ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
on educational program "8D05301 – Chemistry"
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"Development of simple and accurate methods for on-site gas chromatographic determination of volatile organic compounds in environmental objects using solid-phase microextraction"

The relevance of the study.

High-quality environmental monitoring and research on toxic organic compounds are essential for informed decision-making aimed at reducing health risks and supporting sustainable societal development. In routine practice, monitoring typically involves the collection of environmental samples, their transportation to laboratories, and subsequent analysis using gas (GC) or liquid chromatography. Although analytical instruments continue to improve, the entire procedure of analysis remains time-consuming and labor-intensive. During accidental pollution events involving highly toxic compounds – such as a space rocket launch vehicle crash that releases large quantities of toxic fuel – rapid decisions are critical. However, initial analytical results may take days because well-equipped laboratories are often located far from a sampling site. Such delays reduce the efficiency of response measures and can hinder timely mitigation of environmental and public health risks.

A range of approaches can be employed for the extraction and analysis of organic pollutants, including solvent extraction, static and dynamic headspace, solid-phase extraction, and solid-phase microextraction (SPME). Among these approaches, SPME is particularly suitable for on-site analysis in combination with GC because it is simple, does not require organic solvents, and integrates sampling with sample preparation in a single step. In SPME, analytes are extracted by a small polymeric coating either directly or from the headspace of a liquid or solid sample. Most portable GC allow the rapid thermal desorption of fiber-extracted analytes directly in the injection port.

Despite these advantages, only few SPME-based analytical methods have been applied for on-site measurements. Most available SPME-based methods cannot be used in the field without additional optimization because portable GC typically provides lower separation effectiveness of analytes and higher detection limits compared to stationary equipment. On-site analytical methods must be faster and simpler because conducting measurements in the field involves constraints related to time, resources, and equipment availability.

The aim of the study was to develop and test simple and accurate analytical methods for on-site determination of benzene, toluene, ethylbenzene and *o*-/*m*-/*p*-xylene (BTEX) in atmospheric air and eight main transformation products of unsymmetrical dimethylhydrazine (UDMH TPs) in water and soil samples using SPME in combination with a portable SRI 8610C GC.

The following **tasks** were set to accomplish the aim of the work:

Task 1. Development of the method for on-site quantification of BTEX in air using SPME and gas chromatography with photoionization detection (GC-PID).

Task 2. Development of the method for on-site quantification of UDMH TPs in water using vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) and gas chromatography with nitrogen-phosphorus detection (GC-NPD).

Task 3. Development of the method for on-site quantification of UDMH TPs in soil using Vac-HSSPME-GC-NPD.

The objects of the study: methods for on-site gas-chromatographic determination of BTEX in air and UDMH TPs (pyrazine, 1-methyl-1*H*-pyrazole, *N*-nitrosodimethylamine, *N*,*N*-dimethylformamide, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, 1*H*-pyrazole, and 3-methyl-1*H*-pyrazole) in water and soil samples.

The subjects of the research: optimization of sampling, SPME/Vac-HSSPME procedures, desorption parameters for on-site determination of BTEX and UDMH TPs in air, water, and soil using a portable SRI 8610C gas chromatograph with photoionization or nitrogen-phosphorus detectors, with the aim of achieving acceptable trueness (expected recovery 70-130%) and repeatability.

The methods of research.

The scientific method was used to disclose knowledge gaps, formulate research questions and hypotheses, and design experiments for testing hypotheses. Portable SRI 8610C GC with photoionization and nitrogen-phosphorus detectors was used for measurement of analytical signals during the development and optimization of the methods. SPME was chosen as a sampling and sample preparation technique because it combines low cost of analysis and high preconcentration factor. The standard addition and external standard calibration methods were employed to mitigate the matrix effects on SPME. The extraction kinetics of ethylbenzene and xylenes from air samples were simulated using the finite element method in COMSOL Multiphysics®.

The main provisions of the research to be defended:

1. For determination of BTEX (benzene, toluene, ethylbenzene, *m*-/*p*-xylene, and *o*-xylene) in atmospheric air by 15-min solid-phase microextraction in an aluminium foil-covered 250 mL sealed glass bulb using 85 μm Carboxen/polydimethylsiloxane fiber at 40 °C and an SRI 8610C gas chromatograph with photoionization detection, at least four analyses (three samples – not spiked with analytes and one sample – spiked with analytes) are required.
2. Matrix effect during vacuum-assisted headspace solid-phase microextraction of seven transformation products of unsymmetrical dimethylhydrazine (pyrazine, 1-methyl-1*H*-pyrazole, *N*-nitrosodimethylamine, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, 1*H*-pyrazole, and 3-methyl-1*H*-pyrazole) from 5-mL water samples and aqueous soil extracts in 20 mL vials with 1.75 g NaCl using an 85 μm Carboxen/polydimethylsiloxane fiber at 50 °C for 30 min under stirring is not substantial.
3. Preliminary extraction of the eight transformation products of unsymmetrical dimethylhydrazine (pyrazine, 1-methyl-1*H*-pyrazole, *N*-nitrosodimethylamine, *N*,*N*-dimethylformamide, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, 1*H*-pyrazole, and 3-methyl-1*H*-pyrazole) from soil with distilled water prior to vacuum-assisted headspace solid-phase microextraction provides lower matrix effect compared to 1 M NaOH and 1 M HCl.

The main research results:

1. An analytical method for on-site gas-chromatographic determination of BTEX in atmospheric air was developed, providing accurate quantification and low limits of detection for benzene, toluene, ethylbenzene, *m*-/*p*-xylene, and *o*-xylene of 0.07, 0.3, 2, 0.8, and 2 μg/m³, respectively. In Talgar, benzene concentrations determined using the developed method were in the range of 6.8-18.3 μg/m^3, toluene – 5.4-23 μg/m^3. The concentrations of benzene and toluene on February 18 and March 9 were substantially lower than many previously reported values for Almaty air and its suburbs.

2. Described in scientific literature, the method for the gas chromatographic determination of UDMH TPs in water based on Vac-HSSPME and gas chromatography-mass spectrometry (GC-MS) was adapted for a portable gas chromatograph with nitrogen-phosphorus detector. It has been established that calibration using the external standard approach, with standard solutions of the analytes in distilled water, can be used for accurate quantification of seven UDMH TPs (pyrazine, 1-methyl-1*H*-pyrazole, *N*-nitrosodimethylamine, 1-methyl-1*H*-1,2,4-triazole, *N*-methylformamide, 1*H*-pyrazole, and 3-methyl-1*H*-pyrazole) in water samples providing spike recoveries 73.3% - 90.0% from different types of water. Lowest LODs were observed for 1-MPA (0.2 μg/L) and pyrazine (0.5 μg/L), while the highest – for MFA (40 μg/L) and DMF (17 μg/L).

3. Analytical method for on-site gas-chromatographic determination of UDMH TPs in soil based on Vac-HSSPME-GC-NPD was developed. Vac-HSSPME of analytes from aqueous extracts demonstrated a lower variability in extraction effectiveness of analytes and matrix effect compared to extracts obtained using 1 M HCl and 1 M NaOH. The developed method has been successfully applied for study of the contamination of three fall places of first stages of Proton-M carrier rockets in the Ulytau region (Kazakhstan) with UDMH TPs. Prior to the quantitation, screening of UDMH TPs in soils was conducted using Vac-HSSPME of soils without preliminary aqueous extraction for detecting contaminated samples. Quantitation was conducted using matrix-matched external standard calibration and uncontaminated soil collected from the same fall place. LODs determined in the field were 3-60 μg/kg. Concentrations of the analytes were 6.9-150 μg/kg at 50 cm depth and 9.2-139 μg/kg (except for MTA and MFA) at 100 cm depth. The highest concentration (8500 μg/kg) was determined for MTA that is a well-known marker of soil contamination with UDMH. Intraday (2.9-14 %) and interday (3.9-25 %) variability of the GC-NPD based method demonstrate acceptable precision for on-site quantitation.

The scientific novelty of the research lies in the acquisition of new knowledge regarding the application of SPME for on-site determination of VOCs in air, water, and soil. Matrix-matched external standard and standard addition calibration approaches were for the first time employed to more accurate on-site determination of VOCs in environmental samples using SPME. This study is the first to demonstrate the use of Vac-HSSPME for on-site analysis of samples. For the first time in Kazakhstan, gas chromatographic analyses of VOCs in environmental samples were conducted at the sampling sites.

The theoretical and practical significance of the dissertation.

The work advances the understanding of quantitative on-site GC analysis with SPME as a sampling and sample preparation technique, and possible problems of such measurements, such as losses in sensitivity, lack and higher cost of time and other resources. It has been shown that proper method optimization, implementation of simple, fast and reliable calibration approaches and quality control measures are very important for successful on-site measurements using SPME. Vacuum-assisted headspace SPME (Vac-HSSPME) was successfully implemented under field conditions for faster extraction and lower LODs. It only required bringing a low-cost vacuum pump to the field.

Simple and accurate analytical methods for on-site determination of BTEX in atmospheric air and main UDMH TPs in water and soil samples based on SPME in combination with a portable SRI 8610C GC were developed and proposed. The developed methods have practical value for rapid, low-cost, and sufficiently accurate on-site determination of volatile organic compounds in environmental objects. The analytical method for BTEX quantification can be recommended for atmospheric air monitoring, especially at remote sites where prolonged transportation and storage of samples may cause analyte losses and decrease the accuracy of results. The methods based on Vac-HSSPME-GC-NPD can be recommended for quick and accurate on-site quantification of UDMH TPs in water and soil contaminated with rocket fuel and/or in water bodies near the fuel spills, particularly after major accidents. The screening step, involving direct analysis of soil samples without prior aqueous extraction, enables more rapid identification of polluted sites and supports the selection of samples for subsequent quantitative determination.

When evaluating the possible application of the developed method, it is important to consider that analyses in the field are more complex and expensive. Due to the current lack of portable autosamplers, only a limited number of samples can be analyzed in the field. While the developed method offers the advantage of rapid on-site analysis, it has lower performance than conventional laboratory-based approaches in certain aspects, such as detection limits and reproducibility, partly due to a lower sensitivity and stability of the portable GC. In the future, commercial portable GC-MS instruments can be implemented for improved selectivity, lower detection limits and faster separation.

The developed approaches reduce analysis time, eliminate transportation-related sample losses, decrease operational costs, and enable rapid decision-making during environmental monitoring and emergency response. The results are directly applicable to operational environmental control in remote regions and contribute to the modernization of on-site analytical methodologies.

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

Relevance of the dissertation to priority areas of the development of science and state programs.

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Publications (with a description of the personal contribution of the Ph.D. candidate):

1. Kurmanbayeva T., Bukenov B., Rymzhanova Zh., Kazhkenova N., Imangabassov A., Smail A., Karimkyzy N., Kenessov B.; Simple and accurate on-site quantitation of BTEX in atmospheric air using solid-phase microextraction and gas chromatography with photoionization detection; Advances in Sample Preparations (Q1 in the "Chemistry, Analytical" category, IF = 6.5), 2024, 10, 100117. https://doi.org/10.1016/j.sampre.2024.100117. (Input: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization)

2. Kurmanbayeva T., Rymzhanova Zh., Kenessov B.; On-site gas chromatogramphic quantification of transformation products of rocket fuel unsymmetrical dimethylhydrazine in water using vacuum-assisted headspace solid-phase microextraction; International Journal of Environmental Analytical Chemistry (Q3 in the "Chemistry, Analytical" and "Environmental Sciences" categories, IF = 2.5), 2025, 105, p.7673-7682. https://doi.org/10.1080/03067319.2025.2452951. (Input: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization)

3. Kurmanbayeva T., Bukenov B., Imangabassov A., Rymzhanova Zh., Yermakhan M., Karimkyzy N., Smail A., Kenessov B.; On-site gas chromatogramphic quantitation of transformation products of unsymmetrical dimethylhydrazine in soil using vacuum-assisted headspace solid-phase microextraction; Microchemical Journal (Q1 in the "Chemistry, Analytical" category, IF = 5.1), 2025, 215, 114492. https://doi.org/10.1016/j.microc.2025.114492. (Input: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization).