**ABSTRACT**

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

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**“Development of analytical methods for determination of transformation products of unsymmetrical dimethylhydrazine in air”**

**The dissertation is presented** as a series of articles published by the PhD candidate in accordance with the requirements of paragraph 5-1 of the Rules for the Award of Academic Degrees, approved by Order No. 7 of the Minister of Science and Higher Education of the Republic of Kazakhstan dated January 9, 2023.

**The relevance of the study.**

Unsymmetrical dimethylhydrazine (UDMH) is a highly toxic rocket fuel component widely used in launch vehicles. Its use leads to significant environmental contamination, particularly in areas near spaceports such as Baikonur and in rocket stage fall zones. Once released into the environment, UDMH rapidly undergoes various chemical transformations, forming numerous nitrogen-containing transformation products (TPs), including *N*-nitrosodimethylamine (NDMA), *N*,*N*-dimethylformamide (DMF), dimethylaminoacetonitrile (DMAAN), 1-methyl-1*H*-pyrazole (MPA), and 1-methyl-1*H*-1,2,4-triazole (MTA). Among them, compounds such as NDMA and DMF are classified as particularly hazardous due to their potential carcinogenic, mutagenic, and/or teratogenic properties. However, other TPs also contribute to the overall environmental burden and may pose potential risks to human health and ecosystems.

Most of available scientific studies have primarily focused on the investigation and determination of UDMH TPs in soil and water, as these media serve as long-term reservoirs for pollutants and are more convenient for sample collection and storage. However, air represents a critical exposure pathway that has received considerably less attention. UDMH TPs present in the air, as well as those volatilized from soil and water, can travel over long distances and lead to direct exposure of populations on both local and regional scales. Furthermore, air analysis is essential for understanding the initial dispersion and subsequent behavior of these compounds immediately after a rocket stage fall or fuel spill.

Despite the importance of air monitoring, there is a lack of analytical methods capable of simultaneously determining multiple UDMH TPs in air samples at low or trace concentration levels. Most existing methods focus on a single analyte and require complex instrumentation and sample preparation, limiting their practical application and accessibility. Moreover, many of these methods do not offer sufficient sensitivity to detect UDMH TPs at levels relevant to environmental or regulatory standards.

The volatility and potential toxicity of UDMH TPs make air analysis particularly challenging. Sampling and storage can lead to significant losses or transformations of analytes, resulting in inaccurate assessments of contamination. Reliable, comprehensive methods for the quantitative determination of UDMH TPs in air are essential for accurate environmental pollution assessment and for evaluating potential health risks.

Therefore, there is a strong need for the development of sensitive, accurate, and practical analytical methods suitable for air sample analysis. These methods should enable the simultaneous quantification of multiple UDMH TPs, providing essential data for environmental monitoring, risk

assessment, and regulatory control. The development of such methods is particularly relevant for Kazakhstan and other regions where UDMH-based fuels are used.

This study addresses important scientific and practical gaps by developing analytical methods for the determination of multiple UDMH TPs in air. These methods enhance the capabilities of air pollution monitoring related to rocket fuel use, contributing to a more comprehensive understanding of pollutant distribution and their potential impacts. The results of this work can support the development of effective strategies for managing contaminated areas and provide evidence-based support for ensuring environmental and public health safety.

**The aim of this study** was the development of a set of analytical approaches and corresponding methods that are sensitive, reliable, and cost-effective for the quantitative determination of multiple UDMH TPs in air.

**Research tasks:**

1. To develop a method for the quantitative determination of UDMH TPs in air using solid-phase microextraction (SPME) combined with gas chromatography – mass spectrometry (GC-MS), and to optimize the extraction process from air samples using 20 mL vials and 85 μm Car/PDMS SPME fiber.
2. To develop a method for the quantitative on-site determination of UDMH TPs in air using SPME combined with gas chromatography and nitrogen-phosphorus detection (GC-NPD).
3. To develop a method for the quantitative determination of UDMH TPs in air using optimized sorbent tube sampling followed by thermal desorption and analysis by gas chromatography with high-resolution mass spectrometry (TD-GC-HRMS).

**The objects of the study:** determination of a multiple UDMH TPs in air using SPME and sorbent tubes.

**The subjects of the research:** optimization of sampling, extraction, and desorption parameters for the quantitative determination of UDMH TPs in air using SPME and sorbent tube sampling in air using SPME and sorbent tube sampling within acceptable accuracy and repeatability limits.

**The methods of the research**

A rigorous scientific method was applied in the dissertation, involving the formulation and experimental testing of hypotheses. The dependent variables included key performance indicators of the developed methods, such as the analytical signal (peak area), relative standard deviation (RSD), and accuracy of determination (apparent recovery). The independent variables were the optimized methodological parameters, including extraction time, sorbent type, and sampling flow rate.

For the development of analytical methods, selective and sensitive approaches based on gas chromatography were used: GC-MS, GC-NPD, and GC-HRMS (Orbitrap). Sample preparation included SPME from air samples collected in vials and gas sampling bulbs, as well as sampling using sorbent tubes followed by thermal desorption (TD).

**The main provisions of the research to be defended.**

1. The optimal solid-phase microextraction time for the extraction of unsymmetrical dimethylhydrazine transformation products (1-methyl-1*H*-pyrazole, dimethylaminoacetonitrile, *N*-nitrosodimethylamine, *N,N*-dimethylformamide, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, and 1*H*-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.
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-1*H*-pyrazole, *N*-nitrosodimethylamine, *N,N*-dimethylformamide, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, 1H-pyrazole, and 3-methyl-1*H*-pyrazole) from 4–10 to 0.3–2 μg/m³ when using a portable gas chromatograph with nitrogen-phosphorus detection.

3. The use of sorbent tubes packed with 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-1*H*-1,2,4-triazole, dimethylaminoacetonitrile, 1-methyl-1*H*-pyrazole, and *N*-methylformamide) in air among all tested sorbent tubes when analyzed by gas chromatography with high-resolution mass spectrometry.

**The main research results**

1. An automated, solvent-free SPME-GC-MS method was developed for the simultaneous quantitative determination of seven UDMH TPs, with detection limits (LODs) ranging from 0.12 to 0.5 μg/m³ and high precision (apparent recoveries of 88–130%, $R^2 \geq 0.99$). The SPME-GC-MS method demonstrated good stability: air samples containing UDMH TPs remained stable for up to 24 hours at room temperature at concentrations ≥500 μg/m³, whereas significant losses were observed at lower concentrations after just 12 hours.

2. An on-site analytical method for UDMH TPs in air was optimized using SPME combined with a portable GC-NPD. Increasing the sample volume to 250 mL and the extraction time to 15 minutes improved the LODs to 0.3–2 μg/m³. Additionally, a passive air sampling approach was proposed, in which the SPME fiber is placed in a glass liner and exposed to ambient air for 24 hours, providing a low-cost, low-effort pre-screening tool for remote monitoring of UDMH TPs.

3. A highly sensitive analytical method for UDMH TPs in air was developed using sorbent tube sampling followed by thermal desorption and GC-HRMS, achieving detection limits as low as 0.04–0.5 pg/tube, enabling trace-level detection. Among the tested sorbents, Tenax TA and Carbograph 1TD showed the best performance in retaining UDMH TPs, providing high apparent recoveries (76–112%).

**The scientific novelty of the research**

New methods were developed for the simultaneous determination of multiple UDMH TPs in air, including highly toxic compounds such as NDMA, DMF, and MTA (up to seven analytes in total). The study proposes automated SPME-GC-MS method, as well as a portable, field-suitable SPME-GC-NPD method optimized for on-site application, enabling direct measurements in field conditions. In addition, a highly sensitive method based on sorbent tube sampling followed by TD-GC-HRMS analysis was presented, capable of detecting UDMH TPs at the ng/m³ level (with detection limits down to 0.08–1.1 ng/m³). This combination of approaches offers a novel and practical tool for comprehensive environmental monitoring in remote and contaminated areas.

**The theoretical significance of the thesis**

The theoretical significance of this study lies in the development of a set of analytical approaches and corresponding methods for the detection of UDMH TPs in air. The work expands existing scientific knowledge by enabling the simultaneous quantitative determination of multiple toxic UDMH TPs using SPME in combination with both stationary and portable GC systems, as well as GC-HRMS. The study presents field-deployable, sensitive methods with low detection limits, enhancing the efficiency of atmospheric monitoring in rocket stage fall zones. Overall, the dissertation strengthens the theoretical foundation for assessing atmospheric pollution related to rocket fuel emissions.

**The practical significance of the thesis**

The methods developed in this dissertation can be effectively applied for the quantitative determination of UDMH TPs in air, supporting environmental monitoring and risk assessment in areas contaminated by rocket fuel:

1. The SPME-GC-MS method offers sufficient sensitivity (LODs of 0.12–0.5 μg/m³) for assessing air pollution in areas contaminated by rocket fuel, such as rocket stage fall zones. It enables timely and accurate evaluation of environmental impact, including in remote regions, with the possibility of storing samples for up to 24 hours at room temperature at higher concentrations. In addition, the automation of the method allows for the rapid analysis of large numbers of samples, contributing to the collection of comprehensive information on atmospheric conditions.
2. The SPME-GC-NPD method can serve as a practical tool for screening and quantitative analysis of air at "fresh" rocket stage fall sites, allowing the detection of nitrogen-containing TPs shortly after stage separation. Its portability and simplicity make it suitable for preliminary field assessments without the need for advanced laboratory infrastructure.
3. The method based on sorbent tube sampling followed by TD-GC-HRMS analysis offers significant advantages for the analysis of trace-level UDMH TPs in air. It achieves ultra-low detection limits (in the ng/m³ range), making it highly sensitive for monitoring trace concentrations. Sorbent tubes can be reused after proper thermal conditioning, increasing cost-efficiency. Moreover, this approach allows for non-target screening, enabling the identification of previously unknown TPs and other volatile organic compounds in complex environmental matrices, which is particularly valuable for long-term monitoring and in-depth pollution studies.

The developed methods for the quantitative determination of UDMH TPs in air enable the accurate identification of hazardous compounds formed through degradation and oxidation. Monitoring TPs such as NDMA and MTA is crucial for assessing environmental pollution at rocket launch and fall sites. These data can contribute to ensuring environmental safety by identifying zones with elevated contamination levels. The results may be used to assess the long-term impact of space activities on ecosystems, particularly in remote regions. The methods can also aid in protecting public health by helping to evaluate exposure risks, especially for populations living near affected areas.

**The validity and reliability of the results** and obtained data were confirmed using selective, accurate, and modern analytical methods, following scientific method and rigorous scientific principles. To ensure reproducibility and reliability, all experiments were conducted in multiple parallel measurements.

**Relevance of the dissertation to scientific and state programs**

The research 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), and "Development of accurate methods for on-site gas chromatographic determination of volatile organic compounds in environmental objects using solid-phase microextraction" (2022–2024, AP14871374).

**Dissemination of practical results.**

The results of the work were presented at the 43rd International Symposium on Capillary Chromatography, jointly held with the 16th Symposium on Comprehensive Two-Dimensional Gas Chromatography (ISCC & GC×GC, Fort Worth, Texas, USA, 2019), and at the 25th International Symposium on Advances in Extraction Technologies (ExTech, Tenerife, Spain, 2023).

**Publications**

The results of this research were published in international journals ranked in the first and second quartiles according to the Journal Citation Reports (JCR) impact factor: one article in *Microchemical Journal* (Q1 in the "Analytical Chemistry" category, IF = 5.1), and two articles in *Journal of Separation Science* (Q2 in the "Analytical Chemistry" category, IF = 2.8).

**The personal contribution of the Ph.D. candidate to the preparation of each article was as follows:**

In the article "Quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in air using solid-phase microextraction" (Journal of Separation Science, 2022), Bukenov B., and prepared the initial draft of the manuscript. He also participated in its revision following peer review.

In the article "On-site quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in air using solid-phase microextraction" (Journal of Separation Science, 2025), Bukenov B. is the first author, made a significant contribution to the conceptualization of the study, as well as the development and validation of the methodology. He conducted the experimental research, managed data processing, prepared the initial manuscript draft, and contributed to its revision after peer review. Additionally, he created visual materials to enhance the presentation of the results.

In the article "Quantification of rocket fuel transformation products in air using sorbent tube sampling and thermal desorption GC–high-resolution mass spectrometry (Orbitrap)" (Microchemical Journal, 2025), Bukenov B. is both the first and corresponding author. He played a key role in the study: he developed the conceptual framework, designed and validated the methodology, and ensured the integrity of the analytical process. He independently carried out all experiments, conducted formal analysis and investigations, processed the data, and prepared the initial manuscript draft. He was also responsible for submitting the article to the journal, revising it after peer review, and creating graphical materials to effectively present the results.