and presentation are excellent
11.	Notes on a thesis		
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)		The main results on the theme of the thesis are presented in 4 publications: all of them in international peer-reviewed journal with very high impact factor. All of them in Q1 (excluding 1 in Q2). Seven abstracts all in international conferences.
13.	Decision of the official reviewer (pursuant to paragraph 28 of the present Model Regulations)		Summarizing the consideration of scientific research, it should be highlighted the scientific quality and its practical significance. The work gives the impression of a completed scientific work with interesting scientific and practical conclusions, forming the basis for further research. All the tasks are solved in the thesis. Thus, in terms of its relevance. The volume of work, scientific and practical significance, the thesis fully meets the requirements. The author deserves to award of the degree of Doctor of

			Philosophy (PhD) or Doctor of Specialization.

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

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

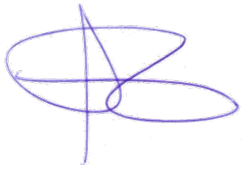
2) send the thesis for revision (except for cases of thesis defense in the form of a series of articles);

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:

University of Santiago de Compostela,
Professor Maria Llompart



(signature)