Review of the local scientific advisor
on the dissertation of Bauyrzhan Omirbekovich Bukenov
"Development of analytical methods for determination of unsymmetrical dimethylhydrazine transformation products in air" submitted for Ph.D. degree
on the educational program "8D05301 – Chemistry"

As a result of spills of rocket fuel unsymmetrical dimethylhydrazine (UDMH), air can be contaminated with volatile UDMH transformation products (TPs) causing health risks. Despite importance of this problem, there was a very limited number of studies on air pollution with UDMH TPs mostly due to the lack of selective and sensitive analytical methods for quantitation of UDMH TPs in air. Most research was focused on soil pollution that was concentrated in the places of UDMH spill, while the area of potential air pollution is much greater resulting in lower concentrations.

Ph.D. dissertation of Bauyrzhan Bukenov aims at the development of novel methods for determination of UDMH TPs in air using gas chromatography. He developed three new analytical methods for: 1) quantification of UDMH TPs in air using SPME from 20-mL vials and gas chromatography-mass spectrometry (GC-MS); 2) on-site quantification of UDMH TPs in air using SPME from 250-mL vials and portable gas chromatograph with nitrogen-phosphorus detector (GC-NPD); 3) quantification of UDMH TPs in air using sorbent tubes and thermal desorption (TD) to gas chromatograph with high-resolution Orbitrap mass spectrometer (GC-HRMS). During the development of these methods, a major focus was on achieving a sufficient accuracy at lowest possible limits of detection (LODs).

For the development of the method based on SPME-GC-MS with 85 μm Carboxen/polydimethylsiloxane (Car/PDMS) fiber, extraction time (5 min), desorption time (3 min), vial type (amber glass) and storage time (<2 h) were optimized. Limits of detection were 0.12-0.5 $\mu g/m^3$. The developed method was applied for the determination of soil-gas distribution constants of UDMH TPs.

For the on-site method based on SPME-GC-NPD with 85 μm Car/PDMS fiber, sample volume and extraction time were increased to 250 mL and 15 min, respectively, to achieve LODs (0.3-2 $\mu g/m^3$). Preliminary screening using 24-hour SPME from the liner (internal diameter 4.6 mm) exposed to the open air has been implemented. According to the modeling with COMSOL Multiphysics, such extraction parameters should provide 2.0-3.5 times greater amounts of analytes in the fiber coating. In 2024, Bauyrzhan Bukenov tested the developed method during expedition to fall places of the first stages of "Proton-M" carrier rockets in Central Kazakhstan.

Development of the method based on sorbent tubes, TD-GC-HRMS was conducted during the internship of Bauyrzhan Bukenov in the Northern Arctic Federal University (Arkhangelsk, Russia) and included selection of tube (Tenax TA) and optimization of sampling flow rate (200 mL/min). For most analytes, LODs ranged from 0.3 to 1.1 ng/m^3. Recoveries depended on the concentrations of analytes and ranged from 76 to 112%. The developed method was applied to analyze changes in UDMH TPs concentrations in air above contaminated soil undergoing decontamination.

Dissertation is presented as a series of three articles published in Journal of Separation Science (Q2 on impact factor in Chemistry, Analytical according to Journal Citation Reports, 2 articles) and Microchemical Journal (Q1 on impact factor in Chemistry, Analytical according to Journal Citation Reports). Bauyrzhan Bukenov is the first author in all these articles.

The research for the dissertation has been conducted under two projects funded by the Science Committee of the Ministry of Education and Science (later - Ministry of Science and Higher Education) of the Republic of Kazakhstan: "Development of analytical methods, materials and equipment for cost-efficient "green" environmental 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) both supervised by me.

Bauyrzhan Bukenov is a prospective young scientist in analytical chemistry with a strong background in gas chromatography, mass spectrometry, solid-phase microextraction and sampling with sorbent tubes. During his work on the dissertation, he showed his ability to conduct novel research on modern analytical instruments. Currently he has 12 articles published in journals indexed in Science Citation Index Expanded (Web of Science) and Scopus including six articles in journals included in Q1 on impact factor. His h-index in Web of Science and Scopus is 5 with total number of citations 364 and 417, respectively. Currently, he participates in the realization of the project AP23484339 "Identification of new potentially hazardous volatile and semi-volatile organic environmental pollutants in Almaty and its suburbs using solid-phase microextraction" (2024-2026).

Based on the published articles, independence, internal unity, scientific novelty, reliability, practical value, and academic honesty, the dissertation meets the requirements of the Rules for Awarding Degrees, and the author deserves to be awarded the degree of Doctor of Philosophy (Ph.D.) in the educational program 8D05301 – Chemistry.

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