Review of the official reviewer
for the dissertation of Mr. Bauyrzhan Bukenov "Development of analytical methods for determination of transformation products of unsymmetrical dimethylhydrazine in air" on 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 dissertation (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 dissertation 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)**	The dissertation was carried out within the framework of projects funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan: "Development of analytical methods, materials and equipment for cost-efficient "green" environ mental monitoring" (2018–2020, AP05133158), "Development of accurate methods for on-site gas chromatographic determination of volatile organic compounds in environmental objects using solid-phase microextraction" (2022–2024, AP14871374), and Ministry of Science and Higher Education of the Russian Federation (Project No. FSRU-2024-0003).
2.	Importance for science	The work **makes** a significant contribution to science, and its importance is **well disclosed**	The dissertation addresses a clear gap in environmental analytical chemistry by developing sensitive and reliable methods for the simultaneous determination of multiple transformation products of unsymmetrical dimethylhydrazine (UDMH) in air. The research combines effective analytical approaches, including solid-phase microextraction, sorbent tube sampling, and gas chromatography with mass spectrometric and nitrogen-phosphorus detection, including high-resolution mass spectrometry, to achieve low detection levels, these approaches can provide new insight into the atmospheric behavior of toxic rocket fuel residues in the environment. Its findings strengthen the scientific basis for monitoring air contamination in regions affected by rocket activity and have both theoretical and practical significance for environmental safety and risk assessment.

3.	The principle of independence	Independence level: 1) **High;**	The dissertation demonstrates a high level of independence. The author confidently applied advanced analytical techniques throughout the research, showing a solid command of modern instrumental methods. The dissertation is presented as a series of peer-reviewed publications, in which the candidate is the first author of three and the corresponding author of one, clearly reflecting his leading role and significant personal contribution to the conceptualization, experimentation, and interpretation of the results.
4.	The principle of inner unity	4.1 Justification of the relevance of the dissertation: 1) **Justified;**	The relevance of the dissertation is well justified. It addresses the lack of reliable analytical methods for determining transformation products of UDMH in air – a key but understudied medium. By developing sensitive and accurate approaches based on solid-phase microextraction, sorbent tube sampling, and gas chromatography with mass spectrometric and nitrogen-phosphorus detection, including high-resolution mass spectrometry, the work fills an important methodological gap and advances environmental analytical chemistry and air monitoring near rocket stage fall sites.
		4.2 The content of the dissertation reflects the topic of the dissertation: 1) **Reflects;**	The content of the dissertation fully reflects its topic. It consistently presents the development, optimization, and validation of analytical methods for determining transformation products of UDMH in air using solid-phase microextraction, sorbent tube sampling, and gas chromatography with various detection systems. The publications forming the dissertation are logically interconnected and collectively contribute to achieving the main research objective, clearly demonstrating that the content accurately reflects the scope and purpose of the dissertation.
		4.3. The purpose and objectives correspond to the topic of the dissertation: 1) **correspond;**	The purpose and objectives of the dissertation fully correspond to its topic. They are clearly defined and aligned with the development of analytical methods for determining transformation products of UDMH in air. Each research task logically contributes to achieving the overall goal, ensuring coherence between the dissertation's topic, its aims, and the obtained results.

		4.4 All sections and provisions of the dissertation are logically interconnected: 1) **completely interconnected;**	All sections and publications of the dissertation are logically compatible and thematically aligned. While each study was conducted independently, they are united by a common scientific objective – the development of analytical methods for determining UDMH transformation products in air. Together, they complement one another conceptually and methodologically, forming a coherent body of work that supports the overall purpose of the dissertation.
		4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions: 1) **critical analysis is presented;**	The new analytical solutions and methodological approaches proposed in the dissertation are well reasoned and evaluated in comparison with existing methods. The dissertation clearly demonstrates the advantages of the developed techniques – such as improved sensitivity, reduced analysis time, and applicability for multi-component determination of UDMH transformation products in air – over previously known approaches. Comparative analysis with literature data confirms the novelty and effectiveness of the proposed methods.
5.	Scientific novelty principle	5.1 Are the scientific results and provisions new? 1) **completely new;**	The research presents original analytical methods for the simultaneous determination of multiple transformation products of UDMH in air. These approaches have not been previously applied to this group of compounds in the atmosphere. The achieved detection limits, methodological optimization, and demonstration of applicability for real and model samples confirm the novelty and scientific significance of the obtained results.
		5.2 Are the dissertation findings new? 1) **completely new;**	The dissertation introduces original analytical methodologies for detecting and quantifying multiple transformation products of UDMH in air, which had not been comprehensively studied before. The developed approaches represent a novel contribution to environmental analytical chemistry by enabling more sensitive and accurate analysis of trace compounds in the air.
		5.3 Technical, technological, economic or management decisions are new and reasonable: 1) **completely new;**	The technical and technological solutions presented in the dissertation are new and well justified. The author proposes optimized analytical approaches, offering improved sensitivity,

			reproducibility, and practicality for air analysis. These solutions enhance existing techniques and provide cost-efficient alternatives suitable for routine and field applications, making them both scientifically and technologically sound.
6.	The validity of the main findings	All main conclusions **are** based on scientifically significant evidence	All main conclusions of the dissertation are based on scientifically significant and experimentally verified evidence. The results were obtained using modern analytical instruments and validated through rigorous method optimization, calibration, and reproducibility studies. The conclusions logically follow from the data presented in the publications and are supported by quantitative results, confirming their reliability and scientific validity.
7.	The main provisions for the defense	It is necessary to answer the following questions for each provision separately: Provision 1: *The optimal solid-phase microextraction time for the extraction of unsymmetrical dimethylhydrazine transformation products (1-methyl-1H-pyrazole, dimethylaminoacetonitrile, N-nitrosodimethylamine, N,N-dimethylformamide, 1-methyl-1H-1,2,4-triazole, N-methylformamide, and 1H-pyrazole) from air in 20 mL vials using a 85 μm Carboxen/polydimethylsiloxane fiber, which provides the best combination of detection limits (0.12–0.5 μg/m³) and apparent recoveries (88–130%) when analyzed by gas chromatography–mass spectrometry, is 5 minutes.* 7.1 Is the provision proven? 1) **proven;** 7.2 Is it trivial? 2) **no**	Provision 1 is experimentally verified through systematic optimization of extraction time, demonstrated by calibration data, recovery, and detection limits obtained using the described SPME-GC-MS method. The result is not obvious, as it was established experimentally for a specific group of UDMH transformation products under optimized analytical conditions. No previous studies have reported optimized extraction parameters for simultaneous determination of multiple UDMH transformation products in air using SPME-GC-MS, making this finding novel. The provision is applicable to analytical and environmental laboratories conducting air quality studies related to rocket fuel contamination but is limited to this class of compounds and matrix type. The proof is provided in the Journal of Separation Science (2022) article, where the optimization experiments, calibration data, recoveries, and detection limits supporting this provision are presented. *Bukenov, B., Baimatova, N., & Kenessov, B. (2022). Quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in air using solid-phase*

		7.3 Is it new? 1) **yes;** 7.4 Application level: 2) **medium;** 7.5 Is it proven in the article? 1) **yes;**	*microextraction. Journal of Separation Science, 45(2), 614–622. https://doi.org/10.1002/jssc.20210068-4*
		Provision 2: *Increasing the air sample volume from 20 to 250 mL and the SPME time from 5 to 15 minutes using an 85 µm Carboxen/polydimethylsiloxane fiber reduces the detection limits for unsymmetrical dimethylhydrazine transformation products (pyrazine, 1-methyl-1H-pyrazole, N-nitrosodimethylamine, N,N-dimethylformamide, 1-methyl-1H-1,2,4-triazole, N-methylformamide, 1H-pyrazole, and 3-methyl-1H-pyrazole) from 4–10 to 0.3–2 µg/m³ when using a portable gas chromatograph with nitrogen-phosphorus detection.* 7.1 Is the provision proven? 1) **proven;** 7.2 Is it trivial? 2) **no** 7.3 Is it new? 1) **yes;** 7.4 Application level: 2) **medium;** 7.5 Is it proven in the article? 1) **yes;**	The provision is experimentally validated through comparative studies showing that increasing sample volume and extraction time leads to lower detection limits when using SPME-GC-NPD. The data are clearly presented and supported by calibration results. Although the general relationship between sample volume and sensitivity is known, its quantitative effect for this specific group of UDMH transformation products and under field-portable GC-NPD conditions is non-trivial and experimentally confirmed. The optimization of SPME parameters for a portable GC-NPD setup applied to multiple UDMH transformation products in air has not been previously reported, demonstrating novelty. The provision has practical value for field and on-site environmental monitoring but is specific to UDMH-related air analysis. The results confirming this provision are presented in the *Journal of Separation Science* (2025) article, which includes detailed optimization data, detection limit comparisons, and method validation. *Bukenov, B., Karimkyzy, N., Smail, A., Kurmanbayeva, T., &Kenessov, B. (2025). On-Site Quantification of Transformation Products of Rocket Fuel Unsymmetrical Dimethylhydrazine in Air Using Solid-Phase Microextraction. Journal of Separation Science, 48(3). https://doi.org/10.1002/jssc.70113*
		Provision 3: *The use of sorbent tubes packed with*	The provision is experimentally supported by systematic

		Tenax TA at an air sampling rate of 200 mL/min provides the highest recovery (82–125%) and the best detection limits (0.04–0.5 pg/tube) for unsymmetrical dimethylhydrazine transformation products (1,1,4,4-tetramethyl-2-tetrazene, N-nitrosodimethylamine, N,N-dimethylformamide, 1-methyl-1H-1,2,4-triazole, dimethylaminoacetonitrile, 1-methyl-1H-pyrazole, and N-methylformamide) in air among all tested sorbent tubes when analyzed by gas chromatography with high-resolution mass spectrometry. 77.1 Is the provision proven? 1) **proven;** 7.2 Is it trivial? 2) **no** 7.3 Is it new? 1) **yes;** 7.4 Application level: 2) **medium;** 7.5 Is it proven in the article? 1) **yes;**	comparison of different sorbent tube types and sampling flow rates, showing that Tenax TA at 200 mL/min yields the best recoveries and detection limits. The result is not trivial, as the optimal sorbent material and flow rate for capturing UDMH transformation products in air were established empirically and had not been determined previously for this compound group. This finding represents a new methodological contribution, as no prior studies have reported optimized sorbent tube parameters for simultaneous determination of multiple UDMH transformation products using TD-GC-HRMS. The method is broadly applicable to analytical laboratories performing environmental air monitoring for rocket fuel residues but remains specific to nitrogen-containing transformation products. The provision is clearly demonstrated in the *Microchemical Journal* (2025) publication, which presents comparative data on sorbent efficiency, recovery rates, and detection limits supporting this conclusion. *Bukenov, B., Kenessov, B., Baimatova, N., Ul'yanovskii, N. V., Popov, M. S., & Kosyakov, D. S. (2025). Quantification of rocket fuel transformation products in air using sorbent tubes sampling and thermal desorption GC – high-resolution mass spectrometry (Orbitrap). Microchemical Journal, 209, 112879. https://doi.org/10.1016/j.microc.2025.112879*
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 details 1) **yes**;	The choice of methodology is well justified, and the analytical procedures are described in sufficient detail. The dissertation clearly explains the selection of analytical methods as the most suitable approaches for determining UDMH transformation products in air. Each methodological step – from sampling and extraction to detection and validation – is thoroughly detailed, ensuring reproducibility and demonstrating a sound scientific basis for the chosen techniques.

		8.2 The results of the dissertation were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) **yes**;	The results of the dissertation were obtained using modern scientific research methods and advanced analytical instrumentation. Data processing and interpretation were carried out with the use of specialized software for chromatographic and mass spectrometric analysis. This ensured high accuracy, reproducibility, and reliability of the obtained results, confirming the use of contemporary and scientifically sound approaches throughout the study.
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research: 1) **yes**;	The theoretical conclusions and identified relationships presented in the dissertation are well supported and confirmed by experimental research. The developed analytical approaches were validated through systematic experimentation, optimization, and comparison with existing methods. The obtained data consistently verify the proposed principles and demonstrate the reliability and reproducibility of the established patterns in determining UDMH transformation products in air.
		8.4 Important statements are **confirmed** by references to current and reliable scientific literature	The author provides an extensive review of relevant sources, including recent international publications on analytical chemistry, environmental monitoring, and rocket fuel transformation products. The cited works are up to date and used appropriately to support the research context, justify methodological choices, and compare results, ensuring the scientific credibility of the dissertation.
		8.5 Used literature sources are **sufficient** for a literature review	The literature sources used in the publications are sufficient for a comprehensive literature review. They cover key international and regional studies on analytical methods for volatile and semi-volatile compounds, as well as research on transformation products of unsymmetrical dimethylhydrazine. The references include recent and relevant publications from high-impact journals, providing a solid scientific foundation for the research and demonstrating the author's thorough understanding of the current state of the field.
9.	Practical value	9.1 The dissertation has theoretical value:	The dissertation has clear theoretical value. It expands the

	principle	1) **yes**;	scientific understanding of the analytical determination of UDMH transformation products in air by establishing methodological principles for their extraction, separation, and detection. The work contributes to the theoretical basis of environmental analytical chemistry, particularly in studying trace nitrogen-containing compounds in complex atmospheric matrices and provides a framework for further research on transformation mechanisms and analytical method development.
		9.2 The dissertation is of practical importance and there is a high probability of applying the results obtained in practice: 1) **yes**;	The dissertation is of clear practical importance, with a high probability of applying the obtained results in practice. The developed analytical methods can be directly used for environmental monitoring of air in areas affected by rocket stage falls and fuel residues. Their simplicity, sensitivity, and adaptability to both laboratory and field conditions make them suitable for routine analyses and regulatory assessments. The results contribute to improving air quality monitoring infrastructure and can support environmental safety programs related to aerospace activities.
		9.3 Are the practice suggestions new? 1) **completely new**;	The practical suggestions presented in the dissertation are new. They propose the use of optimized analytical methods for the simultaneous determination of multiple UDMH transformation products in air. These approaches have not been previously applied to this group of compounds in the atmospheric matrix and offer improved sensitivity, operational simplicity, and suitability for both laboratory and on-site applications, representing novel and practically valuable solutions for environmental monitoring.
10.	The quality of writing and design	Academic writing quality: 1) **high**;	The academic writing quality of the dissertation is high. The text is clear, well structured, and written in a precise scientific style appropriate for analytical chemistry. The author effectively presents complex methodological details in an accessible manner, maintaining logical flow and coherence across sections. Terminology is used accurately, and arguments are supported by data and literature references.

11.	Comments to the dissertation	1) The study remains unclear as to why these seven molecules were specifically quantified, as well as why the list of identified molecules differs across publications. Some components, such as NDMA, may be present in the atmosphere for reasons unrelated to UDMH. 2) The study targets a defined set of seven major transformation products, whereas recent HRMS screening studies indicate the existence of hundreds of possible intermediates and minor by-products not covered here. 3) The study lacks any field demonstration that the method is actually capable of detecting volatile UDMH transformation products at the concentrations they are present in the atmosphere significantly after a rocket launch or crash. A single experiment (JSS article, 2025) at the Proton rocket used stage crash site showed that none of the analytes were detected. An experiment with soil samples from the launch site, collected soon after the launch, showed high concentrations immediately near the launch site (in the restricted-access area), which is less relevant from an ecotoxicological perspective. 4) The study's rationale appears somewhat outdated. Currently, virtually all rockets using UDMH in their lower stages (in significant quantities, measured in tens of tons) are phased out. There have been no Proton rocket launches since 2023, and there likely won't be any in the future. Currently, persistent transformation products with higher molecular weights, which can persist in soil for decades, are of greater importance. 5) It is unclear why on-site analysis using NPD is used instead of delivering samples to the laboratory and using GC-HRMS, especially considering that transformation products were not detected using NPD. 6) The dissertation author frequently mentions recovery rates statistically significantly greater than 100%. This phenomenon may indicate an unreliable estimate of the recovery rates and their uncertainties. 7) In Figure 4 (article MJ 2025), the concentration of some components drops rapidly after the start of decontamination and then remains virtually constant for a long time. It remains unclear what causes this type of dependence and why the decomposition of the substance ceases. This may indicate a false positive detection. 8) The author connects the points on the curves using smooth curves (splines), which is undesirable, although it does not affect the conclusions reached in the work. 9) Stability of target analytes during storage of sorbent tubes or vials over extended periods (weeks to months) was not systematically evaluated, which could affect real-world sampling logistics.
12.	The scientific level of the doctoral student's articles on the research topic	The scientific level of the publications included in the dissertation is high. The first article (JSS, 2022) demonstrates a high scientific level, presenting an original and well-validated SPME-GC-MS method for the quantitative determination of multiple UDMH TPs in air with strong methodological justification and reliable analytical results. The second article (JSS, 2025) is of medium scientific level, extending the approach to on-site GC-NPD analysis and showing originality in adapting SPME for field screening. The third article (MJ, 2025) is of high scientific level, introducing an advanced TD-GC-HRMS method with

		outstanding sensitivity, comprehensive validation, and detailed analytical characterization. Overall, the publications form a coherent, well-structured body of work that demonstrates consistent scientific progress, methodological innovation, and the candidates high research competence and independence.
13.	Decision of the official reviewer	1) **to award the degree of the Doctor of Philosophy (PhD)**; 2) refuse to award the degree of the Doctor of Philosophy (PhD).

Official Reviewer:

Ph.D., senior researcher, head. lab. "smart" methods
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