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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

8D05301 – Chemistry

Dissertation submitted in fulfilment of the requirements for the degree of Doctor of Philosophy (PhD)

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NORMATIVE REFERENCES

In this dissertation, references are made to the following standards:

GOST 7.32-2017. Interstate Standard. Research Report. Effective date: July 1, 2018. Adopted by the Interstate Council for Standardization, Metrology and Certification (Protocol No. 103-P of September 25, 2017).

GOST 7.1-2003. Bibliographic Record. Bibliographic Description. General requirements and rules for compilation. Effective date: July 1, 2004. Adopted by the Interstate Council for Standardization, Metrology and Certification (Protocol No. 12 of July 2, 2003).

US EPA Method TO-14A. Determination of volatile organic compounds in ambient air using canisters.

US EPA Method TO-15. Determination of volatile organic compounds in air collected in canisters.

US EPA Method TO-17. Determination of volatile organic compounds in ambient air using sorbent tubes.

ISO 16017-1/ISO 16017-2. Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography.

ISO 10381/ISO 18400 series. Soil quality – sampling.

ISO 5667 series. Water quality – sampling.

Order of the Minister of Science and Higher Education of the Republic of Kazakhstan dated July 20, 2022 No. 2 "On the approval of the State Compulsory Standards of Higher and Postgraduate Education." Registered with the Ministry of Justice of the Republic of Kazakhstan on July 27, 2022 No. 28916.

MUC 4.1.618-96. Guidelines for chromato-mass spectrometric determination of volatile organic substances in atmospheric air.

LIST OF ORIGINAL PUBLICATIONS

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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,* 10, 100117 (2024), https://doi.org/10.1016/j.sampre.2024.100117.

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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,* 105, p.7673-7682 (2025), https://doi.org/10.1080/03067319.2025.2452951.

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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,* 215, 114492 (2025), https://doi.org/10.1016/j.microc.2025.114492.

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LIST OF ABBREVIATIONS

The following abbreviations and symbols are used in this dissertation:

AD	Amperometric detector
ASE	Accelerated solvent extraction
AQS	Air Quality System
AWASP	Accelerated water sample preparation
BTEX	Benzene, toluene, ethylbenzene, and xylenes
Car/PDMS	Carboxen/polydimethylsiloxane
CEN	European Committee for Standardization
CNEMC	China National Environmental Monitoring Center
COD	Chemical oxygen demand
DELCD	Dry electrolytic conductivity detector
DMF	*N*,*N*-Dimethylformamide
EEA	European Environment Agency
EPA	Environmental Protection Agency
FDMH	1-Formyl-2,2-dimethylhydrazine
FEA	Finite element analysis
FID	Flame-ionization detector
FLD	Fluorescence detector
FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-FID	Gas chromatography with flame-ionization detection
GC-MS	Gas chromatography-mass spectrometry
GC-PID	Gas chromatography with photoionization detection
HPLC	High-performance liquid chromatography
HSSPME	Headspace solid-phase microextraction
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
LC	Liquid chromatography
LLE	Liquid–liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
LSER	Linear solvation energy relationship
MEE	Ministry of Ecology and Environment
MFA	*N*-Methylformamide
MEMS	Microelectromechanical systems
MPC	Maximum permissible concentration
MS	Mass spectrometry
MS/MS	Tandem mass spectrometry
MTA	1-Methyl-1*H*-1,2,4-triazole
MTA-d3	1-(trideuteromethyl)-1*H*-1,2,4-triazole
μ-columns	Microfabricated columns

μ-GC	Micro-gas chromatography
NDMA	*N*-Nitrosodimethylamine
NIST	National Institute of Standards and Technology
NPD	Nitrogen–phosphorus detector
PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PDMS/DVB	Polydimethylsiloxane/divinylbenzene
PID	Photoionization detector
PLE	Pressurized liquid extraction
PTFE	Polytetrafluoroethylene
PTR–MS	Proton-transfer-reaction mass spectrometry
RSD	Relative standard deviation
RT	Retention time
SIFT-MS	Selected-ion flow-tube mass spectrometry
SVOCs	Semi-volatile organic compounds
SPE	Solid-phase extraction
SPME	Solid-phase microextraction
TCD	Thermal conductivity detector
TD-GC	Thermal desorption gas chromatography
TMT	1,1,4,4-tetramethyl-2-tetrazene
U.S.	United States
UDMH	Unsymmetrical dimethylhydrazine
TPs	Transformation products
UV	Ultraviolet detector
Vac-HSSPME	Vacuum-assisted headspace solid-phase microextraction
VALLME	Vortex-assisted liquid–liquid microextraction
VOCs	Volatile organic compounds
1-MPA	1-Methyl-1*H*-pyrazole
3-MPA	3-Methyl-1*H*-pyrazole

INTRODUCTION

Characterization of the work.

This research aimes to develop and implement simple and accurate analytical methods for on-site gas chromatographic determination of benzene, toluene, ethylbenzene, *m*-/*p*-xylene and *o*-xylene (BTEX) in atmospheric air and transformation products (TPs) of unsymmetrical dimethylhydrazine (UDMH) in water and soil samples using solid-phase microextraction (SPME) coupled with portable gas chromatograph.

The work was carried out at the Department of Analytical, Colloidal Chemistry and Technology of Rare Elements and the Center of Physical Chemical Methods of Research and Analysis of Al-Farabi Kazakh National University.

The relevance of the research topic.

High-quality environmental monitoring and research on toxic organic compounds are essential for informed decision-making aimed at reducing health risks and suporting 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 (LC). 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 (SPE), 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 and followed by desorption. 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 BTEX in atmospheric air and eight main

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.

Objects of the research: 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.

Subject of the study: 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 the 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 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 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.

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 results of the study:

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 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. 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.

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

The research was conducted under the project funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan "Development of accurate methods for on-site gas chromatographic determination of volatile organic compounds in environmental objects using solid-phase microextraction" (Grant No. AP14871374, 2022-2024) under the priority area of the development of science "Rational use of water resources, flora and fauna, ecology".

Presentation of the practical results.

The main results of the research were presented at the following international conferences:

– 25th International Symposium on Advances in Extraction Technologies (ExTech, Tenerife, Spain, July 18-21, 2023),

– 3rd European Sample Preparation Conference 2nd Green and Sustainable Analytical Chemistry Conference (EuSPGSAC, Chania-Crete, Greece, September 15-18, 2024),

– International Chemical Congress of Pacific Basin Societies 2025 (Pacifichem, Honolulu, Hawaii, December 15-20, 2025).

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).

The structure of the dissertation.

The dissertation consists of an introduction, a literature review, the main parts, general conclusions, and a list of references. The material is presented in 104 pages of typed text, contains 18 figures and 27 tables, and a list of 131 references.

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1 LITERATURE REVIEW

1.1 Operational environmental monitoring of organic pollutants

Reliable environmental monitoring and accurate quantification of organic contaminants are essential for protecting ecosystems and human health. A broad range of organic pollutants – including pesticides, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), pharmaceuticals, and polychlorinated biphenyls (PCBs) – are associated with adverse effects on respiratory function, neurotoxicity and carcinogenicity [1–3]. Because monitoring data are inevitably affected by measurement uncertainty (e.g. sampling representativeness, losses of analytes during handling, matrix effects, and analytical variability), evidence-based decision-making requires timely measurements.

Many countries have implemented comprehensive environmental monitoring frameworks that integrate advanced technologies, including automated air-quality stations, satellite observations, biomonitoring tools, and high-resolution laboratory analytics. Although automated air-quality stations can provide reliable real-time measurements for a limited number of volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, and xylenes (BTEX), they are fundamentally unsuitable for the determination of most organic pollutants due to insufficient chemical selectivity, inadequate sensitivity, and the inability to sample semi-volatile and particle-bound compounds. Within the European Union, data reported to the European Environment Agency (EEA) [4] are generated by national monitoring authorities using reference methods from the European Committee for Standardization (CEN) and International Organization for Standardization (ISO). The methods are primarily based on air sampling on sorbent tubes (EN ISO 16017-1/2) or whole-air canisters (methodological principles of EPA Compendium Method TO-15) followed by gas chromatography-mass spectrometry (GC-MS) analysis for VOCs, and high-volume sampling followed by GC-MS analysis (EN 15549) for benzo[a]pyrene. The EEA oversees the systematic collection and evaluation of data on air, water, and soil contamination, including the quantification of VOCs, PAHs, and pesticide residues. In the United States, the Environmental Protection Agency (EPA) [5] defines and enforces standardized reference methods used nationwide within the Air Quality System (AQS) and coordinated water-monitoring programs under the National Water Quality Monitoring Council. Ambient air VOCs are routinely monitored using EPA Compendium Method TO-15 and EPA Method TO-17, while PAHs in ambient air are determined using EPA Method TO-13A. For aquatic environments, organic contaminants are quantified using standardized laboratory methods such as EPA Method 525.2 and EPA Method 8270D, as well as EPA Method 1694 and EPA Method 537. China's national environmental monitoring system is coordinated by the China National Environmental Monitoring Centre (CNEMC) under the Ministry of Ecology and Environment (MEE) and operates strictly in accordance with mandatory national standards (HJ series). China has rapidly expanded its network, which currently comprises >2100 air-quality stations, 2767 surface-water monitoring points, 300 automated water-monitoring

stations, and >40000 soil-monitoring locations [6]. Semi-volatile organic compounds (SVOCs) and hydrophobic compounds, including pesticides and PAHs, are routinely determined by solid-phase extraction (SPE) followed by GC-MS according to EPA Methods 525.2 and 8270D. Polar and thermally labile compounds, such as pharmaceuticals and emerging contaminants, are analyzed using SPE-LC-MS/MS (EPA Methods 1694 and 537).

In the Republic of Kazakhstan, environmental monitoring program (according to monthly information bulletins), coordinated by the Republican State Enterprise «Kazhydromet» under the Ministry of Ecology and Natural Resources [7] involves the continuous measurement of the following priority pollutants: suspended particles (dust), PM2.5, PM10, sulfur dioxide, carbon monoxide, nitrogen dioxide, nitric oxide, phenol, formaldehyde, ozone, cadmium, copper, arsenic, lead, chromium (VI), nickel, zinc, benzo[a]pyrene, benzene, ethylbenzene, chlorobenzene, *p*-xylene, *m*-xylene, cumene, *o*-xylene, and hydrogen sulfide. Bicarbonates, sulfates, chlorides, calcium and sodium ions were determined in samples of atmospheric precipitation and snow cover. Monitoring of surface water quality includes: suspended solids, dissolved oxygen, major ions of salt composition, chemical oxygen demand (COD), phosphorus, petroleum products, phenols, pesticides, and heavy metals. Sediment and soil quality monitoring includes heavy metals as chromium, lead, cadmium, arsenic, manganese, zinc, and copper.

As shown in Table 1, the analytical methods applied by Kazhydromet are methodologically equivalent in sampling strategy and chromatographic separation to the reference approaches used by the US EPA and CEN/ISO within the European Union. The primary distinction between Kazhydromet methods and EPA or CEN/ISO reference methods lies in the level of detection and confirmation rather than in the analytical workflow itself. While EPA and CEN/ISO methods formally rely on mass-spectrometric detection as the standard for compound identification, Kazhydromet predominantly applies robust, non-spectrometric detectors (GC-FID, GC-PID, spectrophotometric and infrared techniques) for routine nationwide monitoring, reserving GC-MS for confirmatory and investigative analyses conducted in centralized laboratories. In addition, whole-air canister sampling, standardized in the United States under EPA Method TO-15, is not implemented within the Kazhydromet monitoring network.

In addition to the routine monitoring methods employed by Kazhydromet, numerous simple and accurate analytical methods for the determination of organic pollutants in the environment based on GC-MS have been developed in Kazakhstan within research laboratories and project-oriented investigations [8–11]. Although these methods provide high analytical performance and detailed compound identification, they are typically implemented only in well-equipped stationary laboratories and are applied periodically rather than continuously.

Table 1 – Correlation of analytical methods used by Kazhydromet with EPA and CEN/ISO reference methods

Procedure	EPA and CEN/ISO reference methods			Kazhydromet (routine practice)		
	Ambient air	Ambient air	Ambient air	Ambient air	Surface water	Soil and sediments
Sampling	Sorbent tubes, whole-air canisters, high-volume samplers	Grab sampling	Grab/ limited composite	Sorbent tubes, high-volume samplers	Grab sampling	Grab/core sampling
Preparation	-	LLE/SPE	Soxhlet extraction/ PLE/ASE/ Ultrasonic extraction	Solvent extraction	LLE/SPE	Solvent extraction
Detection	TD-GC-MS, GC-MS or HPLC	GC-MS	GC-MS	GC-FID/ GC-PID/ GC-MS for confirmatory analysis	IR spectrometry, UV-Vis, GC-FID/ECD (GC-MS for confirmatory analysis)	GC-FID/ECD (GC-MS in targeted or investigative studies)
Note: GC – gas chromatography; GC-FID – gas chromatography with flame ionization spectrometry; GC-PID – gas chromatography with photoionization detection; TD-GC – thermal desorption gas chromatography; GC-MS – gas chromatography – mass spectrometry; HPLC – high-performance liquid chromatography; LLE – liquid-liquid extraction; SPE – solid-phase extraction; PLE – pressurized liquid extraction; ASE – Accelerated solvent extraction;						

Emergency scenarios involving high levels of contamination, such as a space rocket crash releasing hundreds of tons of toxic fuel [12], require immediate action to protect the environment and human health. Having delayed or limited results for these pollutants makes this complicated. Civil protection frameworks rely on rapid situational awareness to inform decisions regarding evacuation, access control, the deployment of remediation resources, and protection of first responders. Data collection during standard environmental monitoring is highly energy- and time-intensive, as it usually involves sample collection, transportation, and laboratory analysis. Typically, it can take days to receive initial analytical results because well-equipped laboratories are often located far from the sampling site. This delay in obtaining data can lead to less efficient decisions, hampering efforts to mitigate environmental and human health risks effectively. Ideally, continuous on-site monitoring would be used to assess pollution levels (e.g. using proton-transfer-reaction mass spectrometry, PTR-MS or selected-ion flow-tube mass spectrometry, SIFT-MS), however, such techniques are expensive and suitable only for a limited number of substances and sample types. However, even with these advanced

systems, instrumental accuracy may be compromised, while overall quantitative accuracy remains strongly dependent on sample representativeness and the minimization of pre-analytical errors. Alternatively, portable instruments, such as GC or GC-MS, are more cost-effective solutions. Recent advances in analytical instrumentation have increased the potential of portable technologies for on-site environmental emergency assessment. Nonetheless, the availability of rapid field-ready analytical methods for organic pollutants remains limited. Existing approaches include portable Fourier-transform infrared (FTIR) spectroscopy [13], Raman spectroscopy [14], and portable gas chromatography [15–20] for both environmental and forensic applications. Capillary gas chromatography provides high resolving power for complex mixtures, while gas chromatography-mass spectrometry enables unambiguous analyte identification using EPA, NIST, Wiley, and other spectral libraries [21]. Portable GC and GC-MS instruments are commercially available and can determine a wide range of VOCs and SVOCs. Although portable gas chromatographs generally have lower analytical performance than laboratory instruments due to design limitations, they are invaluable in emergency contamination scenarios where rapid results are required.

For reactive and highly volatile compounds, representativeness errors dominate over instrumental precision. Total quantitative reliability – accuracy of the reported concentration – depends on: 1) analytical performance of the method/instrument, 2) representativeness of the sample, and 3) preservation of analyte integrity from sampling to measurement. Eurachem explicitly treats sampling and sample handling as part of the measurement process, each adding uncertainty [22]. Analytical performance includes the limit of detection (LOD) or limit of quantification (LOQ), precision (characterized by relative standard deviation, RSD), bias, selectivity, calibration model, matrix effects and robustness. For portable GC/GC-MS, this terms can be “lower” than for laboratory GC-MS due to constraints on column efficiency, detector stability and thermal control. However, even if analytical performance of portable instruments is slightly worse, it might not be the dominant contributor to total error for VOCs – because the next two terms can dominate.

On-site analysis improves the accuracy of VOCs by preserving representativeness over time and space, which is often lost through laboratory sampling. While off-site analysis ensures superior analytical performance for individual samples, on-site measurements significantly increase spatial data density, leading to a higher overall information value for environmental assessment (Figure 1).

On-site analytical methods are not intended to replace laboratory-based analysis, but rather to complement it. They enable a rapid in situ assessment during emergency scenarios, where immediate information is critical for effective risk management and decision-making. Recent advances in analytical instrumentation have increased the potential of portable technologies for on-site environmental emergency assessment. Nevertheless, rapid, field-ready analytical methods for determining organic pollutants remain limited.

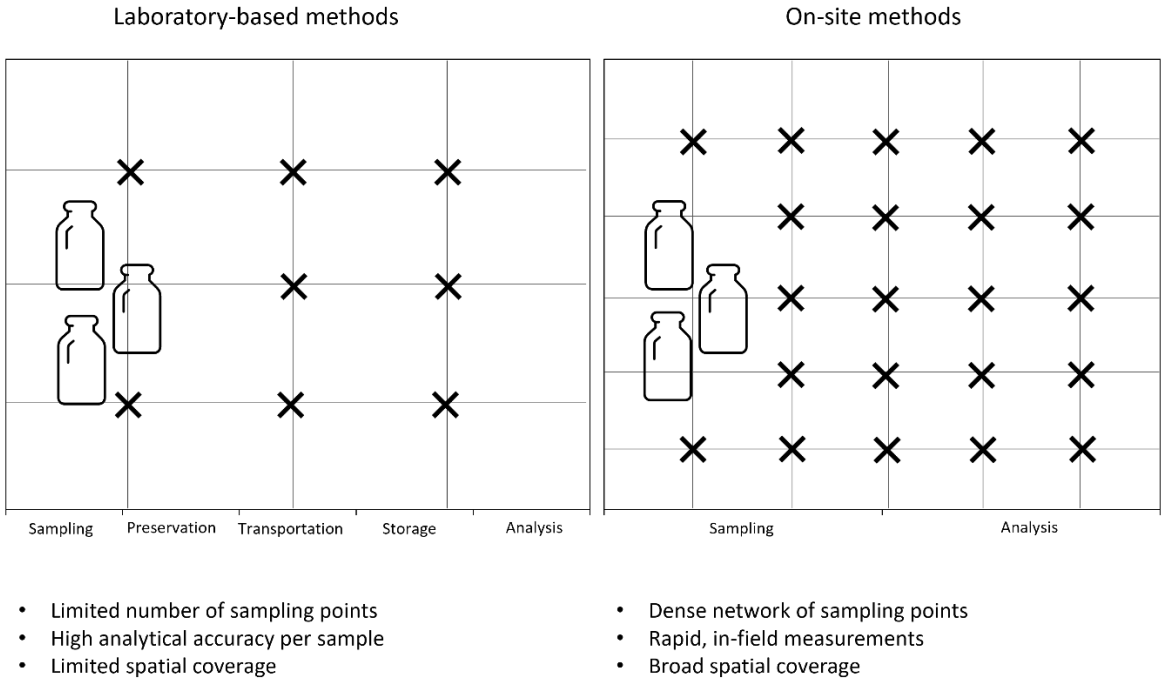


Figure 1 – Conceptual comparison of on-site and laboratory-based measurements (Note – Compiled based on source [23])

1.2 Portable gas chromatographic systems for on-site monitoring

Field-deployable analytical methods do not require the same level of validation as full-scale laboratory procedures. However, analytical performance of available portable gas chromatographs remain critically important for developing accurate on-site methods. In addition, such systems must satisfy the following requirements [23,24]:

– low weight and compact dimensions;
– sufficient sensitivity for detecting and quantifying pollutants;
– generation of data comparable to laboratory-grade results;
– simple hardware infrastructure;
– integrated battery or compatibility with a portable power source;
– high analysis speed;
– low energy consumption;
– ease of operation;
– adaptability to environmental conditions.

Based on instrument weight, the authors of [25] proposed classifying portable GC systems into three categories: 1) microchip chromatographs (0.2-3 kg), 2) field-portable/transportable systems (5-15 kg), and 3) compact systems (10-25 kg).

A conventional gas chromatograph consists of a thermostated (1) injection device, (2) chromatographic column, and (3) detector [26]. Accordingly, portable GC incorporate minituarized injectors, mini/μ-columns, and mini/μ-detectors.

Micro-gas chromatography (μ-GC) is the most advanced form of chromatographic miniaturization, achieved using microelectromechanical systems (MEMS) and microfabrication technologies [27,28]. Due to their compact

dimensions (typically <5 kg), low power consumption, and rapid analysis times, μ-GC systems are often described as 'truly portable' chromatographs, suitable for autonomous field measurements [29,30]. These instruments integrate miniaturized injectors, microfabricated columns (μ-columns), and compact detectors, such as miniaturized photoionization detectors (PID), thermal conductivity detectors (TCD), or micro-mass spectrometers. The primary advantage of μ-GC is its ability to perform fast separations – often in just 1-10 minutes – while operating under severe constraints in size, energy demand, and infrastructure. Microfabricated injectors and preconcentrators differ fundamentally from traditional split/splitless inlet systems. In conventional and most portable GC, injectors are heated chambers of several milliliters in volume and require external pumps for sample introduction. In μ-GC, injectors often integrate both preconcentration and sample introduction, frequently relying on passive diffusion sampling without pumps or using microfabricated pumping systems [27]. Preconcentration factors can reach up to 2500 for granular commercial adsorbents [31] and up to 14800 when thin-film or foam-structured adsorbents are used [32], enabling ppb-level detection even without external pumps [27]. For example, the μCOIN (microcollector-injector) system for VOC sampling operates through passive diffusion governed by Fick's laws, eliminating energy consumption during sampling and requiring only short thermal pulses (≤ 300 ms) for desorption [33]. Using a heating rate of 4 °C/ms to 250 °C in 60 ms, followed by a 60-ms hold, the μCOIN injector yielded a sharp chromatographic peak for *m*-xylene with a full width at half maximum (FWHM) of 190 ms, achieved even without a separation column – demonstrating minimal dead volume and reduced band broadening. Another design, the Microfabricated Integrated Sampler-Injector (MISI) [34], supports temperature programming from 30 °C to 250 °C in 230 ms, with a power consumption of only 1 W. MISI consists of a two-layer structure: (1) an upper layer with microchannels for diffusion-based vapor collection, and (2) a lower layer containing Carbopack X adsorbent, integrated Ti/Pt heater, and a resistive temperature sensor. Leak-tightness and thermal insulation are ensured by an epoxy seal. Performance tests demonstrated that MISI released 590 ng of toluene during thermal desorption. A second desorption under stopped-flow conditions produced a peak corresponding to 33 ng, indicating 95% desorption efficiency. For an introduced concentration of 640 ppb toluene over 30 minutes, the theoretical captured mass was 754 ng (at 10.5 mL/min), corresponding to an error < 18%.

Nevertheless, extreme miniaturization imposes fundamental limitations on chromatographic performance. Compared with conventional fused-silica capillary columns that are typically tens of meters long and can routinely deliver very high separation efficiency, μ-columns are confined to much shorter channel lengths, which directly limits the attainable number of theoretical plates. Conventional capillary GC columns, such as those with 20-50 m lengths and narrow inner diameters, can deliver on the order of 5×10^4-2×10^5 theoretical plates under optimal conditions, and specialized high-efficiency columns have been documented to exceed several hundred thousand plates in total for detailed analyses [35]. In contrast, silicon-based μ-columns with etched microchannels in the 10-100 cm range

typically yield on the order of 10^3-10^4 theoretical plates because of their limited length and microfabrication constraints. Modern MEMS-based designs with optimized channel geometries and microstructures can improve separation performance to roughly 2×10^4-3×10^4 plates under favorable operating conditions, although this remains below the efficiency routinely achievable in bench-top capillary GC [28,36]. Reduced separation efficiency in μ-columns arises from shortened channel length, increased axial diffusion, enhanced hydrodynamic resistance, and challenges in achieving uniform stationary-phase coatings within complex microgeometries [28].

Detector miniaturization further constrains μ-GC performance. While compact PID and TCD detectors are readily integrated, full miniaturization of flame ionization detectors or high-performance mass spectrometers remains technically challenging due to safety, vacuum, and power requirements. As a result, μ-GC systems typically exhibit higher detection limits and reduced quantitative robustness compared to laboratory-scale GC and GC-MS instruments, particularly when analyzing complex or multicomponent environmental samples.

Consequently, while current μ-GC systems are primarily optimised for the rapid screening and targeted detection of a limited number of volatile compounds, ongoing advances in micro-column design, stationary phases, and miniature detectors are establishing μ-GC as a promising and increasingly powerful platform for future quantitative analysis. As these developments continue, μ-GC systems are expected to overcome current limitations in terms of separation efficiency and detector performance. This will allow for the more reliable identification of complex mixtures of VOCs and SVOCs in on-site and field-deployable applications.

Nowadays, when accurate on-site quantification is required, compact portable GC or GC-MS systems provide a more balanced compromise between portability and analytical performance, retaining sufficient column length, detector flexibility, and quantitative robustness.

In this study, the portable SRI 8610C gas chromatograph (SRI Instruments, USA) was selected as a balanced platform for quantitative on-site environmental analysis, offering substantially higher separation efficiency than micro-GC systems while avoiding the complexity, logistical constraints, and higher cost of portable GC-MS. The instrument supports conventional stationary gas chromatography using a 30-m capillary column in combination with selective detectors (PID and NPD), enabling reliable determination of aromatic VOCs and nitrogen-containing compounds, including transformation products (TPs) of unsymmetrical dimethylhydrazine (UDMH). The 8610C GC is a more cost-effective solution for routine field deployment than portable GC-MS, while also maintaining fit-for-purpose quantitative performance.

1.3 SPME opportunities for on-site quantitative analysis

On-site analysis require a rapid and straightforward sample preparation method. Several approaches can be employed for the extraction and analysis of organic pollutants, including solvent extraction, static and dynamic headspace,

solid-phase extraction (SPE), coiled microextraction (CME), and solid-phase microextraction (SPME). Among these approaches, SPME stands out as one of the most suitable techniques for field analysis with combination of GC and GC-MS due to its simplicity, needlessness of organic solvent use, and its combination of sampling and sample preparation in a single step [20,37–40]. This method does not require organic solvents and is considered a 'green' sample preparation technique [41]. Despite the advantages of SPME, there are only few SPME-based analytical methods, the use of which for on-site analysis was reported in the literature – BTEX in water [42], tetrachloroethylene in soil vapour air and water [16], volatile organic compounds in air [43–46], organic pollutants in water [47], polychlorinated biphenyls in soil [19], chemical warfare agents and stimulants in water [48]. This can be caused by the complexity of developing methods that have sufficient accuracy and detection limits.

SPME is non-exhaustive extraction and governed by partition equilibrium between the polymeric coating and the surrounding phases. At equilibrium, the extracted mass is determined using distribution constants between phases. For air, the polymeric coating extracts the mass of an analyte from the two-phase (coating and gas phase) system. For water or soil, it becomes a three-phase system where the analyte must first partition from the matrix into the gas headspace and only then into the coating, making extraction strongly matrix-dependent.

The mass extracted in coating (SPME fiber) is related to the overall equilibrium of the analyte in systems [49]:

1) air:

$$n_0 = C_0 V_a = C_f^{\infty} V_f + C_a^{\infty} V_a \quad (1)$$

where n_0 is initial mass of an analyte in air sample, C_0 is the initial concentration of the analyte in air, C_f^{∞} and C_a^{∞} are the equilibrium concentrations of the analyte in fiber coating and air sample, respectively; V_a and V_f are the volumes of the air sample (vessel) and the coating. Considering that the distribution constant between fiber and air is expressed as $K_{fa} = C_f^{\infty}/C_a^{\infty}$, the mass of the analyte adsorbed by the coating can be calculated as follows:

$$n = C_f^{\infty} V_f = C_0 \frac{K_{fa} V_f V_a}{K_{fa} V_f + V_a} \quad (2)$$

2) water (or soil):

$$n_0 = C_0 V_s = C_f^{\infty} V_f + C_h^{\infty} V_h + C_s^{\infty} V_s \quad (3)$$

where C_h^{∞} and C_s^{∞} are the equilibrium concentrations of the analyte in headspace and sample, respectively; V_s and V_h are the volumes of the sample and the headspace. Assuming that the distribution constant between water and the gas headspace is given by Henry's law constant $K_{hs} = C_h^{\infty}/C_s^{\infty}$, and distribution constant between

fiber and air is expressed as $K_{fh} = C_f^{\infty}/C_h^{\infty}$, the mass of analyte adsorbed by the coating can be determined as follows:

$$n = C_f^{\infty} V_f = C_0 \frac{K_{fh} K_{hs} V_f V_s}{K_{fh} K_{hs} V_f + K_{hs} V_h + V_s} \quad (4)$$

An SPME device consists of a thin fiber (up to 100 µm) coated with an extraction polymer or composite phase and deposited on an inert support within a syringe-type holder. When the exposed fiber comes into contact with a sample containing organic molecules, the analytes are absorbed or adsorbed, depending on the chemical nature of the coating. When the fiber is inserted into a GC injector that is heated to a high temperature, the analytes are thermally desorbed from the coating (Figure 2) [49,50].

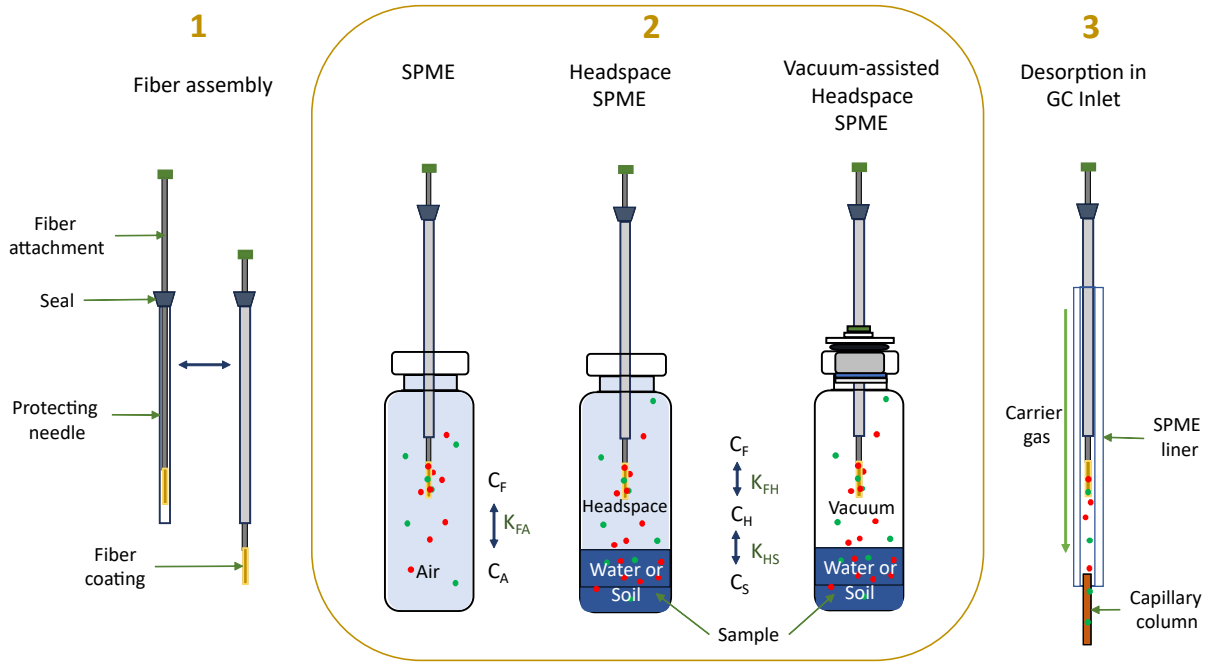


Figure 2 – Solid-phase microextraction of VOCs and SVOCs from air, water and soil samples

For field experiments, the authors of [47] developed a method for determining VOCs and SVOCs in wastewater after a fire using SPME coupled with a portable Torion® T-9 GC-MS. Comparing two SPME modes with a polydimethylsiloxane/divinylbenzene (PDMS/DVB) coating – headspace solid-phase microextraction (HSSPME) and direct immersion SPME – showed that HSSPME provides higher responses for volatile organic compounds. However, heavier compounds were only detected when the fiber was directly immersed in the water sample. Combining these two SPME approaches enables comprehensive analysis of contaminants under emergency conditions. Prior to direct immersion of the fiber into liquid samples, it is necessary to filter out fine particles that could damage the fiber or block adsorption sites, thereby reducing extraction efficiency.

In contrast, this step is not required for HSSPME and a single fiber can withstand over 200 extraction/desorption cycles.

HSSPME coupled with a portable Guardion 8 gas chromatography – mass spectrometry system (Torion Technologies, American Fork, UT, USA) was optimised for the determination of persistent organic pollutants in soil, specifically PCBs [19]. To enhance the extraction efficiency of the target compounds, 2.5 mL of potassium permanganate in an acidic medium were added to 0.5 g of soil. Extraction was performed using a 100 μm polydimethylsiloxane (PDMS) fiber in a 10 mL glass vial at 100 °C for 30 minutes. The chromatographic run time was 6.5 minutes. Quantification was carried out using external standard calibration with Aroclor 1260, which is the most commonly used standard for developing PCB determination methods. However, the signals obtained (chromatographic peak areas) were less reproducible on the portable GC-MS, with relative standard deviations of around 20%. However, the linearity of the calibration curves obtained using the Guardion 8 GC-MS was expressed as a correlation coefficient of 0.96, indicating a positive linear relationship between signal intensity and retention time. On a stationary GC-MS, the correlation coefficients were greater than 0.98. The reduced linearity ($R = 0.96$) can be mainly due to poor ion statistics at low analyte concentrations. In portable GC-MS systems such as the Guardion 8 GC-MS, a smaller vacuum capacity and reduced ion transmission efficiency may result in lower signal intensity and higher baseline noise. Consequently, the signal-to-noise ratio decreases at low concentration levels, thereby increasing relative measurement error. Analysis of real soil samples showed that the detection limits of the portable GC-MS were significantly higher than those of stationary instruments. This is generally associated with limitations in hardware and/or software for data acquisition. Additionally, the authors noted that accurate quantitative determination was complicated by variations in soil moisture content.

Most existing analytical methods based on portable GC-MS systems are limited to qualitative detection and semi-quantitative determination. Accurate and reliable quantitative methods for organic pollutants are often unavailable due to the complexity of their development. While portable GC-MS systems are invaluable in critical situations due to their capabilities and performance, their high cost often restricts access for many routine laboratories.

Most SPME-based analytical methods reported in the literature are designed for stationary GC or GC-MS systems and cannot be directly applied under field conditions without additional optimization, as portable instruments generally provide lower separation efficiency and higher detection limits. On-site methods should be faster and simpler because the field time is more expensive [50].

2 DEVELOPMENT OF THE ANALYTICAL METHOD FOR ON-SITE DETERMINATION OF BENZENE, TOLUENE, ETHYLBENZENE AND XYLENES IN ATMOSPHERIC AIR USING SOLID-PHASE MICROEXTRACTION

Preamble

The materials in this article have been partially published as research article: Tolkyn Kurmanbayeva, Bauyrzhan Bukenov, Zhansaya Rymzhanova, Nargiz Kazhkenova, Aibolat Imangabassov, Aruzhan Smail, Nurbi Karimkyzy, Bulat Kenessov; 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,* 2024, 10, 100117. Materials for all sections of this current Chapter are reprinted from this research article with the permission from the Advances in Sample Preparations. The copyright for this work remains with Elsevier and any further requests for reuse of this information should be made directly to them.

2.1 Importance of the development of the analytical method for on-site quantification of BTEX in atmospheric air using SPME

Benzene (B), toluene (T), ethylbenzene (E), and *o*-,*m*-,*p*-xylenes (X) are mono-aromatic volatile organic compounds and known anthropogenic toxicants contributing to air pollution and human health [51]. BTEX originate from various industrial processes, vehicular emissions, solid fuel combustion, and the use of organic solvents [52,53]. Exposure to BTEX can lead to severe respiratory problems, skin irritations, and long-term diseases such as cancer [54–56]. Benzene is classified by IARC as 'carcinogenic to humans', and exposure to benzene coincides with a development of acute and chronic lymphocytic leukemias, myelomas and non-Hodgkin lymphoma [57]. Along with health risks, BTEX affect the environment by contributing to formation of ozone and secondary organic aerosols due to photochemical reactions [58]. Thus, it is crucial to evaluate the levels of BTEX in the environment and raise awareness about the significant health hazards posed by exposure to BTEX. For quantification of BTEX, air samples are typically collected to containers or sorbents and transported to a laboratory for analysis using gas chromatography (GC) with mass spectrometric (MS), photoionization (PID), flame-ionization (FID) or another type of detection. However, on-site quantitation of BTEX is often required for faster data collection and decision-making. Long transportation of air samples can result in major losses of analytes: this problem was experienced by our research group when studying air in Kalachi village, where people suffered from a 'sleep illness' [59]. Moving the instrument to the field allows making the analytical method greener [60]. Such measurements can be conducted using a direct injection of air to a portable GC-PID equipped with a 6-port valve, mass flow controller and vacuum pump [61]. Reported limits of detection (LODs) for this method are 0.7-2.6 ppb, but it was only tested on indoor air samples (Table 2). Calibration was conducted by mixing standard gas containing known

concentration of BTEX with nitrogen at known mass flow rates and supplying the known mass flow rate of the prepared gas to a GC using a vacuum pump. LODs 2-4 ppb can be achieved using US Environmental Protection Agency (EPA) TO-14A method [62] based on a portable GC-PID with a built-in dual adsorbent trap [63]. Air samples are collected to deactivated canisters and introduced to a GC at a known mass flow rate. Calibrated air pumps are required for supplying air to/from a canister. For calibration, nitrogen with known BTEX concentration is prepared in the canister. Solid-phase microextraction (SPME) developed by Prof. Pawliszyn from the University of Waterloo (Canada) represents a simple and cost-efficient alternative for on-site quantitation of VOCs in air samples [49]. SPME is based on extraction of analytes directly from sample to a small sorbent coating with subsequent thermal desorption in a GC inlet. Koziel et al. [64] quantified BTEX in air using portable GC with in-series PID, FID and dry electrolytic conductivity (DELCD) after 1-min extraction with 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) SPME fiber exposed to open air (grab sampling). External standard calibration was obtained using air with different BTEX concentrations generated using National Institute of Standards and Technology (NIST) traceable certified permeation tubes. Koziel et al. [64] estimated LODs at 10 ppt, but such values can be achieved only on model samples and below capabilities of the standard gas generation system [18]. Jia et al. [18] achieved LODs 1.3-1.9 ppb using the method of Koziel et al. [64] (Table 2). The method proposed by Baimatova et al. [65] based on air sampling into 20-mL vials with subsequent SPME-GC-MS allowed to collect a large amount of data on BTEX concentrations in atmospheric air in Almaty, the largest and one of the most polluted city of Kazakhstan, which were used to assess influence of COVID-19 lockdown on the improvement of air quality [66]. A simpler calibration based on BTEX standard addition to vials filled with air was implemented. Despite great results obtained using these methods, concentrations of analytes in samples can change during sample storage and transportation before the analysis, e.g., due to oxidation, adsorption, photolysis, and leaks [9]. In 2018-2019, Serik et al. [67] collected air samples in Taldykorgan, Almaty oblast, Kazakhstan and analyzed them using SPME-GC-MS in the laboratory located in Almaty, >250 km from the sampling location. In 2016, Orazbayeva et al. [68] collected air samples in Astana, Kazakhstan and analyzed them days later using SPME-GC-MS in the laboratory located in Almaty, >1200 km from the sampling location.

The purpose of our study was to simplify the method of Koziel et al. [64] for the on-site quantification of BTEX in air using the SRI 8610C GC-PID and apply it in the town of Talgar, Almaty oblast, Kazakhstan. Air was collected to 250 mL gas sampling bulbs, and on-site standard addition calibration was for the first time used for quantification in the field. The simplified method did not require a standard gas generator and traceable certified permeation tubes, which were used by Koziel et al. [64] for instrument calibration. The inlet of SRI 8610C GC was slightly modified to work with 78.5 mm × 6.35 mm glass liners (from Agilent 7890 GC) and allow faster and more efficient desorption of analytes from the fiber and their transfer to the column.

Table 2 – Sampling and calibration characteristics, and on-site method analytical performance of BTEX quantification

Technique	Sampling procedure	Calibration approach	Total time of analysis of 1 sample	LODs ($\mu g/m^3$)	Reported concentrations ($\mu g/m^3$)	Reference
8610C GC-PID-FID-DELCD (SRI, USA)	1-min SPME from open air with 65 µm PDMS/DVB	Standard gas generator with traceable certified permeation tubes	<15 min (per replicate, w/o calibration)	PID: 0.04 at NTP (10 ppt) FID: 3.8 at NTP (1 ppb)	T: 94-140 at NTP (24.1-35.8 ppb)	[64]
8610C GC-PID-FID-DELCD (SRI, USA)	1-min SPME from open air with 65 µm PDMS/DVB	Standard gas generator with traceable certified permeation tubes	<15 min (per replicate, w/o calibration)	B: 6.2 at NTP (1.9 ppb) T: 5.0 at NTP (1.3 ppb) E: 7.1 at NTP (1.6 ppb) X: 7.5 at NTP (1.7 ppb)	B: Min = 3.6 at NTP (1.1 ppb) Max = 1861 at NTP (573 ppb) T: Min = 14.6 at NTP (3.8 ppb) Max = 2042 at NTP (533 ppb) E: Min = 10.2 at NTP (2.3 ppb) Max = 503 at NTP (114 ppb) *m*-/*p*-X: Min = 11.5 at NTP (2.6 ppb) Max = 821 at NTP (186 ppb)	[18]
GC-PID with two temperature-controlled sorbent traps and vacuum pump (for EPA TO-14A method)	Air pumping to sorbent trap(s) located in the GC	Pumping air with known BTEX concentrations to the trap(s)	About 30 min (GC separation time of one replicate)	B: 6.5 at NTP (2 ppb) *m*-/*p*-X: 17.7 at NTP (4 ppb) *o*-X: 13.2 at NTP (3 ppb)	-	[62,63]

Continued from Table 2

Technique	Sampling procedure	Calibration approach	Total time of analysis of 1 sample	LODs ($\mu g/m^3$)	Reported concentrations ($\mu g/m^3$)	Reference
Portable miniaturized GC-PID	Air pumping to 6-port valve with 200 µL loop for	Dilution of certified BTEX gas mixture with nitrogen by mass flow controllers, pumping of the prepared gas to the 6-port valve	10 min (per replicate)	B: 2.3-3.1 at NTP (0.72-0.96 ppb) T: 3.8-4.4 at NTP (0.98-1.16 ppb) E: 6.3-9.3 at NTP (1.42-2.10 ppb) *m*-/*p*-X: 3.4-6.2 at NTP (0.76-1.40 ppb) *o*-X: 7.8-11.6 at NTP (1.76-2.63 ppb)	T: 3.8-68.9 at NTP (1-18 ppb) E, X: 0.4-2.2 at NTP (0.1-0.5 ppb) From [61]	[69]
Compact GC/µGC-PID with temperature-controlled sorbent trap containing Carbopack B, Carbopack X and Carboxen 1000 and miniature diaphragm pump	Air pumping to a sorbent trap for 10 min	Dilution of VOCs mixture with zero air in 3 L Tedlar bags and sampling by compact GC directly through the exit port of the Tedlar bags	15 min (per replicate)	B: 0.06 at NTP (0.02 ppb) T: 0.11 at NTP (0.03 ppb) *m*-X: 0.31 at NTP (0.07 ppb)	-	[70]
8610C GC-PID	Pumping air to 250 mL bulb, bulb heating to 40 °C in thermostat, depressurization, 15-min SPME with 85 µm Car/PDMS	Standard addition (analysis of one extra air sample with added known BTEX mass)	45 min (per replicate) Total 240 min for 3 sample replicates + 1 sample with added BTEX	B: 0.07 (0.02 ppb at NTP) T: 0.3 (0.08 ppb at NTP) E: 2 (0.45 ppb at NTP) *m*-/*p*-X: 0.8 (0.18 ppb at NTP) *o*-X: 2 (0.45 ppb at NTP)	B: 6.8-18.3 T: 5.4-30 E: 4.4-5.5 *m*-/*p*-X: 2.1-12.6 *o*-X: 6.8-10.6	This study
Note: NTP – Normal Temperature and Pressure; B – Benzene; T – Toluene; E – Ethylbenzene; *m*-/*p*-X – *m*-/*p*-Xylene; *o*-X – *o*-Xylene; X – Xylenes						

2.2 Materials and methods

2.2.1 Reagents and materials

Benzene (≥99.6%), REACHEM (Moscow, Russia);
Toluene (≥99.8%), REACHEM (Moscow, Russia);
Ethylbenzene (≥99.0%), Sigma-Aldrich (St. Louis, MO, USA);
o-Xylene (≥99.3%), REACHEM (Moscow, Russia);
m-Xylene (≥99.0%), Sigma-Aldrich (St. Louis, MO, USA);
Helium, >99.995%, Orenburg-Tehgas (Russia);
Nitrogen, >99.999%, Orenburg-Tehgas (Russia);
Calibrated gas sampling bulbs for 250 mL, Sigma-Aldrich (St. Louis, MO, USA);
Pump, DC12V 3M Micro (China);
SPME fiber 85 μm Carboxen/polydimethylsiloxane (Car/PDMS), Supelco (Bellefonte, PA, USA);
8610C gas chromatograph with photoionization detector (GC-PID), SRI Instruments (USA);
Capillary column Rtx-VRX (30 m x 0.25 mm x 1.4 μm), Restek (Bellefonte, PA, USA);
Crimp-top headspace vials for 20 mL, HTA (Italy);
Cylindrical septum with a half-hole, Thermogreen® LB-1, Supelco (USA);
SPME glass liner, Supelco (USA);
Gas sensor, G3388B, Agilent Technologies, Santa Clara (USA);

2.2.2 Sampling

Air sampling was conducted in aluminum foil-covered 250-mL calibrated gas sampling bulbs connected in parallel to the pump for 15 min at ambient temperature in a private house yard in Talgar (sampling location provided in ANNEX A), Almaty oblast, Kazakhstan in February and March 2024. For BTEX concentrations comparison, air in Almaty was sampled in front of the Center for Physical Chemical Methods of Research and Analysis on March 1 and 11 (Table 3). Sampling on March 11 at 2:30 p.m. was performed near three parked cars with running engines: 1998 Honda Accord, 2021 Lada Granta, and 2023 Kia Cerato.

2.2.3 Extraction

Before the first extraction, 85 μm Car/PDMS fiber was pre-conditioned in the modified inlet of the 8610C GC-PID at 250 °C for >5 min. The SPME fiber (85 μm Car/PDMS) was chosen because it provides high selectivity to BTEX and their low detection limits [9,49]. Prior to each extraction, the retracted fiber was cooled for 5 min in a nitrogen-filled 20-mL vial at ambient temperature. A bulb with sampled air was placed in a lab-made air thermostat heated to 40 °C for 10 min.

Table 3 – Air sampling parameters and conditions in Talgar, Almaty oblast and the city of Almaty

Sampling date	Number of samples	Sampling time	Sampling height (cm)	Ambient temperature (°C)	Ambient pressure (kPa)	Analysis location
Talgar						
February 17	3	10:30 p.m.	50	–20±2	92.8	on-site
February 18	4	12:00 p.m.	50	–12±2	91.8	on-site
February 18	4	3:30 p.m.	50	–12±2	91.8	laboratory
March 8	4	2:00 p.m.	150	12±2	90.7	on-site
March 9	4	09:00 a.m.	150	13±2	90.5	on-site
Almaty						
March 1	4	10:00 a.m.	150	0±2	91.8	laboratory (near sampling site)
March 11	4	09:30 a.m.	150	4±2	90.5	
March 11	4	2:30 p.m.	150	4±2	90.5	

During February analyses, for maintaining stable pressure of SPME, excess pressure was released by quickly opening and closing one bulb valve before extraction, and in March analyses overpressure relief was performed 5 min before extraction. Increase in the temperature after moving a bulb with cold air to a heated thermostat results in the increase of the total pressure in the bulb and partial pressures of analytes, which can lead to the increase of extraction effectiveness [49]. Without pressure relief, minor leaks in one or several bulbs can result in pressure differences during extraction from different bulbs and problems with reproducibility.

Extraction was conducted by introducing an SPME device into a bulb located in the thermostat through a cylindrical septum with a half-hole and exposing the coating in the center of the bulb. Extraction of BTEX from air sampled in February was performed during 5 min, and from samples collected in March – for 15 min. Since the thermostat lid had to be opened when releasing the excess pressure and introducing the SPME device into a bulb, the temperature in the bulb dropped to 30-35 °C, and after closing the lid it increased to 40 °C within 1-2 minutes. During February sampling, the thermostat was placed inside the house at 20±2 °C; during March sampling, the thermostat was in the house yard at ambient air temperature. Desorption was conducted in the GC inlet at 250 °C for 1 min followed by opening the split valve for 1 min. The SPME device was left in the GC inlet at 250 °C for 36±2 min.

2.2.4 Chromatographic analysis

To allow more efficient desorption of analytes at low flow rates and their transfer to the column, a GC inlet was modified to work with glass liner from an Agilent 7890A GC with a length of 78.5 mm, an outer diameter of 6.35 mm and an inner diameter of 0.75 mm (Supelco, USA) (Figure 3). The 1/4" mm x 1/16" x 1/16" in-house made stainless steel tee was used for connecting the liner with column and

a split valve. Liner was connected to the tee using a 1/4" Swagelok nut and 1/4" graphite ferrule (CRS, USA). The column was connected to the tee using a 1/16" Swagelok nut and 1/16" graphite ferrule with a 0.4 mm hole (Agilent, USA). The in-house made stainless-steel inlet cap included four outlets: 1) for an 8 mm diameter septum and nut from Agilent 7890A GC split/splitless inlet; 2) for liner with Swagelok nut and 1/4 graphite ferrule (CRS, USA); 3) for 1/16" carrier gas supply line; 4) for 1/16" septum purge restrictor. An aluminium block with an internal diameter of 6.4±0.1 mm was produced for the liner. The heater and temperature sensor from an SRI 8610C GC split/splitless inlet were then inserted into the block.

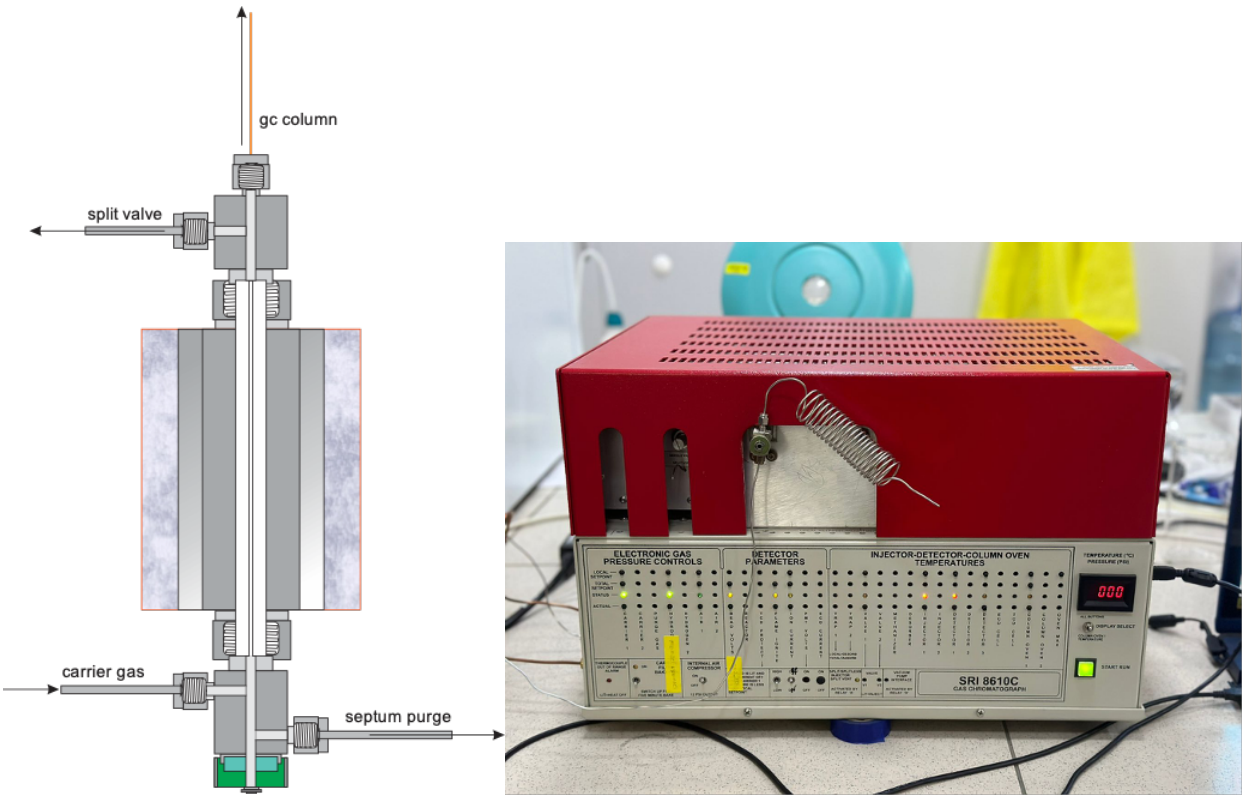


Figure 3 – The SRI 8610C GC with modified inlet using glass liner from an Agilent 7890A GC

Before analyzing the air samples, the GC was checked for leaks with a gas sensor, and 5.00 µL of nitrogen sample with concentrations of benzene and toluene 0.501±0.013 ng/µL, ethylbenzene and xylenes 0.250±0.013 ng/µL was analyzed.

Separation was performed on a 30 m x 0.25 mm Rtx-VRX column with a film thickness of 1.4 µm at a constant helium flow rate of 1.5 mL/min and GC oven temperature program: 40 °C (held for 10 min), heating at a rate of 5 °C/min to 60 °C (5 min), heating at a rate of 10 °C/min to 80 °C (5 min), heating at a rate of 40 °C/min to 240 °C (10 min). The total run time was 40 min. A constant helium flow rate was provided by pressure programming: 15.62 psi (held for 10 min), increasing at 0.324 psi/min to 16.93 psi (5 min), increasing at 0.648 psi/min to 18.23 psi (5 min), increasing at 2.591 psi/min to 28.57 psi (10 min).

Detection was performed at a voltage of 10.6 eV, temperature 150 °C, and current 0.70 mA. Chromatograms were recorded at a medium level of detector gain in the PeakSimple data acquisition and processing system (version 4.98, SRI Instruments, USA). The detector lamp window was cleaned on February 28 to remove a stationary phase from column bleeds and restore detector sensitivity.

For on-site measurements, 8610C GC-PID, 5L helium cylinder and laptop were installed into a trank of a crossover car (Figure 4). Voltage (220 V) to the GC and other electric units was supplied from a private house.



Figure 4 – The crossover car with installed SRI 8610C GC-PID, 5L helium cylinder and laptop during on-site measurements in March 2024

2.2.5 Calibration and quantitation

2.2.5.1 Laboratory calibration

Calibration standards of nitrogen with benzene and toluene concentrations of 0; 10; 25; 50; 100 μg/m^3, ethylbenzene and xylenes concentrations of 0; 5; 12.5; 25; 50 μg/m^3 were prepared in calibrated 250-mL gas sampling bulbs from the initial BTEX gas standard with concentrations of benzene and toluene 0.501±0.013 ng/μL, ethylbenzene and xylenes 0.250±0.013 ng/μL. The initial gas standard was prepared by injecting 2.00 μL (with a 5.00 μL gas-tight microsyringe) of the mixture (density of 0.859 g/mL) of benzene (≥99.6%), toluene (≥99.8%), ethylbenzene (≥99.0%), *m*-xylene (≥99.0%), *o*-xylene (≥99.3%) at a volumetric ratio of 2:2:1:1:1, respectively, into an aluminum foil-covered gas sampling bulb for 1 L that was kept for 30 min at room temperature before the use. Before preparation of calibration standards, bulbs were washed with distilled water, pre-conditioned at 150 °C for 120 min and covered with aluminium foil (to minimize photochemical processes). To prepare calibration standards with the above concentrations, 0; 5.0; 12.5 μL (with a 10.0 μL gas-tight

microsyringe); 25.0 and 50.0 µL (with a 100.0 µL gas-tight microsyringe) of the initial BTEX gas standard were injected into the bulbs filled with nitrogen. Extraction and chromatographic analysis of calibration standards were performed at room temperature (23±2 °C) 1-2 days before the on-site analyses according to the procedure described in Sections 2.2.3-2.2.4. During the on-site air sampling and analyses (February 17), chromatograms of a nitrogen sample with concentrations of benzene and toluene 80.8 µg/m^3, ethylbenzene and xylenes 40.4 µg/m^3 after depressurizing were obtained for checking the sensitivity and reproducibility. Dependencies of an analyte peak area on its concentration in the calibration standard after depressurization were used as calibration plots. The BTEX concentration in a bulb after depressurization (C, µg/m^3) at extraction temperature (313 K) was calculated using:

$$C = \frac{C_0 \cdot T_0}{313\ K} \quad (5)$$

where C_0 is an analyte concentration (µg/m^3) at ambient temperature T_0 (K).

The outliers of obtained results (peak areas) were discarded based on Grubbs test.

2.2.5.2 Standard addition calibration

To the fourth air sample in the bulb, 50.0 µL of BTEX gas standard in nitrogen with concentrations of benzene and toluene 0.501±0.013 ng/µL, ethylbenzene and xylenes 0.250±0.013 ng/µL were added using a 100.0 µL gas-tight microsyringe. Extraction and GC analysis of calibration standards were carried out according to the procedure described in Sections 2.2.3-2.2.4. Calibration plots included two points corresponding to the peak areas of the analyte in the air sample: 1) without (mean of the triplicate measurements), and 2) with the addition of the standard.

2.2.6 Comparison of on-site and laboratory analyses

The bulbs with four air samples collected on February 18 were placed in a polypropylene container and transported with the instrument to the laboratory. The samples were analyzed on February 19 after 18±1 hours after collection according to the method described in Sections 2.2.3-2.2.4.

2.2.7 Identification of BTEX peaks on chromatograms

Peak identification was performed using retention times (RTs) determined for nitrogen samples (250 mL in gas bulb) with concentrations of benzene and toluene 50.0±1.3 µg/m^3, ethylbenzene and xylenes 25.0±1.3 µg/m^3 after SPME with 85 µm Car/PDMS fiber. The retention times were 8.69±0.15 for benzene, 16.41±0.05 for toluene, 23.58±0.12 for ethylbenzene, 24.58±0.15 for *m*-/*p*-xylene, and 26.38±0.10 min for *o*-xylene.

2.2.8 Determination of limits of detection and limits of quantification

Limits of detection (LODs) corresponding to a 3:1 signal-to-noise ratio and limits of quantitation (LOQs) corresponding to a 10:1 signal-to-noise ratio were calculated using:

$$LOD = \frac{C \cdot N}{S} \cdot 3 \quad (6)$$

$$LOQ = \frac{C \cdot N}{S} \cdot 10 \quad (7)$$

where C is the concentration of the analyte in the analyzed sample (μg/m^3), S and N are the signal (mV) and noise (mV) of the analyte peak on the chromatogram, respectively. Noise for benzene and toluene was determined at the baseline near the corresponding peak, while for ethylbenzene and xylenes – in the regions of their retention times in chromatograms where these analytes were not detected. The LODs and LOQs of ethylbenzene and xylenes on February 17-18 were determined using a chromatogram of a nitrogen sample with concentration of benzene and toluene of 100 μg/m^3, ethylbenzene and xylenes of 50 μg/m^3, while, for benzene and toluene, the LODs and LOQs were calculated from concentrations found in air samples. The LODs and LOQs of all analytes in March were determined from the concentrations found in real air samples.

2.2.9 Modelling in COMSOL Multiphysics®

Optimization of SPME parameters is a critical step in developing an analytical method, directly influencing extraction efficiency, sensitivity, reproducibility, and total analysis time. This process involves adjusting the extraction time temperature, pH, salt content, the ratio of sample to headspace volume, agitation rate, system pressure (particulary for vacuum-assisted HSSPME), desorption time and temperature. Comprehensive experimental evaluation of all these factors through classical one-factor at a time or fractional design is complex and resourse-demanding. In this content, numerical modelling has emerged as a powerful alternative to purely empirical optimization. COMSOL Multiphysics has been established as an effective tool for simulating the SPME of organic compounds from air, water and soil. Using finite element analysis (FEA), the software solves coupled mass- and energy balanced equations that describes diffusion and interfacial partitioning processes. This enabled the prediction and visualisation of time-dependent analyte concentration fields and extraction profiles under different conditions [71–74].

Simulated ethylbenzene and xylenes extraction profiles were obtained using the model developed by Kenessov et al. [73] and two-dimensional axisymmetric geometry in COMSOL Multiphysics 5.6 (Burlington, MA, USA). A cylinder with a diameter of 5 cm and a volume of 250 mL was used as the extraction vessel. Car/PDMS porous extraction coating (on a 130 μm diameter core) with a thickness

of 80 μm, density of 760 kg/m^3 and a porosity of 0.3658 was placed in the center of the vessel (Figure 5).

SPME was characterized using 'Transport of Diluted Species' and 'Transport of Diluted Species in Porous Media' physics in a 'time-dependent' mode. Main parameters of the geometry, coating and compound were described in Table 4. All other parameters of the model was kept as in the work [73].

In air inside the bulb mass transport of analytes was described using the Fick's second law of diffusion:

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{8}$$

where: C – the concentration of analyte (mol/m^3); D – the diffusion coefficient (m^2/s); t is the time. Diffusion coefficients were calculated using the method of Fuller et al. [75].

In Carboxen Knudsen diffusion occurs because the pore diameter is smaller than the mean free path of the molecules, meaning that mass transfer is controlled by collisions between molecules and the walls of the pores [73]. This makes internal transport of analytes the rate-limiting step of SPME, and mass transport of the analytes was modelled using:

$$(\varepsilon + \rho K_{fh})\frac{\partial c}{\partial t} = D\nabla^2 C \tag{9}$$

where: ε – a porosity of the porous material (fiber coating); ρ – a density of the coating (kg/m^3); K_{fh} is a distribution constant of the analyte between coating and headspace (air); and D is the diffusion coefficient of an analyte in the gas inside the coating (e.g., air) and has a dimention m^2/s.

K_{fh} at 23 °C was calculated by the LSER approach according to Car/PDMS equation [76]:

$$logK_{fh} = 3.92(0.13) + 0.35(0.09)S - 0.36(0.14)A + 0.43(0.05)L \tag{10}$$

where S (solute dispolarity/polarizability), A (solute hydrogen-bond acidity), and L (gas-liquid partition coefficient in n-hexadecane at 298 K) are the solute descriptors, that represents non-specific electrostatic interactions, H-bond donor strength, and dispersion/cavity interactions, respectively. Values of S, A and L were obtained from the UFZ-LSER database v3.2.1 [77].

For gas-phase mass transfer modelling in SPME, the binary diffusion coefficient in air (D_{AB}) is a key parameter determining equilibration kinetics and flux through the boundary layer. Fuller, Schettler and Giddings equiation is the most suitable for quick and accurate (5-10% error) estimation of D_{AB}:

$$D_{AB} = \frac{0.001T^{1.75}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)^{\frac{1}{2}}}{p\left[(\sum V_A)^{1/3}+(\sum V_B)^{1/3}\right]^2} \quad (11)$$

where T *(K)* and p *(atm)* are the temperature and pressure of the system, M_A and M_B – molar masses of diffusing substances (e.g. analyte and air (M_{air}=28.97 g/mol)), g/mol; V_A and V_B are specific molecular diffusion volumes, V_{air}=20.1.

The difusion volume of a molecule is determined by:

$$\sum V = \sum n_i V_i \quad (12)$$

where n_i – number of atoms or structural groups, V_i – tabulated diffusion volume increment.

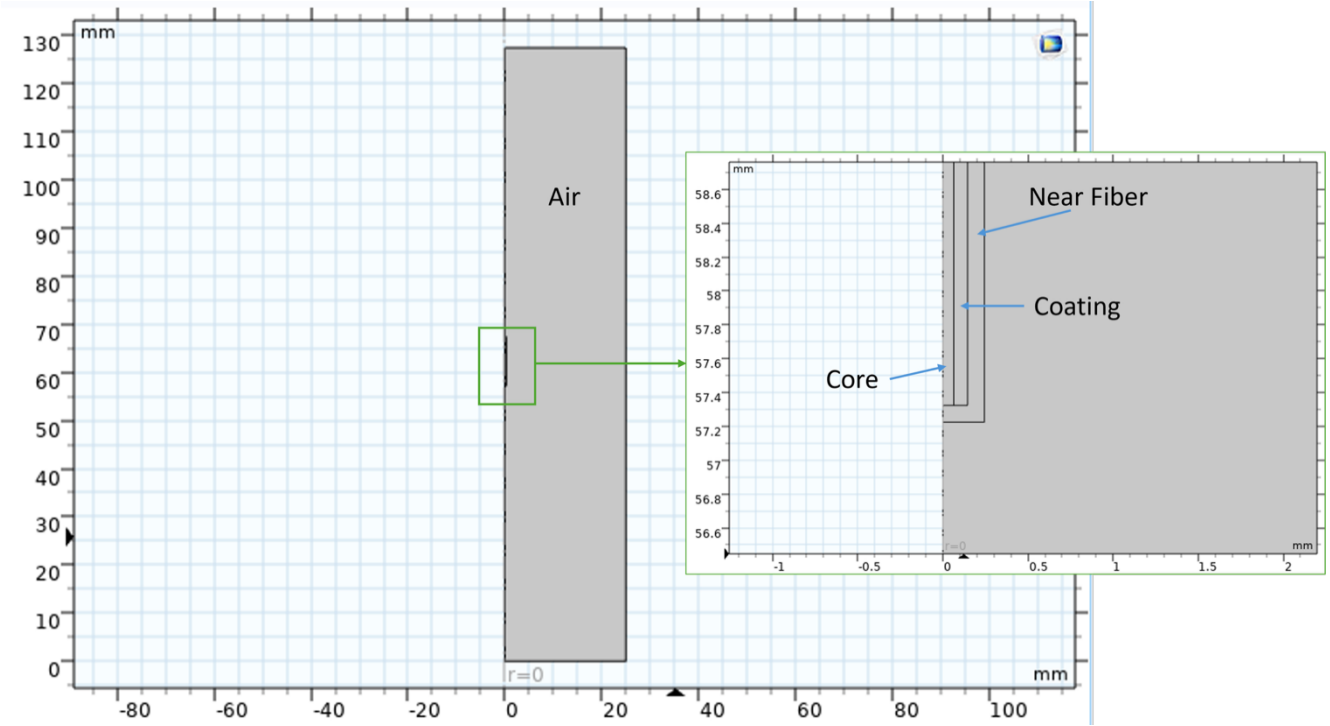


Figure 5 – Two-dimensional axisymmetric geometry in COMSOL Multiphysics 5.6 for modelling air sampling with a retracted SPME fiber

Table 4 – Main parameters of the geometry, coating and compound

Parameter Name	Expression	Value	Description
NFV	((CoreD+CoatTh*2+0.2[mm])^2) /4*pi*(CoatL+0.2[mm])	1.92E-9 m^3	Volume of the Near Fiber (gas-phase area where initial concentration was set to zero)
T	(TC+298.15)[K]	313.15 K	Temperature
TC	40	40	
p	0.9[atm]	91193 Pa	Pressure
CoatTh	0.08[mm]	8E-5 m	Coating thickness
CoreD	0.13[mm]	1.3E-4 m	Core diameter
CoatL	10[mm]		Coating length
VialD	50[mm]	0.05 m	Vial diameter
VialV	250[cm^3]	2.5E-4 m^3	Vial volume
VialH	VialV*4/pi/VialD^2	0.12732 m	Vial height
FiberDepth	70[mm]	0.07 m	Fiber insertion depth
CoatDen	760[kg/m^3]	760 kg/m^3	Coating density
CoatPor	0.3658	0.3658	Coating porosity
CoatTort	CoatPor+1.5*(1-CoatPor)	1.3171	Coating tortuosity factor
M_G	28.97[g/mol]	0.02897 kg/mol	Molar mass of air
Vd_G	20.1	20.1	Fuller diffusion volume of air
M	106.17[g/mol]	0.10617 kg/mol	Molar mass of ethylbenzene and *m*-/*p*-xylenes
V	132		Fuller diffusion volume of ethylbenzene and xylenes
ModTime	60[min]	3600 s	Modelling time

For ethylbenzene and xylenes, calculated K_{fh} was >500000 (Table 5). For model generalization, the fiber/headspace distribution constant for ethylbenzene and xylenes were neglected and a common value of K_{fh} = 500000 was applied. Since there are no formulas for calculating the distribution constant at 40 °C, modelling was also carried out at a constant of 200000, because these constants are known to decrease with increasing temperature [49]. The pressure was set to 0.9 atm. The 'extremely fine free triangular' mesh was used for the modelling. To provide better meshing at the coating-air interface, the resolution of narrow regions was increased to '10'. The modelling was conducted at extraction times up to 60 min. For better accuracy, the maximum step in the time-dependent solver settings was limited to 0.02*t.

Table 5 – The main physico-chemical properties of BTEX [78] and solute descriptors and distribution constants of BTEX between the coating and air at 23 °C calculated using LSER method

Compound	CAS number	Formula	Molecular weight (Da)	Density (g/cm^3)	Half-life, h	Boiling point (°C)	*S*	*A*	*L*	K_{hs}	Diffusion volume (V_A)
Benzene	71-43-2	C_6H_6	78.11	0.877	~220-260	80.1	0.52	0	2.79	199517	90.7
Toluene	108-88-3	C_7H_8	92.14	0.867	~40-50	110.6	0.52	0	3.33	340212	111.1
Ethylbenzene	100-41-4	C_8H_{10}	106.17	0.867	~30-40	136.2	0.51	0	3.78	528494	131.6
m-Xylene	108-38-3	C_8H_{10}	106.17	0.864	~11-15	139.1	0.52	0	3.84	565939	131.6
p-Xylene	106-42-3	C_8H_{10}	106.17	0.861	~12-16	138.4	0.52	0	3.84	565939	131.6
o-Xylene	95-47-6	C_8H_{10}	107.17	0.880	~8-12	144.4	0.56	0	3.94	645312	131.6

2.3 Results and discussion

2.3.1 Description and comparison of chromatograms

Peaks of benzene (RT = 8.57±0.03 min) and toluene (RT = 16.37±0.14 min) were detected on all obtained chromatograms of samples analysed on February 17-18 (Figure 6). The peaks of ethylbenzene and xylenes were not detected, apparently due to the large number of non-separated peaks and noise (1-4 mV) around their retention times. One of the samples was classified as an outlier because a significant deviation of the detector signal around the toluene affecting its area was observed (Figure 6). This may be attributed to inadequate conditioning of the extraction coating before analysis.

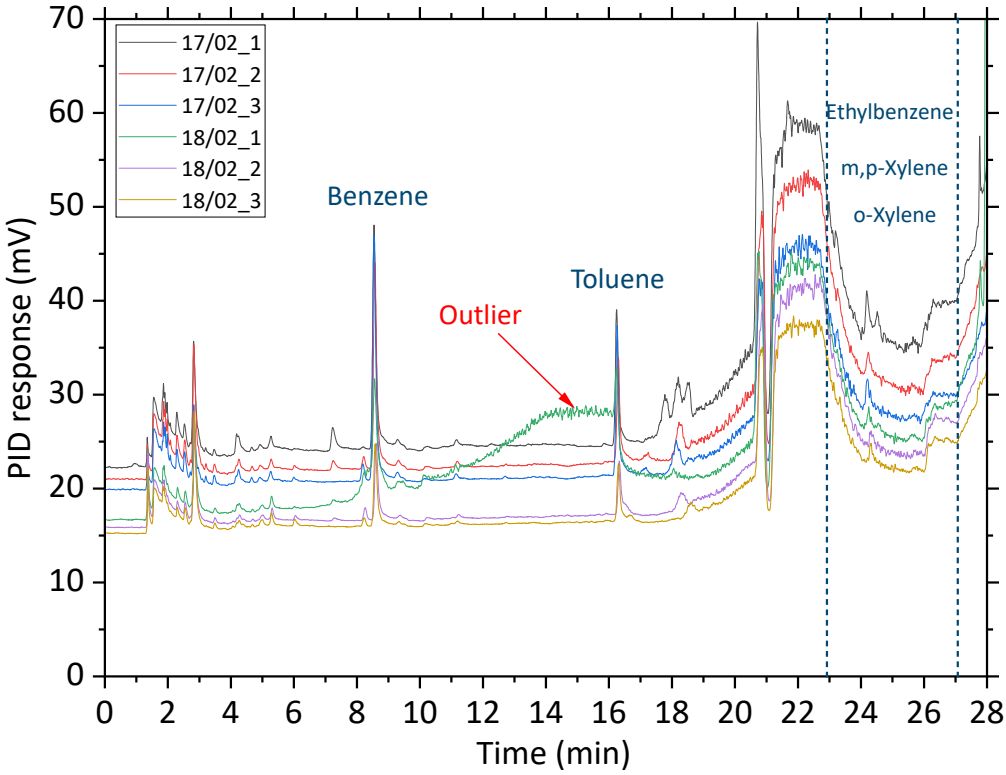


Figure 6 – Chromatograms of six ambient air samples obtained using a portable SRI 8610C GC-PID after 5-min SPME with 85 µm Car/PDMS fiber on February 17 and 18 in Talgar

According to the analysis of nitrogen with concentrations of benzene and toluene 100 µg/m^3, ethylbenzene and xylenes 50 µg/m^3, LODs and LOQs of benzene, toluene, ethylbenzene, and xylenes were 0.9-2.9, 2.2-7, 15-25 and 8-15 µg/m^3, respectively. (Table 6).

Table 6 – Slopes of calibration plots obtained using laboratory calibration in February 2024, and LODs and LOQs of BTEX

Analyte	Linear range (µg/m^3)*	R^2	Mean slope*	RSD of slope (%)	LOD** (µg/m^3)	LOQ** (µg/m^3)
Benzene	0-94	0.995	13.2	5.0	0.9	2.9
Toluene	0-94	0.998	7.8	8.4	2.2	7
Ethylbenzene	0-47	0,999	3.0	4.1	15	25
m-/*p*-Xylene	0-47	0.992	2.2	6.6	9	15
o-Xylene	0-24	0.977	3.1	5.1	8	14
Note: *Concentrations after depressurization; **LODs and LOQs of benzene and toluene were calculated using real air samples collected in February, while LODs and LOQs of ethylbenzene, *m*-/*p*-xylene, and *o*-xylene were determined from nitrogen sample with concentrations of benzene and toluene 100 µg/m^3, ethylbenzene and xylenes 50 µg/m^3.						

The results show that 5-min extraction is insufficient for detecting ethylbenzene and xylenes in real air during on-site analyses. COMSOL Multiphysics® simulations demonstrated that increasing extraction time from 5 to 15 min should lead to a more than 1.9-2.2-fold increase in extracted mass of the analytes. After 15-min extraction, their concentration in the fiber should equal to 59-78% of its equilibrium concentration (Figure 7).

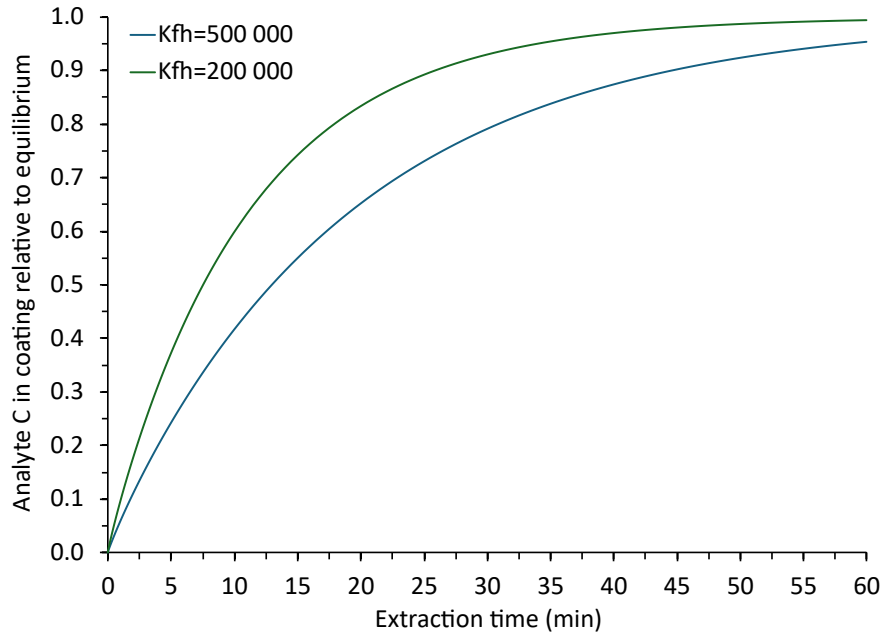
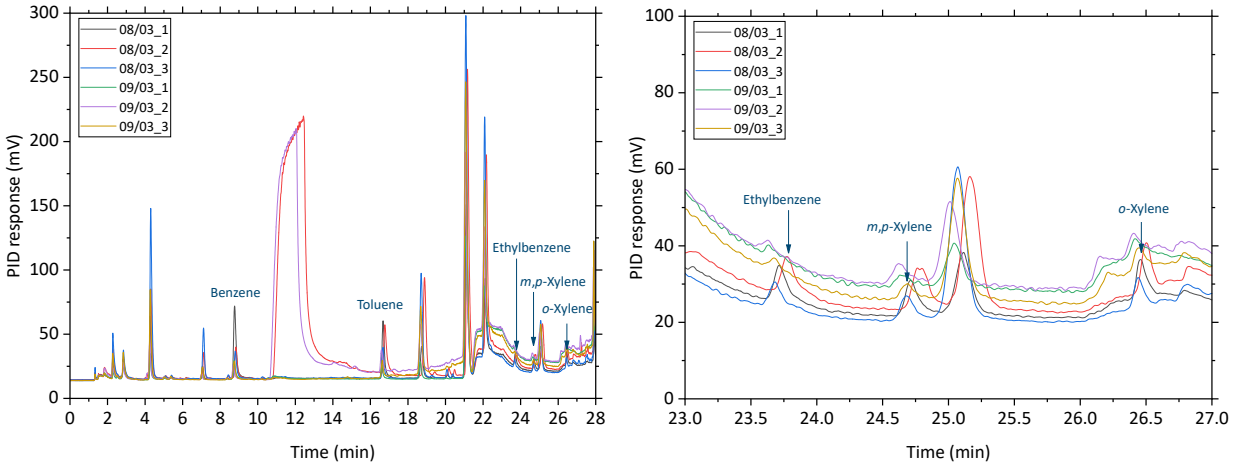


Figure 7 – Dependence of ethylbenzene and xylenes equilibrium concentrations in the SPME coating on extraction time

After 15-min extraction of March samples (Figure 8), peaks of ethylbenzene (RT 23.68±0.05 min), *m*-/*p*-xylene (RT 24.69±0.06 min) and *o*-xylene (RT 26.44±0.03 min) were detected; their LODs were 2 µg/m^3, 0.8 µg/m^3 and 2 µg/m^3, respectively (Table 7). Thus, extraction time 15 min was proven to be the shortest optimal time to detect all analytes.



(a) (b)

Figure 8 – (a) Chromatograms of six ambient air samples obtained using a portable SRI 8610C GC-PID after 15-min SPME with 85 µm Car/PDMS fiber on March 8 and 9 in Talgar, and (b) same chromatogram in the range of retention times of ethylbenzene and xylenes

Table 7 – Limits of detection (LODs) and quantification (LOQs) of BTEX estimated using concentrations determined in March 2024 in air samples of Talgar

Parameter	Benzene	Toluene	Ethylbenzene	*m*-/*p*-Xylene	*o*-Xylene
LOD (µg/m^3)	0.07	0.3	2	0.8	2
LOQ (µg/m^3)	0.2	1.1	8	3	8

2.3.2 Comparison of slopes

Before the first on-site analysis in Talgar, calibration plots for linear range (concentrations after depressurization determined using Eq. (5)) of benzene and toluene 4.7-94 µg/m^3, ethylbenzene, *m*-/*p*-xylene – 2.4-47 µg/m^3, *o*-xylene – 2.4-24 µg/m^3 were obtained in the laboratory on February 15 and 16. The determination coefficients were 0.977-0.999. Slopes presented in Table 6 were used to calculate benzene and toluene concentrations in air analysed on February 17. Slopes obtained on-site by standard addition method on February 18 (Table 8) for benzene and toluene were 23-24% lower than those obtained in the laboratory on February 15-16. For ethylbenzene and *m*-/*p*-xylene, on-site slopes were 50% and 14% higher, respectively, while slopes for *o*-xylene were 29% lower. Such a difference could be due to the use of nitrogen instead of air for preparing calibration standards, i.e. the matrix effect. The standard addition method allows to control a matrix effect [79]

and improve the accuracy because calibration is performed at the same conditions as analysis of real samples, hence it was chosen for subsequent analyses. The higher slopes in March (Table 8) were caused by the increased sensitivity of the detector after cleaning the lamp window, as well as by threefold increase in the extraction time.

Table 8 – Slopes of calibration plots obtained using standard addition calibration at on-site analyses in February and March 2024 in Talgar

Date	Slope				
	Benzene	Toluene	Ethylbenzene	*m*-/*p*-Xylene	*o*-Xylene
February 18	10.1	5.9	4.5	2.5	2.2
March 1	21.4	18.5	14.7	13.3	14.1
March 8	19.5	19.3	14.9	15.2	13.8
March 9	18.4	19.2	15.1	11.8	11.6
March 11	16.3	13.3	10.6	9.9	9.4
March 11	15.8	14.0	11.1	10.7	10.8

2.3.3 Comparison of concentrations

In Talgar, benzene concentrations were in the range of 6.8-18.3 μg/m^3, toluene – 5.4-23 μg/m^3 (Table 9). The lowest concentrations were found in the morning of the second weekend, when population activity and emissions were minimal. Benzene and toluene concentrations on February 17 and March 8 in Talgar were at the same level as lowest concentrations determined in Almaty between March 31 to April 4, 2015 [65]. The concentrations of benzene and toluene on February 18 and March 9 were substantially lower than concentrations ever previously reported for Almaty air and its suburbs. In the afternoon of February 18, despite the low air temperature (-12 °C) and the need to heat houses, the level of air pollution was minimal. This could be due to the gasification of Talgar carried out in the last five years. The higher concentrations on 17 February night could be caused by lower air temperatures (-20 °C), as well as greater activity of residents and heating systems. Elevated concentrations of benzene and toluene on 8 March afternoon could be caused by cooking holiday meals over an open fire during sampling. Xylenes were only detected in the March samples, while ethylbenzene was only detected on March 8. Ethylbenzene and *m*-/*p*-xylene concentrations were 5.5 and 2.1-3.6 μg/m^3, respectively, slightly above their detection limits. Concentrations of *o*-xylene were in the range of 6.8-10.6 μg/m^3. Concentrations of *m*-/*p*-xylene and *o*-xylene in Almaty were higher than in Talgar (8.5-12.6 μg/m^3 and 8.5-9.6 μg/m^3 for *m*-/*p*-xylene and *o*-xylene, respectively) in all samples (Table 9).

Benzene concentrations in Almaty on March 1 and 11 were generally comparable to those in Talgar, while toluene concentrations in Almaty were significantly higher. The toluene-to-benzene (T/B) concentration ratios in Talgar were 0.73-1.9, while in Almaty – from 2.0 to 3.0. In all samples except two (on February 17 and March 9 in Talgar), T/B were greater than 1.0, which indicates that

the main source of emissions of analytes during these sampling periods was traffic. The lower T/B in Talgar could be due to the essentially lower intensity of vehicular traffic compared to Almaty. In addition, sampling in Talgar was conducted on weekends and public holidays, while in Almaty – on weekdays.

Table 9 – Measured BTEX concentrations in ambient air of Talgar and Almaty in February and March 2024

Date	Concentration (μg/m^3)				
	Benzene	Toluene	Ethylbenzene	*m*-/*p*-Xylene	*o*-Xylene
Air samples from Talgar					
February 17	18.3	15.7	nd	nd	nd
February 18	6.8	8.5	nd	nd	nd
March 8	12.3	23	5.5	3.6	6.8
March 9	7.4	5.4	nd	2.1	10.6
Air sampes from Almaty					
March 1	9.3	19.6	4.4	8.5	9.6
March 11, 09:30	14.7	30	4.9	12.6	8.5
March 11, 14:30	8.7	26	4.9	10.3	8.9
nd – not detected.					

2.3.4 Comparison of on-site and laboratory analyses

Air samples from February 18 in Talgar were also analysed in the laboratory >18 hours later. Concentrations of benzene and toluene were 9.1 and 6.5 μg/m^3, respectively, which were 34% higher for benzene and 24% lower for toluene than those determined on-site. This difference may reflect a combination of real temporal variability of ambient BTEX concentrations and possible changes in sample composition during transportation and overnight storage.

2.3.5 Comparison of the developed method with SPME-based alternatives and other methods

Compared to the most similar method based on SPME [64], the developed method (Figure 9) has a simpler standard addition calibration and does not require a gas generation system with predetermined analyte concentrations. The developed method requires longer run time (40 min vs 15 min), mainly due to the use of capillary column with greater inner diameter and stationary phase film thickness. To analyse three replicate air samples and one calibration sample (air with added BTEX standard), the method requires about four hours including instrument preparation, conditioning, and checking. The detection limits of the developed method are lower than for the Koziel et al. [64] method reported by Jia et al. [18]. In contrast to the EPA TO-14A methodology, the developed method does not require air extraction canisters and pumps with precise flow rate control. The developed method allows sampling and analysis of air from a smaller (approximately three times) number of points in one day, but the accuracy of such analysis should be higher due to the

shorter time between sampling and analysis, especially when analysing air from locations remote from the laboratory, as compared to the methods of BTEX determination in the laboratory [65] based on SPME from 20 mL vials and GC-MS [9]. In addition, the performance of the developed method can be substantially improved by upgrading to one of the commercially available portable GC-MS instruments due to their higher selectivity and sensitivity.

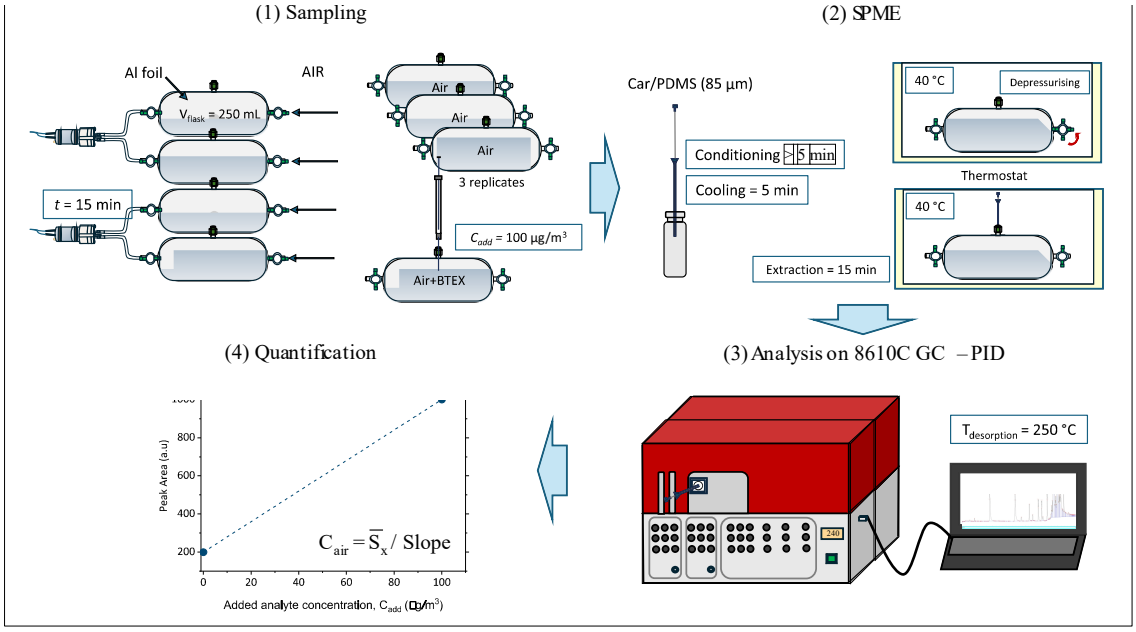


Figure 9 – Schematic illustration of the developed method for BTEX quantitation in atmospheric air

2.4 Chapter conclusion

In this study, a simple on-site analytical method based on SPME was enhanced allowing reliable measurements of BTEX in atmospheric air at ppb levels. Using the developed method and an SRI 8610C GC with a modified inlet, BTEX concentrations in Talgar, Almaty oblast, Kazakhstan, were determined for the first time. Quantitation was conducted using standard addition calibration on four replicate air samples in 250 mL calibrated gas bulbs, one of which was spiked with BTEX standard. All the procedure was conducted in the field. Optimal extraction time for detecting lower concentrations of ethylbenzene and xylenes was 15 min.

In Talgar, benzene concentrations 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.

The developed method can be recommended for quick and low-cost on-site quantification of BTEX in atmospheric air, particularly at remote locations when long transportation of samples can result in losses of analytes and poor accuracy.

3 ADAPTATION OF A SPME-BASED ANALYTICAL METHOD FOR ON-SITE DETERMINATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE TRANSFORMATION PRODUCTS IN WATER

Preamble

The materials in this article have been partially published as research article: Tolkyn Kurmanbayeva, Zhansaya Rymzhanova, Bulat Kenessov; 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,* 2025, 105 (19), p.7673-7682. Materials for all sections of this current Chapter are reprinted from this research article with the permission from the International Journal of Environmental Analytical Chemistry of Taylor & Francis. The copyright for this work remains with Taylor & Francis and any further requests for reuse of this information should be made directly to them.

3.1 Selection of SPME-based analytical method for on-site determination of unsymmetrical dimethylhydrazine transformation products in water

Unsymmetrical dimethylhydrazine (UDMH) is a highly toxic rocket propellant released to the environment during landing of stages of heavy carrier rockets [80]. As a result of UDMH spills, water can be contaminated with UDMH transformation products (TPs), most of which are hydrophilic and have high water solubility [81,82]. Monitoring of UDMH TPs in water typically includes collection of water samples and transportation to laboratories equipped with gas or liquid chromatography instruments with mass spectrometric detectors providing high sensitivity, selectivity and versatility [83]. On-site quantification of UDMH TPs in water samples is important because fast results can be needed, particularly after major accidental fuel spills, but analytical methods for on-site quantification of UDMH TPs in water are not available in scientific literature.

UDMH TPs can be quantified in water using LC without sample preparation, but such instruments have limited applicability and reliability in the field. Analytical methods based on GC use liquid-liquid extraction (LLE) [84,85], solid-phase extraction (SPE) [86–88], accelerated water sample preparation (AWASP) [89], vortex-assisted liquid-liquid microextraction (VALLME) [90], and headspace solid-phase microextraction (HSSPME) [10,91–94]. Methods based on HSSPME [93,94] are the most prominent for on-site quantification of environmental pollutants because they offer a great combination of limits of detection and simplicity [39,50,95] (Table 10). These methods are based on GC-MS but potentially could be upgraded for an on-site application with one of the commercially available portable GC or GC-MS instruments. The method developed by Orazbayeva et al. [94] is based on vacuum-assisted HSSPME (Vac-HSSPME) and provides lower LODs (0.5-6000 ng/L) due to higher diffusion coefficients of analytes in headspace and faster extraction [96,97]. This can be important for on-site methods due to a lower sensitivity of portable instruments and time restrictions in the field. The method

includes a 2-min evacuation of a 20-mL vial, addition of 5.0 mL water sample, preincubation for 10 min at 50 °C and HSSPME for 30 min at 50 °C [94]. Quantitation was conducted using external standard calibration. Accuracy of the method can be decreased due to a matrix effect caused by different extraction effectiveness of analytes from different samples [49,50]. For matrix effect control, Orazbayeva et al. [94] studied the applicability of multiple HSSPME. Extraction effectiveness of analytes from studied water sample varied from 3.0 to 27%.

In this study, the method based on Vac-HSSPME for quantitation of UDMH TPs in water was adapted for application in combination with portable GC with a nitrogen-phosphorus detector. Pyrazine, 1-methyl-*1H*-pyrazole (1-MPA), *N*-nitrosodimethylamine (NDMA), *N*,*N*-dimethylformamide (DMF), 1-methyl-*1H*-1,2,4-triazole (MTA), *N*-methylformamide (MFA), *1H*-pyrazole and 3-methyl-*1H*-pyrazole (3-MPA) were chosen as analytes because they are most toxic and/or stable, and were used for the development of SPME-based methods [93,94]. Method linearity, LODs and LOQs were estimated for the chosen UDMH TPs. Spike recoveries of the analytes from different water samples were studied. The developed method has been applied for on-site analyses of two water samples collected near the UDMH spills in Central Kazakhstan.

Table 10 – Comparison of the analytical performance of methods for quantification of UDMH TPs in water based on HSSPME

Instrument	Sample preparation approach	Analytes	LOD (µg/L)	LOQ (µg/L)	Spike recovery (%)	Reference
GC-ITMS	HSSPME	Nitrosoamines (including NDMA)	0.0032-0.0035	nd	92-122	[91]
GC-ITMS	HSSPME	Nitrosoamines (including NDMA)	0.001-0.005	0.010-0.015	nd	[92]
GC-MS	HSSPME	FADMH	0.5	nd	nd	[10]
GC-MS	HSSPME	Pyrazine, MPA, NDMA, DMF, MTA, MIA	0.005-0.5	0.01-1.3	75-125	[93]
GC-QQQ	HSSPME	Pyridine, Pyrazine, NDMA, DMF, MTA, MFA, FDMH, MIA, FA, 2-Furaldehyde dimethylhydrazone, 1*H*-Pyrazole, 3-Methyl-1*H*-pyrazole, 3,5-Dimethyl-1*H*-pyrazole	0.001-0.14 (Q1 SIM) 0.01-3 (MRM)	0.002-0.42 (Q1 SIM) 0.02-10 (MRM)	nd	[93]
GC-MS	Vac-HSSPME	Pyrazine, MPA, NDMA, DMF, MTA, FDMH, MIA, FA, 1*H*-Pyrazole	0.0005-6	nd	80-119	[94]
Portable GC-NPD	Vac-HSSPME	Pyrazine, MPA, NDMA, DMF, MTA, MFA, 1*H*-Pyrazole, 3-MPA	0.2-40	0.7-130	73-90	This study

Note: LOD, limit of detection; LOQ, limit of quantification; HSSPME, headspace solid-phase microextraction; ITMS, ion trap MS; NDMA, *N*-nitrosodimethylamine; FADMH, formaldehyde dimethylhydrazone; Vac-HSSPME, vacuum-assisted headspace solid-phase microextraction; MPA, 1-methyl-1*H*-pyrazole; 3-MPA, 3-methyl-1*H*-pyrazole; DMF, *N*,*N*-dimethylformamide; MTA, 1-methyl-1*H*-1,2,4-triazole; FDMH, 1-formyl-2,2-dimethylhydrazine; MIA, 1-methyl-1*H*-imidazole; FA, formamide; QQQ, triple quadrupole MS; MFA, *N*-methylformamide; nd, not detected.

3.2 Materials and methods

3.2.1 Chemicals and materials

The purity and origin of UDMH TPs is provided in Table 11. NaCl (>99%, Russia) was dried at 150 °C for 2 h before using. Prior to experiments, vials and flasks were washed with distilled water and preconditioned at 150 ºC for 2 h. Disposable plastic syringe (Bioject, China) for 5.0 mL were used with a manually blunted needle.

Table 11 – List of analytes and their main physicochemical properties

Analyte	CAS number	Elemental composition	Molecular weight (Da)
Pyrazine (99.0%, Meryer, China)	290-37-9	$C_4H_4N_2$	80
1-Methyl-*1H*-pyrazole (98.0%, Meryer, China)	930-36-9	$C_4H_6N_2$	82
N-Nitrosodimethylamine (99.0%, Meryer, China)	62-75-9	$C_2H_6N_2O$	74
N,N-Dimethylformamide (98.0% Sigma-Aldrich, USA)	68-12-2	C_3H_7NO	73
1-Methyl-*1H*-1,2,4-triazole (99.0%, Meryer, China)	6086-21-1	$C_3H_5N_3$	83
N-Methylformamide (99.0%, Meryer, China)	123-39-7	C_2H_5NO	59
1H-Pyrazole (99.0%, Meryer, China)	288-13-1	$C_3H_4N_2$	68
3-Methyl-*1H*-pyrazole (97.0%, Meryer, China)	1453-58-3	$C_4H_6N_2$	82

The following materials and reagents were also used in the study:

Amber glass screw-top vials for 2 mL with PTFE/rubber septa, Zhejiang Aijiren Technology Co (China);

Volumetric flasks for 25mL, class A, ISOLAB (Germany);

Microsyringes for 5.0, 10.0 µL (for liquids), Agilent (USA);

Microsyringe for 50 µL (gas-tight), Agilent (USA);

Microsyringe for 100 µL (gas-tight), Gerstel (Germany);

Single-channel micropipette for 1000 µL, Eppendorf (Germany);

Single-channel micropipette for 5000 µL, Sartorius (Germany);

3-Picoline, 99.0%, Meryer (China);

Crimp-top glass vials for 20 mL, Zhejiang Aijiren Technology Co (China);

Aluminium caps with PTFE/silicone septa, Zhejiang Aijiren Technology Co (China);

SPME fiber 85 µm Carboxen/polydimethylsiloxane (Car/PDMS), Supelco (Bellefonte, PA, USA);

Needle heater, GERSTEL (Germany);

Modified Mininert® valves, Supelco (USA);

Cylindrical septum with a half-hole, Thermogreen® LB-1, Supelco (USA);

SPME glass liner, Supelco (USA);

Single-stage rotary vane pump (Russia);

In-house manufactured thermostat located on the top of the magnetic stirrer PE-6100, Ecros (Russia);

PARAFILM® M, Bemis (USA);

HP-INNOWax 30 m × 0.25 mm × 0.25 μm, Agilent Technologies (Santa Clara, USA);

Helium, >99.995%, Orenburg-Tehgas (Russia);

Hydrogen generator QL-M150, Shandong Saikesaisi Hydrogen Energy Co., Ltd. (China);

8610C gas chromatograph with nitrogen-phosphorous detector (GC-NPD), SRI Instruments (USA);

Centrifuge CM-12, TAGLER (Russia);

Gas sensor, G3388B, Agilent Technologies (Santa Clara, USA);

3.2.2 Preparation of standard solutions and calibration standards

Standard solutions of analytes were prepared in 2-mL amber glass screw-top vials with PTFE/rubber septa.

Stock solutions of analytes (with concentrations of analytes provided in Table 12) were prepared by injecting 5.00 μL of an analyte into the vial containing 995 μL of distilled water, sealing with PTFE/rubber septa and vortexing for 1-2 min.

Solution 1 (Table 12) was prepared in the vial containing 740 μL of distilled water by adding 5.00 μL of stock solutions of pyrazine and 1-MPA, 25 μL of stock solutions of NDMA, DMF, MTA, 1*H*-pyrazole and 3-MPA, and 125 μL of the stock solution of MFA.

Calibration standards were prepared in 25 mL volumetric flasks with distilled water by adding 5.00 μL, 10.0 μL, 20 μL, 30 μL, 40 μL of Solution 1 (Table 12) and filling the flask to a graduation mark.

Table 12 – Concentration of UDMH TPs products in water solutions used in this study

Analyte	Concentration in		
	Stock solutions (mg/L)	Solution 1 (mg/L)	Control sample (μg/L)
Pyrazine	5100±50	25.5±0.4	102
1-MPA	4840±50	24.2±0.4	97
NDMA	4950±50	124±3	99
DMF	4630±50	116±3	93
MTA	5450±60	136±3	109
MFA	4950±50	619±12	99
1H-Pyrazole	4950±50	124±3	99
3-MPA	4950±50	124±3	99

3.2.3 Vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME)

Extraction of analytes was conducted from the headspace of water samples in evacuated 20-mL glass vial using SPME fiber with 85-μm Carboxen/polydimethylsiloxane (Car/PDMS) coating. Before each extraction, 85

μm Car/PDMS was pre-conditioned in the GC inlet or the needle heater of MPS2 autosampler (GERSTEL, Germany) at 250 °C for ≥10 min.

Vials with NaCl (1.75 g), polytetrafluoroethylene (PTFE)-coated magnetic stir bar (10 × 6 mm) were sealed with a modified Mininert® valve [98], which have been [99] proven to provide stable responses of analytes even after long waiting times (up to 24 h) [94]. Then the vial was evacuated for 120 s inserting stainless steel needle of a disposable plastic syringe tightly connected to the tubing of a single-stage rotary vane pump through the cylindrical Thermogreen® LB-1 septum. A water sample (5.0 mL) containing UDMH TPs was added to the vial using disposable plastic syringe. The vial was then placed on a stirring plate inside the in-house manufactured thermostat [94] heated to 50 °C and pre-incubated for 10 min at 1500 RPM. Upon sample equilibration, 85 μm Car/PDMS fiber was introduced into the vial by piercing the septum, and Vac-HSSPME sampling was performed for 30 min at the same temperature and agitation speed. After extraction, the fiber was retracted, and the SPME device was quickly transferred into the portable GC inlet for 3 min desorption of analytes at 250 °C.

3.2.4 Gas chromatography with nitrogen phosphorus detection (GC-NPD)

GC-NPD analyses were conducted on a portable 8610C gas chromatograph equipped with a nitrogen-phosphorous detector and a built-in air compressor. The GC inlet was modified to work with a 0.75 mm×6.35×78.5 SPME glass liner according to our previous study [99]. Before analyses, GC was checked for leaks using 'pressure drop' test and using a gas sensor. Sensitivity of GC system was controlled by analyzing 5.0 mL of the control sample using Vac-HSSPME (Section 3.2.3). Control sample was prepared by injecting 5.0 μL of solution of analytes (Solution 1, Section 3.2.2) into a 20-mL vial containing 4995 μL of distilled water. GC separation was conducted on an HP-INNOWax fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness) with polyethylene glycol stationary phase using helium (>99.995 %) as a carrier gas. Constant flow rate (1.5 mL/min) of helium provided by pressure programming: 16.98 psi to 25.76 psi (held for 7 min) at 0.306 psi/min. Column temperature was programmed from 60 °C to 200 °C (held for 7 min) at 5 °C/min. Total run time was 35 min. NPD was conducted at 2 psi air flow (corresponding to 100 mL/min) and 10 psi (corresponding to 2 mL/min) hydrogen flow from a hydrogen generator. The temperature was set at 250 °C, the bead current was -350 mV, detector gain was at HIGH level. Chromatograms were recorded and processed using the PeakSimple application (version 4.98, SRI Instruments, USA). Identification of the analytes were performed using their retention times on the chromatograms (Table 13).

Table 13 – Retention times of analytes on chromatograms and their confidence intervals obtained using the methods based on Vac-HSSPME-GC-NPD

Analyte	Retention time ± confidence interval (min)
Pyrazine	5.50±0.02
1-MPA	6.20±0.02
NDMA	7.59±0.01
DMF	7.90±0.03
MTA	13.52±0.01
MFA	14.98±0.01
1H-Pyrazole	18.54±0.01
3-MPA	19.23±0.01

3.2.5 Calibration

Stock and standard solutions of the analytes (Table 12) were prepared by dissolving pure analytes in distilled water and a subsequent serial dilution according to the procedures described in Section 3.2.2. Calibration standards (Table 14) were analysed using Vac-HSSPME-GC-NPD according to the parameters provided in Sections 3.2.3-3.2.4. Slopes (determined by the least squares method), their relative standard deviations (RSDs), and determination coefficients of calibration plots were calculated using LINEST function of MS Excel.

Table 14 – Concentrations of UDMH TPs products in calibration standards

Analyte	Concentration (μg/L) in calibration standard				
	1	2	3	4	5
Pyrazine	5.1	10.2	20	31	41
1-MPA	4.8	9.7	19.4	29	39
NDMA	25	50	99	149	198
DMF	23	46	93	139	185
MTA	27	55	110	163	220
MFA	125	250	500	740	990
1H-Pyrazole	25	50	99	149	198
3-MPA	25	50	99	148	198

3.2.6 Study of the matrix effect

Eight different samples of water including two aqueous extracts from soil (pH 5.7-8.0) were used for evaluation of the matrix effect (Table 15).

Table 15 – Water samples used for evaluation of the matrix effect

Sample	Type	pH	Sampling date	Sampling location
1	Snow	5.7	06/02/2024	43°15'08.8"N, 76°55'41.3"E
2	Tap	7.6	05/04/2024	43°15'08"N, 76°55'42"E
3	Rain	6.2	09/04/2024	43°15'08.8"N, 76°55'41.3"E
4	Puddle	7.8	10/04/2024	43°14'34"N, 76°55'11"E
5	Mountain river	6.4	10/04/2024	43°12'07.7"N, 76°53'23.1"E
6	Mountain river	8.0	10/04/2024	43°15'08.8"N, 76°55'41.3"E
7	Soil extract	7.3	10/04/2024	43°15'06.4"N, 76°55'43.1"E
8	Soil extract	7.0	10/04/2024	43°15'08.8"N, 76°55'41.3"E

Prior to analysis, the samples were filtered through a blue-ribbon paper and stored at 4°C. Then samples in 25-mL volumetric flasks were spiked with 15 µL of Solution 1 (Section 3.2.2) and filled to the mark. All solutions were analysed using Vac-HSSPME-GC-NPD according to the parameters provided in Sections 3.2.3-3.2.4. Spike recoveries (%) of analytes were calculated based on their concentrations in the solution determined from calibration plots, which were obtained one day before the experiment. The outliers of obtained results were discarded based on Grubbs test.

3.2.7 On-site analysis of real water samples

The proposed procedure (Figure 10) has been applied for on-site analyses of two water samples collected near the UDMH spills during a scientific expedition to the fall regions of the first stages of Proton-M carrier rockets (47°18'39"N, 66°46'43"E, Ulytau region, Kazakhstan) organized in June 2024. GC, with all equipment, was located under the 3 × 3 m tent. Samples were collected in 20-mL vial just before the analysis on June 22 and 24. Samples were analysed using Vac-HSSPME and GC-NPD as described in Sections 3.2.3-3.2.4.

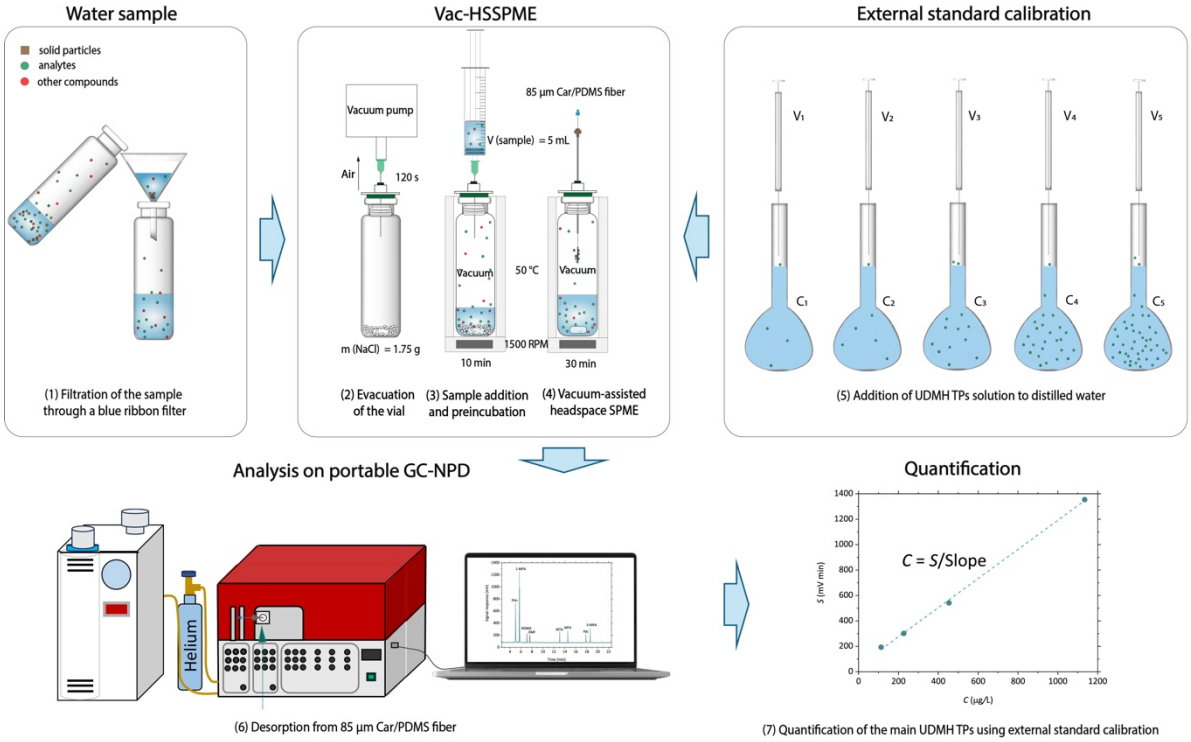


Figure 10 – Schematic illustration of the analytical procedure for on-site quantification of UDMH TPs in water

3.3 Results and discussion

3.3.1 Figures of merit of the on-site method based on Vac-HSSPME-GC-NPD

For application of the method of Orazbayeva et al. [94] with a portable GC-NPD instrument, 30 m column with a 0.25 µm film was used instead of 60 m column with a 0.50 µm film. Volumetric flow rate was increased from 1.0 mL/min to 1.5 mL/min because NPD works under atmospheric pressure, while MS detector uses vacuum. All other method parameters (except detector parameters) were the same.

Linear calibration plots (R^2 = 0.979-0.999) were obtained using standard solutions of analytes in distilled water (Table 16). Chromatogram of the calibration standard 4 (Table 14) is shown in Figure 11. Calibration slopes varied from 0.015 (for MFA) to 7.45 (for 1-MPA) because of different detector sensitivity to different analytes and their different extraction effectiveness. 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).

Table 16 – Analytical performance of the method based on Vac-HSSPME-GC-NPD

Analyte	Linear range (µg/L)	R^2	Slope	RSD of slope (%)	LOD* (µg/L)	LOQ* (µg/L)
Pyrazine	5.1-41	0.9984	3.54	2.0	0.5	1.6
1-MPA	4.8-39	0.9995	7.45	1.2	0.2	0.7
NDMA	25-198	0.9901	0.149	5.0	7	20
DMF	23-185	0.9788	0.077	7.4	17	60
MTA	27-218	0.9974	0.150	2.5	8	30
MFA	124-990	0.9831	0.015	6.6	40	130
1H-Pyrazole	25-198	0.9973	0.319	2.6	2	8
3-MPA	25-198	0.9994	0.465	1.3	7	25
Note: *LODs and LOQs were calculated using signal-to-noise (*S/N*) ratios of 3:1 and 10:1, respectively. *S/N* were measured in calibration standards prepared in distilled water with lowest concentration of each analyte.						

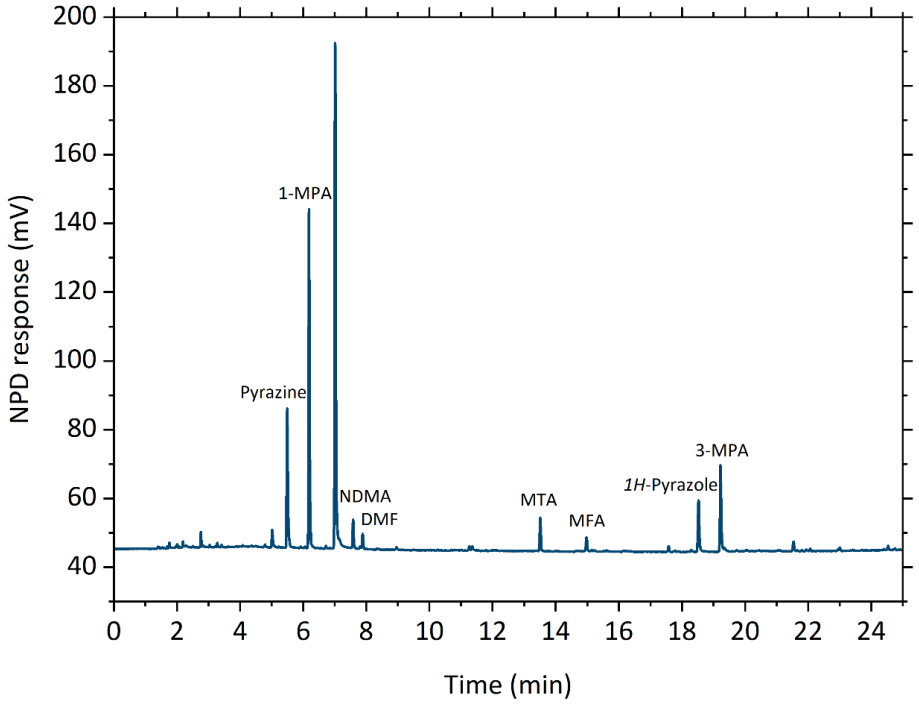


Figure 11 – Chromatogram of the standard solution of analytes in distilled water obtained in a laboratory after Vac-HSSPME with 85 µm Car/PDMS (volume of sample 5 mL, preincubation at 50 °C for 10 min at 1500 RPM, extraction at 50 °C for 30 min at the same agitation speed)

Compared to the method based on a Vac-HSSPME-GC-MS [94], LODs with a portable GC-NPD were from 133 (for MTA) to 700 (for NDMA) times higher. Compared to the method based on a HSSPME-GC-MS [93], LODs with a portable GC-NPD were from 27 (for MTA) to 340 (for DMF) times higher. Despite much lower LODs of the method based on Vac-HSSPME-GC-NPD, they are lower than

the values of maximum permissible concentrations for DMF (10 mg/L) and even NDMA (10 μg/L) established in Kazakhstan [100,101].

3.3.2 Evaluation of the matrix effect

Extraction effectiveness of analytes from different water samples using HSSPME can vary because of different affinities of analytes to the samples resulting in matrix effect and lower accuracy. The goal of this experiment was to study the matrix effect by estimating spike recoveries of the analytes from six different water samples and two aqueous extracts from soils (Table 15).

Spike recoveries of DMF for water samples 1-3 and 7 were significantly (more than two times) higher than for other samples (Table 17), which can be caused by its peak overlap with other matrix compounds with the same retention times. Using Grubbs test, outliers were detected for MFA in sample 3 and 3-MPA for sample 4. After discarding all these outliers, mean spike recoveries of analytes were in range from 73.3% (for MTA) to 90.0% (for DMF). RSDs of the recoveries varied from 10% (for DMF) to 21% (for 1-MPA). These results indicate that the external standard calibration can be used for accurate quantitation of all UDMH TPs (except DMF) in water samples using Vac-HSSPME-GC-NPD.

Table 17 – Spike recoveries (%) of analytes calculated using the slopes of calibration plots

Sample	Analyte							
	Pyrazine	1-MPA	NDMA	DMF	MTA	MFA	*1H*-Pyrazole	3-MPA
1	60.3	62.4	102.2	221*	59.6	69.9	74.5	60.7
2	77.4	85.3	81.8	229*	64.0	71.5	78.0	68.6
3	95.8	93.1	81.0	338*	85.9	119.4*	94.7	85.3
4	73.3	71.0	71.5	80.9	67.8	78.2	74.3	195.3*
5	101.7	100.9	92.6	101.4	93.6	89.9	104.1	105.8
6	80.8	70.1	76.9	85.1	77.3	73.0	77.8	69.7
7	76.8	75.7	68.6	267*	73.2	92.5	63.7	75.1
8	68.1	53.0	65.4	92.8	65.2	69.1	69.0	72.8
Mean	79.3	76.4	80.0	90.0	73.3	77.7	79.5	76.9
SD	13.7	15.9	12.4	9.0	11.7	9.7	13.4	14.8
*Outlier								

3.3.3 Method application

The method based on Vac-HSSPME-GC-NPD has been applied for on-site analyses of two water samples collected from the river at the distance of ~200 m from the UDMH spills in Central Kazakhstan on 22 and 24 June 2024. DMF peak was observed in both samples, but the laboratory experiment showed that matrix compounds can have similar retention time. MFA was detected in the first sample, while 1-MPA – in the second sample. The quantification of these analytes was not conducted because their signal-to-noise ratios were below 10 (Figure 12). Such low

levels of water pollution can be explained by the low levels of soil pollution in the place of UDMH spill [102] and high distance between the river and this place.

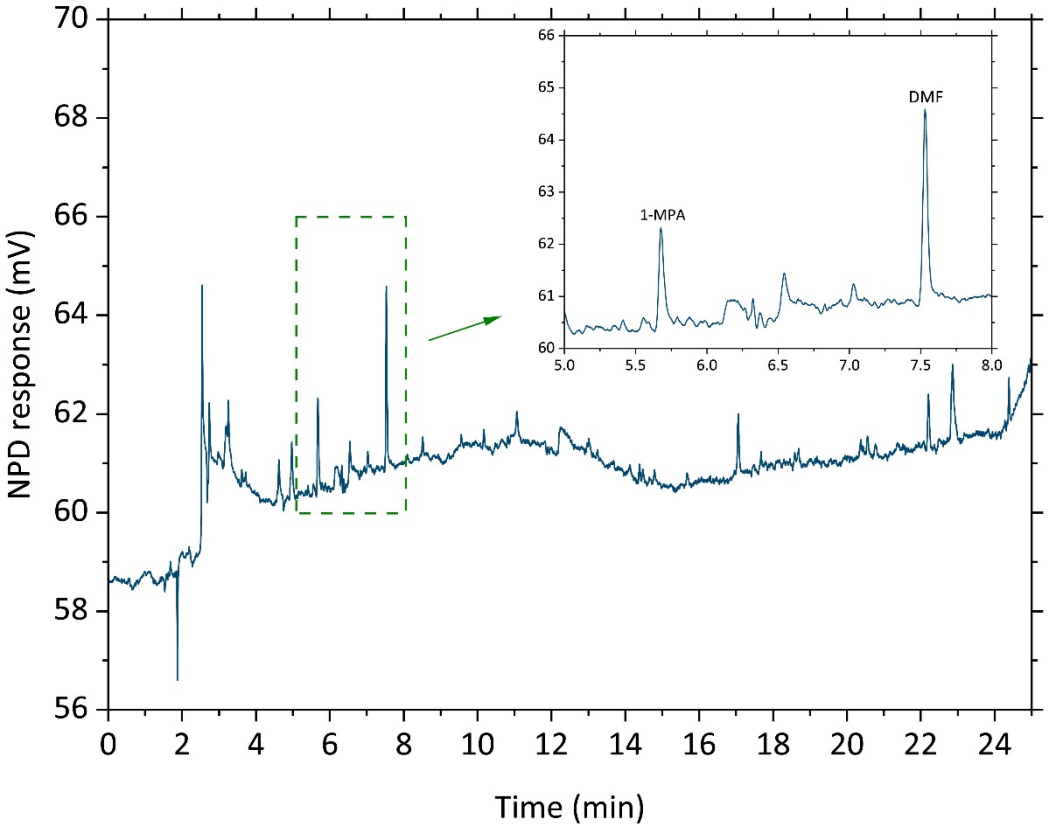


Figure 12 – Chromatogram of real water sample collected near the UDMH spills obtained in the field after Vac-HSSPME with 85 µm Car/PDMS (volume of sample 5 mL, preincubation at 50 °C for 10 min at 1500 RPM, extraction at 50 °C for 30 min at the same agitation speed)

3.4 Chapter conclusion

The analytical method based on Vac-HSSPME-GC-MS [94] has been adapted for the on-site quantification of eight transformation products of unsymmetrical dimethylhydrazine in water using the portable GC-NPD. Compared to Vac-HSSPME-GC-MS, the method based on GC-NPD provided 133-700 times higher LODs, most probably, due to a lower selectivity and higher noise of the NPD compared to the MS detector in selected ion monitoring (SIM) mode. 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). External standard calibration using standards of analytes prepared in distilled water can be used for accurate quantitation of all UDMH TPs (except DMF) in water samples providing spike recoveries 73.3% - 90.0% from different types of water.

On-site testing of the method based on Vac-HSSPME-GC-NPD for analysis of water samples from the river located ~200 m from the UDMH spill in Ulytau region, Kazakhstan, allowed to detect 1-MPA and MFA, but their concentrations were below LOQs. Vac-HSSPME was used for the first time for on-site water

analysis. The air-evacuation of vials was easily implemented on-site because it only required a low-cost vacuum pump, the modified Mininert® valve, Thermogreen® septum and 2 min of time per vial.

The method based on Vac-HSSPME-GC-NPD can be recommended for quick and accurate on-site quantification of UDMH TPs in water contaminated with rocket fuel and/or in water bodies near the fuel spills, particularly after major accidents. The main limitation of the method is its relatively high LODs compared to the methods based on GC-MS. However, the LOD for NDMA is lower than the value of its maximum permissible concentration established in Kazakhstan, and the method can be used for quick evaluation whether analysed water meets this value. For lower LODs and LOQs, this method can be improved by using one of the commercially available portable GC-MS instead of the GC-NPD.

4 DEVELOPMENT OF THE ANALYTICAL METHOD FOR ON-SITE DETERMINATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE TRANSFORMATION PRODUCTS IN SOIL USING SOLID-PHASE MICROEXTRACTION

Preamble

The materials in this article have been partially published as research article: Tolkyn Kurmanbayeva, Bauyrzhan Bukenov, Aibolat Imangabassov, Zhansaya Rymzhanova, Nurbi Karimkyzy, Aruzhan Smail, Bulat Kenessov; On-site gas chromatographic quantitation of transformation products of unsymmetrical dimethylhydrazine in soil using vacuum-assisted headspace solid-phase microextraction; *Microchemical Journal,* 2025, 215, 114492. Materials for all sections of this current Chapter are reprinted from this research article with the permission from the Microchemical Journal. The copyright for this work remains with Elsevier and any further requests for reuse of this information should be made directly to them.

4.1 Importance of the development of an analytical method for on-site quantification of unsymmetrical dimethylhydrazine transformation products in soil using solid-phase microextraction

Despite its high toxicity (Class I hazard [103], Group 2B human carcinogen [104]), unsymmetrical dimethylhydrazine (UDMH) is still widely used as a rocket fuel, resulting in environmental and human health risks. UDMH can be released to the environment during transportation and refuelling of rocket systems, remaining fuel spillage from falling burned-out stages. In the last decade (2014-2023), 36 Proton-M carrier rockets fueled with UDMH and nitrogen tetroxide were launched from Baikonur Cosmodrome [105], and their first stages fell in Central Kazakhstan with 10-30 kilograms of residual UDMH [106]. The last major accident was in 2013 when the Proton-M carrier rocket crashed with several hundred tons of the residual fuel [107]. Rocket fuel spills result in the contamination of soil, air, water and plants with UDMH and its transformation products.

N-nitrosodimethylamine (NDMA), 1,1,4,4-tetramethyl-2-tetrazene (TMT), 1-formyl-2,2-dimethylhydrazine (FDMH), *N,N*-dimethylformamide (DMF), 1-methyl-*1H*-1,2,4-triazole (MTA) are the most common markers of environmental contamination with UDMH [83,101,108,109]. Soil contamination with UDMH TPs at regular fall places of the first stages of Proton carrier rockets was detected only near the epicenters of the UDMH spill [80,108] at the depths of up to 150 cm [106,108]. Reported concentrations of MTA in soil one day after an accidental Proton-M crash were up to 608±15 mg/kg [110], while the highest reported concentration in soil at the regular fall place of the first stage of the rocket was 57.3 mg/kg [108].

Screening and quantitation of UDMH TPs in soil are required to monitor and map their contamination levels. Most known analytical methods for quantitation of UDMH TPs in soil use stationary gas chromatography with mass spectrometric

detector (GC-MS) [110–119] (Table 18), or liquid chromatography (LC) with MS, ultraviolet (UV), fluorescence (FLD) and amperometric (AD) detectors [82,120–124]. For quantitation of UDMH TPs in soil using GC, sample preparation is required using solvent extraction (Soxhlet, Randall, pressurized solvent or supercritical fluid extraction), headspace sampling, headspace solid-phase microextraction (HSSPME) or vortex-assisted liquid-phase microextraction. For LC, solvent (including water) extraction or basic distillation are commonly applied [83].

For analysis, soil samples are typically transported to laboratories located hundreds of kilometers from sampling locations [108,125,126]. In many cases, particularly after major accidents, results of analysis are needed quickly after sampling for decision making. However, collection of soil samples and their transportation to a laboratory typically take several days. Such delays can also result in the loss of accuracy due to a degradation of some UDMH TPs. Due to the high reactivity of UDMH and varying stability of transformation products, it is recommended that soils are transported at low temperatures (+2 to +5 °C) and analyzed within three days of sampling to obtain more reliable results [127]. Nowadays, commercial analytical equipment [15,24] and methods [19,47,64] are available for on-site quantitation of organic pollutants. Such methods are considered to be 'greener' because they provide lower energy consumption, chemical waste and emissions. However, the results of on-site quantitation of UDMH TPs in soil and proper analytical methods are not reported in the literature. Zhubatov et al. [110] developed the method based on GC-MS for quick quantitation of MTA in soil after solvent extraction and recommended it for on-site application, but this method has not been tested with a portable instrument.

HSSPME in combination with GC provide great combination of simplicity and limits of detection (LODs) for screening and quantitation of UDMH TPs, and this approach has been successfully applied for on-site quantitation of other VOCs in environmental samples [19,47,128]. The major problem in soil analysis using HSSPME is the matrix effect caused by different extraction effectiveness of analytes from various soil samples, and the proper matrix effect minimization and/or control are required for sufficient quantitation accuracy [50]. Several approaches are available for quantitation of UDMH TPs in soil using HSSPME. Yegemova et al. [116] developed an isotope dilution method with 1-(trideuteromethyl)-*1H*-1,2,4-triazole (MTA-d3) for the quantitation of MTA using HSSPME-GC-MS. After spiking of a soil sample with MTA-d3, equilibration at elevated temperatures for several hours was required to ensure a uniform distribution of the internal standard in the sample and sufficient accuracy. Bakaikina et al. [117] extended this method to a larger number of analytes, resulting in lower detection limits for NDMA, DMF and MTA (Table 18), and combined it with a standard addition approach to achieve greater precision and accuracy. Orazbayeva et al. [118] developed the method for the quantitation of UDMH TPs in aqueous extracts from soil based on vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME).

Table 18 – Analytical methods for quantitation of UDMH TPs in soil samples based on GC-MS

Sample preparation	Analyte(s)	Limit(s) of detection (LODs) (µg/kg)	Recovery (%)	Reference
Soxhlet extraction, evaporative preconcentration, filtration	MTA	5	80–95	[111]
Soxhlet extraction	MTA FADMH	20	58–72	[112]
Solvent extraction, isotope dilution	MTA	<2000	67-131	[110]
PHWE, HSSPME	*N*-nitrosamines	0.03-0.15	nd	[113]
MAE, SPE	*N*-nitrosamines and amines	0.03-0.35	<94-96	[114]
HSSPME	23 and 36 TPs	nd	nd	[115]
HSSPME, isotope dilution	MTA	<1000	91-121	[116]
HSSPME	MTA DMF NDMA	14 12 1	91-117 85-123 64-132	[117]
Vac-HSSPME	Pyrazine 1-MPA NDMA MTA *1H*-Pyrazole	0.035 0.17 0.22 3.6 0.35	112±8 119±10 114±11 103±12 107±9	[119]
Aqueous extraction, Vac-HSSPME	 Pyrazine 1-MPA NDMA DMF MTA MIA *1H*-Pyrazole	LODs (mg/L) 0.3 0.2 1.8 4 9 4 2	 91±2 99±11 90±8 96±14 100±13 103±10 93±12	[118]

Continued from Table 18

Sample preparation	Analyte(s)	Limit(s) of detection (LODs) (μg/kg)	Recovery (%)	Reference
Aqueous extraction and Vac-HSSPME (on-site)		LODs (μg/kg)		This study
	Pyrazine	6	82±8	
	1-MPA	3	84±5	
	NDMA	27	85±7	
	DMF	10	104±16	
	MTA	9	100±16	
	MFA	60	123±17	
	1H-Pyrazole	14	89±5	
	3-MPA	4	91±4	

Note: PHWE, pressurized hot water extraction; MAE, microwave-assisted extraction; SPE, solid-phase extraction; HSSPME, headspace solid-phase microextraction; Vac-HSSPME, vacuum-assisted headspace solid-phase microextraction; MTA, 1-methyl-*1H*-1,2,4-triazole; FADMH, formic acid dimethylhydrazine; DMF, *N,N*-dimethylformamide; NDMA, *N*-nitrosodimethylamine; 1-MPA, 1-methyl-*1H*-pyrazole; MIA, 1-methyl-imidazole; MFA, *N*-methylformamide; 3-MPA, 3-methylformamide; nd, not detected.

Compared to HSSPME, Vac-HSSPME of UDMH TPs from aqueous samples provided faster extraction and lower LODs [94]. Zhakupbekova et al. [119] developed the method for quantitation of trace UDMH TPs in sand using Vac-HSSPME without preliminary aqueous extraction, but its accuracy for other soil types has not been studied. Recently, the method based on Vac-HSSPME [94] has been successfully adapted for on-site quantitation of UDMH TPs in water using a portable GC with nitrogen-phosphorus detector (NPD) [129], but a substantial increase in detection limits compared to a stationary GC-MS was reported.

In this work, the method of Orazbayeva et al. [118] was optimized for on-site quantitation of UDMH TPs in soil using Vac-HSSPME in combination with a portable GC-NPD. The developed method was applied for the on-site quantitation of UDMH TPs in soil samples collected at the fall site of the first stage of a Proton-M carrier rocket in the Ulytau Region, Kazakhstan.

4.2 Experimental

4.2.1 Chemicals and materials

Pyrazine, 1-MPA, NDMA, DMF, MTA, MFA, *1H*-pyrazole and 3-MPA were chosen as analytes (Table 11). All analytes, except DMF (Sigma-Aldrich, USA), were purchased from Meryer (China) and had a purity greater than 97%. Aqueous standards and model solutions of analytes were prepared using distilled water. Sodium chloride (>99%, Russia) was dried at 150 °C for 2 h before use. Disposable plastic syringes (Bioject, China) for 5.0 and 10.0 mL were used with a manually blunted needle.

The following materials and reagents were also used in the study:

Amber glass screw-top vials for 2 mL with PTFE/rubber septa, Zhejiang Aijiren Technology Co (China);

Volumetric flasks for 25mL, class A, ISOLAB (Germany);

Microsyringes for 5.0, 10.0 μL (for liquids), Agilent (USA);

Microsyringe for 50 μL (gas-tight), Agilent (USA);

Microsyringe for 100 μL (gas-tight), Gerstel (Germany);

Single-channel micropipette for 1000 μL, Eppendorf (Germany);

Single-channel micropipette for 5000 μL, Sartorius (Germany);

3-Picoline, 99.0%, Meryer (China);

Crimp-top glass vials for 20 mL, Zhejiang Aijiren Technology Co (China);

Aluminium caps with PTFE/silicone septa, Zhejiang Aijiren Technology Co (China);

SPME fiber 85 μm Carboxen/polydimethylsiloxane (Car/PDMS), Supelco (Bellefonte, PA, USA);

Modified Mininert® valves, Supelco (USA);

Cylindrical septum with a half-hole, Thermogreen® LB-1, Supelco (USA);

SPME glass liner, Supelco (USA);

Single-stage rotary vane pump (Russia);

In-house manufactured thermostat located on the top of the magnetic stirrer PE-6100, Ecros (Russia);

PARAFILM® M, Bemis (USA);

HP-INNOWax 30 m × 0.25 mm × 0.25 μm, Agilent Technologies, Santa Clara (USA);

Helium, >99.995%, Orenburg-Tehgas (Russia);

Hydrogen generator QL-M150, Shandong Saikesaisi Hydrogen Energy Co., Ltd. (China);

8610C gas chromatograph with nitrogen-phosphorous detector (GC-NPD), SRI Instruments (USA);

Centrifuge CM-12, TAGLER (Russia);

Gas sensor, G3388B, Agilent Technologies (Santa Clara, USA);

4.2.2 Preparation of standard solutions and calibration standards

Stock solutions of analytes were prepared in 2-mL amber glass screw-top vials with PTFE/rubber septa. Calibration standards were prepared in 25-mL volumetric flasks. The vials and flasks were washed with distilled water and preconditioned at 150 °C for 2 h prior to analysis.

Stock solutions of analytes (Table 19) and 3-picoline were prepared by injecting 5.00 μL (with a 5.0 μL microsyringe) of an analyte into a 2-mL vial containing 995 μL (injected with a 1000 μL single-channel micropipette) distilled water, sealing with PTFE/rubber septa and vortexing for 1-2 min. Stock solutions were stored at 4 °C for no more than two weeks. Solution 1 (Table 19) was prepared in 2-mL vial containing 740 μL of distilled water by adding 5.00 μL (with a 5.0 μL microsyringe) of stock solutions of pyrazine and 1-MPA; 25 μL (with a 50 μL microsyringe) of stock solutions of NDMA, DMF, MTA, *1H*-pyrazole and 3-MPA; 125 μL (with a 1000 μL single-channel micropipette) of the stock solution of MFA. Solution 2 (Table 19) was prepared in 2-mL vial containing 440 μL of distilled water by injecting 5.00 μL (with a 5.0 μL microsyringe) of stock solutions of pyrazine and 1-MPA; 25 μL (with a 50 μL microsyringe) of stock solutions of NDMA and *1H*-pyrazole, and 125 μL (with a 1000 μL single-channel micropipette) of stock solutions of DMF, MTA, MFA and 3-MPA. Solution 3 was prepared by diluting 200 μL of solution 2 in 800 μL of distilled water.

Control sample was prepared by adding 10.0 μL (with a 10.0 μL microsyringe) of solution 1 to 6.0 mL of distilled water (measured with a 10-mL disposable injection syringe) in a 20-mL glass vial.

For the preparation of calibration standards for GC-MS analysis, solutions 4 and 5 (Table 19) were prepared by 10× and 100× serial dilution of solution of 2, respectively. In the first three extracts (6.0 mL measured with a 10-mL disposable injection syringe) in 20-mLvials, 4.80 μL, 24 μL, and 96 μL of solution 5 were added. In the next three vials with 6.0 mL extracts, 24 μL, 48 μL, and 96 μL of solution 4 were added. Last three vials were spiked with 24 μL, 48 μL, and 144 μL of solution 2.

Table 19 – Concentrations of UDMH TPs products in water solutions used in this study

Analyte	Concentration in						
	Stock solutions (mg/L)	Solution 1 (mg/L)	Solution 2 (mg/L)	Solution 3 (mg/L)	Control sample (µg/L)	Solution 4 (mg/L)	Solution 5 (mg/L)
Pyrazine	5100±50	25.5±0.4	25.5±0.5	5.10±0.12	43±2	2.55±0.05	0.255±0.005
1-MPA	4840±50	24.2±0.4	24.2±0.4	4.84±0.12	40.3±1.9	2.42±0.05	0.242±0.005
NDMA	4950±50	124±3	124±3	24.8±0.7	206±10	12.4±0.3	1.24±0.03
DMF	4630±50	116±3	578±13	116±3	193±9	57.8±1.3	5.78±0.14
MTA	5450±60	136±3	681±15	136±4	227±11	68.1±1.6	6.81±0.16
MFA	4950±50	619±12	619±13	124±3	1030±50	61.9±1.4	6.19±0.15
1*H*-Pyrazole	4950±50	124±3	124±3	24.8±0.7	206±10	12.4±0.3	1.24±0.03
3-MPA	4950±50	124±3	618±13	124±3	206±10	61.8±1.4	6.18±0.15

4.2.3 Vac-HSSPME

SPME was conducted in 20-mL crimp-top glass vials with 85-µm Car/PDMS fiber. Before the first extraction, SPME fiber was preconditioned in the inlet of the 8610C GC-NPD at 250 °C for >10 min.

Vac-HSSPME was conducted according to the method of Orazbayeva et al. [118], which was optimized for on-site analyses. The vials with 1.75 g NaCl and polytetrafluoroethylene (PTFE)-coated magnetic stirring bar (10 × 6 mm) were sealed using a modified Mininert® valve with a 6 mm diameter × 9 mm length cylindrical septum containing a half-hole, and 1.5 mm fluorocarbon O-ring [98]. Vials were air-evacuated using a low-cost single-stage rotary vane pump for 120 s [118] followed by the addition of 5.0 mL of a soil extract or a solution of analytes in water. The vial was placed inside the in-house manufactured thermostat located on the top of the magnetic stirrer PE-6100 [118] and heated to 50 °C. The samples were incubated for 10 min at a maximum stirring speed (1500 RPM), and extraction was performed with an 85-µm Car/PDMS fiber, which was exposed in the headspace above the sample for 30 min at the same stirring speed. After extraction, SPME fiber was retracted and introduced into the GC inlet for >25 min desorption of analytes at 250 °C.

4.2.4 Gas chromatography with nitrogen-phosphorus detection

GC-NPD analyses were performed using 8610C GC with a nitrogen-phosphorous detector, which can be converted to flame ionization detector, and a built-in air compressor. To ensure rapid transfer of the analytes desorbed from the

fiber to the column, the GC inlet was modified to work with a SPME glass liner 0.75 mm×6.35×78.5 [99]. Before analyzing the samples, the GC was checked for leaks with a gas sensor and for sensitivity by analyzing 5.0 mL of the control sample (Table 19) using Vac-HSSPME.

Chromatographic separation was achieved on a 30 m × 0.25 mm HP-INNOWax fused silica capillary column with a 0.25-μm film thickness of the polyethylene glycol stationary phase. High-purity (>99.995 %) helium was used as the carrier gas with constant flow rate of 1.5 mL/min provided by pressure programming: 16.98 psi to 25.76 psi (held for 7 min) at 0.306 psi/min. The oven temperature was programmed from 60 °C to 200 °C (held for 7 min) at 5 °C/min. Total duration of the analysis was 35 min. Detection was conducted at 100 mL/min air flow measured with Flow Tracker 2000 (Agilent Technologies, Santa Clara, USA) and 10 psi (corresponding to 2 mL/min) hydrogen flow from a QL- M150 hydrogen generator (Shandong Saikesaisi Hydrogen Energy Co., Ltd., China). NPD temperature was set at 250 ◦C, the bead current was −350 mV, detector gain was at HIGH level. The PeakSimple (version 4.98, SRI Instruments, USA) was used for recording and processing of chromatograms.

4.2.5 Method optimization

4.2.5.1 Aqueous soil extracts preparation

A 20-mL vial with a 10 × 6 mm PTFE-coated magnetic stirring bar was placed in a thermostatically controlled heating device (40 °C) with magnetic stirrer (1500 RPM) [94]. Distilled water (10.0 mL) was added to the vial, and 1.00 ± 0.01 g of soil sample was dispersed on top of it. The vial was quickly crimped using aluminium caps with PTFE/silicone septa and returned to the stirrer for 15 min. Then the vial was opened, the suspension was transferred to a 15-mL plastic tube and centrifuged at 4000 RPM for 5 min. The supernatant (6.0 mL) was aspirated to a 10-mL disposable injection syringe and dispensed into a clean vial, and the vial was sealed with PARAFILM® M. The optimized scheme of the analytical method is presented in Figure 13.

4.2.5.2 Study of the effects of water pH and matrix effect

Six different soil samples (m = 1.00 ± 0.01 g) collected at six different locations in Almaty, Kazakhstan with pH = 5.2-9.8 not containing analytes were extracted with 10 mL of distilled water, 1M HCl and 1M NaOH according to Section 4.2.5.1. To each 5.0 mL of an extract, 10.0 μL of solution 2 (Section 4.2.2) and 5.00 μL of standard solution of 3-picoline with concentration 4.74±0.07 mg/L were added and analyzed using Vac-HSSPME-GC-NPD. The standard solution of 3-picoline was prepared by diluting its stock solution (Section 4.2.2) with distilled water.

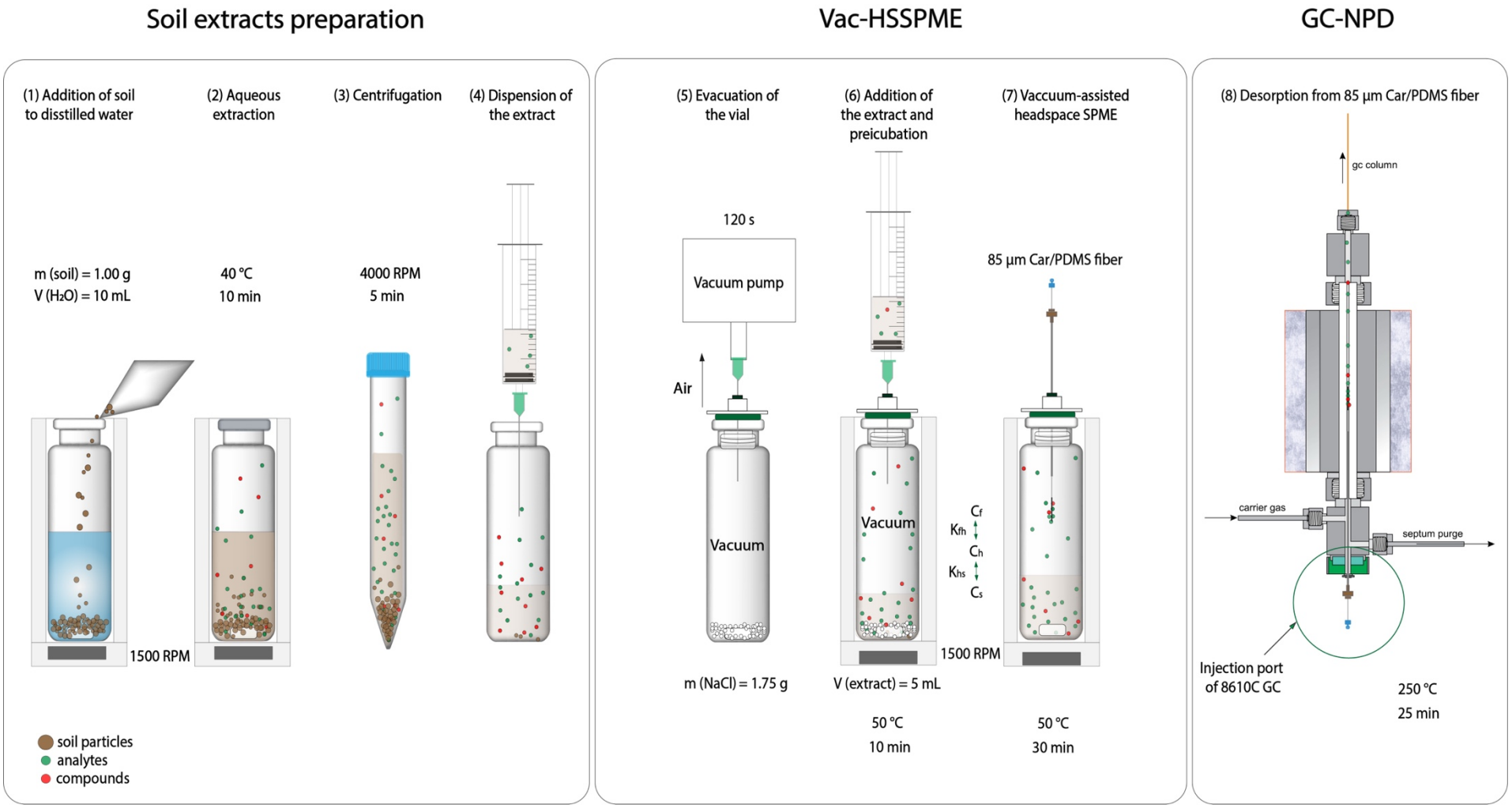


Figure 13 – Schematic illustration of the analytical method for on-site quantitation of UDMH TPs in soil

4.2.6 On-site analyses

4.2.6.1 Scientific expedition to the fall region of the first stages of Proton-M carrier rockets

GC with all equipment were transported using 2015 Toyota Hilux pickup truck and located at the distance ~100 m from one of the fall places under the 3x3 m tent (Table 20 and Figure 14). Samples from two other fall places (located at the distance of about 10 km, Table 20) were transported to this site using the pickup truck. Electricity was supplied to the GC and other necessary equipment from the 4-kW gasoline-fueled generator (Zubr, Russia). Total power consumption of the GC and all sample preparation equipment was always less than 1 kW. In the first day of the on-site measurements, there was a noticeable increase in baseline noise on the chromatograms. The noise was 1.9±0.5 mV, which was 3.6 times higher than the laboratory noise (0.5 mV) recorded before the expedition (16-17 June 2024). In the second day, the noise level returned to the laboratory levels.

Table 20 – Sampling sites of soil (map is provided in ANNEX B) during a scientific expedition to the fall places of first stage of Proton-M carrier rockets (Ulytau region, Kazakhstan)

Site code	Payloads	Samples	Sampling depth (cm)	Sampling date	Launch date	Location
Site 1 (with GC)	Luch-Kh/ Olimp-K 2	1_1-1_9	50	20-21/06/2024	13/03/2023	47°18'39"N 66°46'43"E
		1_10-1_12	100			
Site 2	Elektro-L 4	2_1-2_4	50	22/06/2024	05/02/2023	47°21'54"N 66°47'48"E
		2_5	0-20			
Site 3	JCSat 11	3_50_1-3_50_4	50	23/06/2024	06/09/2007	47°16'20"N 67°05'02"E
		3_100_1-3_100_4	100			



Figure 14 – 8610C GC-NPD with all equipment under the 3x3 m tent during on-site measurements on 20-26 June 2024

4.2.6.2 Sampling of soil at the fall regions of the first stages of Proton-M carrier rockets

From Site 1, nine samples (1_1 - 1_9) (approx. 0.2 kg of each) were collected on June 20, one meter apart at a depth of 50 cm. On June 21, three additional samples (1_10 - 1_12) were taken at 100 cm depth. From Site 2, four samples (2_1 - 2_4) one meter apart at a depth of 50 cm and one sample (2_5) from the surface were collected on June 22. On June 23, eight soil samples from four boreholes (3_50_1 - 3_50_4) at a depth of 50 cm and 100 cm (considering possible deep migration of UDMH and its transformation products) were collected at Site 3. After sampling, soils were immediately passed through a 1 mm sieve, placed in airtight polyethylene zip-lock bags and stored in the dark until analysis. Soils with high water content (samples from 100 cm depth), where separation was not possible, were not sieved.

4.2.6.3 Sampling and screening of analytes

For application of the developed method, a scientific expedition to the fall region of the first stages of Proton-M carrier rockets (Ulytau region, Kazakhstan) was organized in June 2024 (Section 4.2.6.1). Soil samples were collected from three fall places (Table 20). Sampling from the depth was conducted using Edelman augers (Eijkelkamp, The Netherlands) (Figure 15).



Figure 15 – Soil sampling using the Edelman auger

On-site screening of UDMH TPs in collected soil samples was conducted on the sampling days, except samples from Site 3, which were tested one day later. Soil sample (1.00 ± 0.01 g) was placed into a 20-mL vial, then was sealed with a modified Mininert® valve and air-evacuated for 20 s [119]. The vial was located in the thermostat heated to 50 °C. The sample was incubated for 10 min and extracted with 85-µm Car/PDMS fiber exposed in the headspace above a sample for 15 min. After

extraction, the SPME fiber was introduced into the 8610C GC inlet for >25 min desorption of analytes at 250 °C and analysis using the parameters provided in Section 4.2.4. Retention times of the analytes on chromatograms of the control sample were used for their identification (Table 21).

Table 21 – Retention times of analytes on chromatograms obtained on-site using 8610C GC-NPD

Analyte	Retention time ± SD (min)
Pyrazine	5.03±0.06
1-MPA	5.76±0.07
NDMA	7.12±0.08
DMF	7.65±0.11
MTA	13.15±0.11
MFA	14.63±0.12
1*H*-Pyrazole	17.93±0.13
3-MPA	18.80±0.15

4.2.6.4 Quantitation of the analytes in soil using external standard calibration

For on-site quantitation of UDMH TPs in soil samples, obtained aqueous extracts were analyzed using Vac-HSSPME-GC-NPD. Samples only from Site 1 were quantified: three samples from 50 cm depth (1_7-1_9) and three samples from 100 cm depth (1_10-1_12). Concentrations of analytes in soil (C_s, μg/kg) were calculated using:

$$C_s = \frac{C_e V}{m} \quad (13)$$

where: C_e is the concentration of an analyte in aqueous extract (μg/L), V is the volume of distilled water added to soil (L), m is the mass of a soil sample (kg). Concentrations of analytes in aqueous extracts were determined using matrix-matched external standard calibration. Calibration standards were prepared in six aqueous extracts (obtained using the procedure described in Section 4.2.5.1) from soil sample 1_6 (where analytes were not detected during screening): 5.00 μL, 10.0 μL, 20 μL, 50 μL and 100 μL of solution 1 were added to 6.0 mL of soil extracts in a 20-mL glass vial. Obtained standards were analyzed using Vac-HSSPME-GC-NPD according to Sections 4.2.3-4.2.4. The results were used for construct external standard calibration plots "$S = k\ C_e$". LODs were defined as the concentration at which the analyte signal reached a signal-to-noise (S/N) ratio of 3:1. LODs were calculated by multiplying the lowest real analyte concentrations determined in the aqueous extracts by a peak height, and dividing by an average noise near the peak and 3. Similarly, LOQs were established using a S/N 10:1.

4.2.7 Analyses in the laboratory

Soil samples collected in the field were transported to the laboratory in Almaty, Kazakhstan (located about 1500 km driving distance from the sampling sites) and analyzed using 6890N/5975C GC-MS (Agilent, USA) equipped with a Combi-PAL (CTC Analytics AG, Switzerland) autosampler and split/splitless injection port at the parameters described below.

Analytes were desorbed in the GC inlet equipped with SPME glass liner (Supelco, USA) in splitless mode for 5 min at 240 ºC. Septum purge at 50 mL/min was activated 5 min after the fiber introduction to the inlet. The 30 m × 0.25 mm × 0.25 μm HP-INNOWax column was used for the separation under the constant flow rate of helium (1.0 mL/min). Oven temperature was programmed from 40 °C (held for 5 min) to 100 °C at 5 °C/min ramp, to 140 °C at 10 °C/min ramp, and to 240 °C (held for 5 min) at 20 °C/min ramp. Total run time was 31 min. MS detection was conducted in selected ion monitoring (SIM) mode. All ions were split to six groups at 100 ms dwell time for quantification and 50 ms for confirmation ions (Table 22). Temperatures of interface, ion source and quadrupole were 250, 230 and 150°C, respectively. Solvent delay was set to 7 min.

Screening of UDMH TPs in collected samples was conducted according to the procedure described in Section 4.2.6.2, and for quantitation of UDMH TPs, aqueous extracts of samples were prepared (Section 4.2.5.1). For calibration, nine aqueous extracts of soil sample 1_6 were obtained using the procedure described in Section 4.2.5.1 and spiked with UDMH TPs (Section 4.2.2). The results were used for construct external standard calibration plots "$S = k\,C_e$".

Table 22 – MS detection program for the UDMH transformation products in the SIM mode

Analyte	Retention time (min)	*m/z* of quantification ion (dwell 100 ms)	*m/z* of confirmation ion (dwell 50 ms)	Group	Start time (min)
Pyrazine	11.07±0.08	80	53	1	7.00
1-MPA	12.41±0.11	82	54		
NDMA	14.40±0.10	74	42	2	14.00
DMF	15.09±0.16	73	44		
MTA	20.47±0.06	83	56	3	20.00
MFA	21.43±0.04	59	-	4	21.00
1*H*-Pyrazole	23.00±0.04	68	41	5	22.30
3-MPA	23.28±0.03	82	54	6	23.20

4.2.8 Study of spike recoveries of the analytes from different soils

Six soil samples from the fall places (without or with a negligible content of the analytes) were chosen for the experiment: 1_7, 1_9, 2_3, 2_4, 3_50_1, and 3_50_3. A sample (1.00 ± 0.01 g) was weighed in 20-mL vial and spiked with 10.0 μL of aqueous solution of analytes with concentrations ranging from 460 mg/L (DMF) to 550 mg/L (MTA). After spiking, the vials were left in darkness to

equilibrate for 18 h at room temperature. Then the aqueous extracts of prepared samples were analyzed using Vac-HSSPME-GC-MS. For preparation of the standard solution of analytes in distilled water with the same concentration as should be after exhaustive (100% recovery) extraction of spiked soil, 25 µL of the aqueous solution used for soil spiking were injected into a 25-mL volumetric flask that was immediately filled to the graduation mark. The standard solution was analyzed by Vac-HSSPME-GC-MS in two replicates at the same parameters. Spike recoveries (R, %) of analytes from soil aqueous extracts was determined using:

$$R = \frac{S_e}{S_s} \times 100\% \quad (14)$$

where: S_e is the analyte peak area for aqueous extract, S_s is the mean analyte peak area for standard solution.

4.2.9 Greenness evaluation of the analytical method

Analytical Greenness (AGREE, the calculator is available at https://mostwiedzy.pl/AGREE) [60] and Analytical Greenness Metric for Sample Preparation (AGREEprep, http://mostwiedzy.pl/AGREEprep) [130] metrics were used to assess the environmental sustainability of the analytical method.

AGREE is based on twelve principles of Green Analytical Chemistry (GAC), including the minimisation of energy and reagent consumption, the reduction of waste and the enhancement of safety [60]. The AGREEprep software requests data for ten assessment steps, ranging from the location of the sample preparation, the use of hazardous and renewable materials, the time spent and the energy consumption of the method [130]. The result of the method evaluation was provided by a visual representation in a radar chart (AGREE) and a circular pictogram (AGREEprep) with a circle in the centre, with cumulative scores varying between 0 and 1, with higher scores indicating greater adherence to green chemistry practices.

4.3 Results and discussion

4.3.1 Effects of water pH on Vac-HSSPME responses and matrix effect

Matrix effect in HSSPME is caused by different extraction effectiveness of analytes from different samples. Preliminary extraction of analytes from soil with water decreases the effect of soil moisture content [118], but extracts could be obtained with water of different pH, particularly, basic [90]. The goal of this experiment was to study the variability of the Vac-HSSPME effectiveness of analytes from soil extracts obtained using distilled water, 1M HCl and 1M NaOH and spiked with analytes and internal standard (3-picoline). The responses of all UDMH TPs except DMF and MFA for extracts obtained using 1M HCl were more than five times lower than from other extracts (Figure 16), which can be caused by basic properties of most UDMH TPs and lower volatilities of their protonated (at lower pH) forms [90]. Therefore, 1 M HCl was excluded from further consideration.

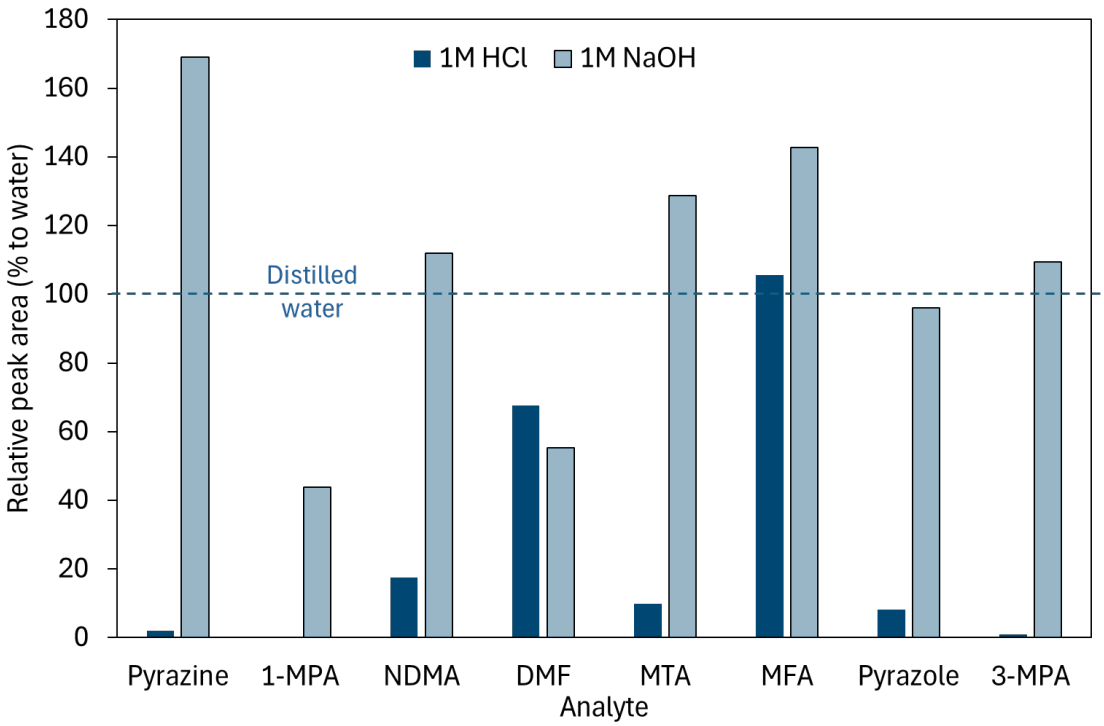


Figure 16 – Relative peak areas of analytes obtained after Vac-HSSPME of 1M HCl, distilled water and 1M NaOH extracts from six different soils (extracts were spiked with analytes)

Relative standard deviations of peak areas between six different soil extracts were used as the dependent variable indicating the matrix effect (Figure 17). RSDs of UDMH TPs peak areas between six different soil extracts obtained with distilled water varied from 22% (NDMA and DMF) to 38% (MFA). For extracts obtained using 1M NaOH, RSDs ranged from 21% (MFA) to 55% (pyrazine). For 1M HCl, the RSDs were from 15% (pyrazine) to 116% (*1H*-pyrazole). The obtained results indicate that the Vac-HSSPME effectiveness of UDMH TPs from soil extracts obtained using distilled water is less variant, and the matrix effect should be lower.

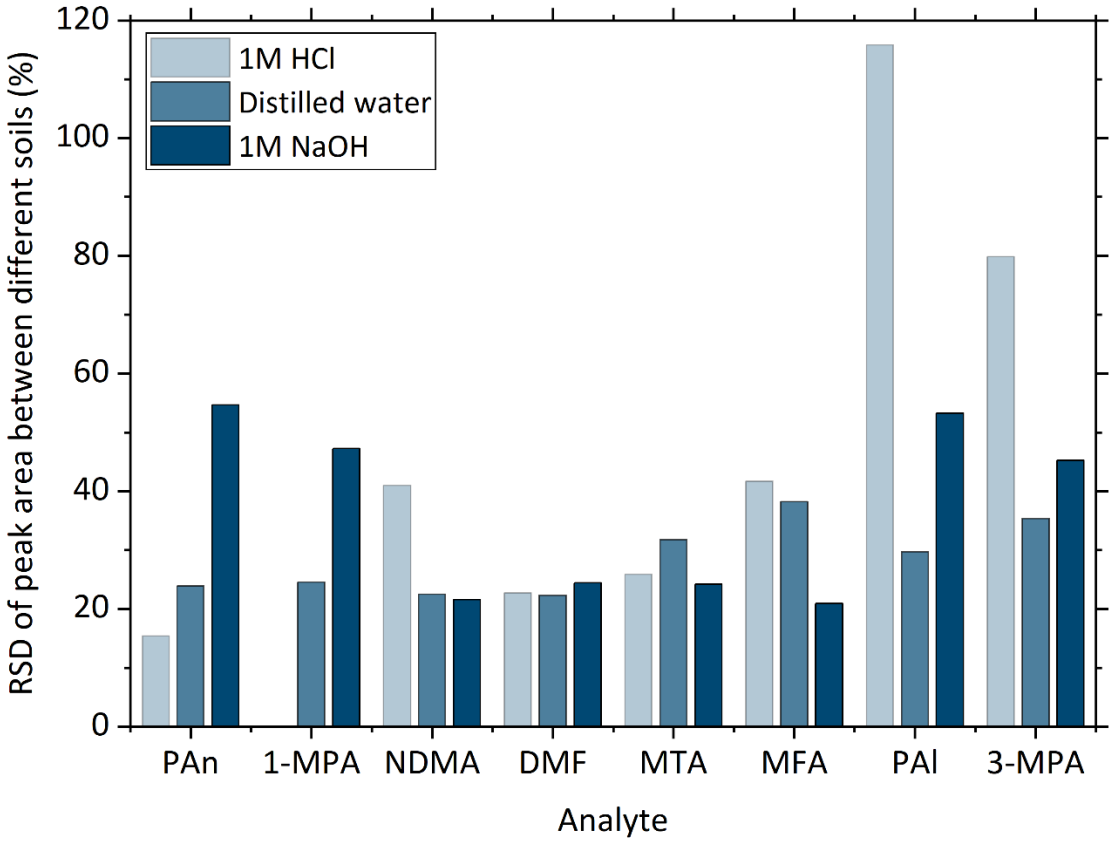


Figure 17 – Relative standard deviations of UDMH TPs peak areas obtained after Vac-HSSPME from 1 M HCl, distilled water and 1 M NaOH extracts from six different soils (extracts were spiked with analytes)

Internal standards are often used for matrix effect control and more accurate quantitation of VOCs in soil samples using HSSPME [50]. However, the physicochemical properties of the potential internal standard must be similar to the properties of analytes. 3-Picoline, that was previously used as the internal standard for the quantitation of UDMH TPs [131], has been tested for the matrix effect control in this study. The results of the experiment showed that RSDs of the ratios of peak areas of the analytes and 3-picoline (S_a/S_{is}) were much higher than RSDs of the peak areas of analytes: 89-117% for distilled water, 103-218% for 1M NaOH and 77-138% for HCl (Table 23). They indicate that the use of 3-picoline as an internal standard for the quantitation of UDMH TPs in soil extracts using Vac-HSSPME is not feasible because it does not allow effective matrix effect control.

Table 23 – RSDs of the ratios of peak areas of analytes and 3-picoline (Sa/Sis) in chromatograms of extracts from soils obtained using Vac-HSSPME

Extractant	RSDs (%) of the ratios of peak areas of analytes and 3-picoline (S_a/S_{is})							
	Pyrazine	1-MPA	NDMA	DMF	MTA	MFA	1*H*-Pyrazole	3-MPA
H_2O	117	112	99	106	108	89	106	114
1M NaOH	103	218	196	217	200	212	216	190
1M HCl	138	-	94	97	87	77	85	81

4.3.2 On-site screening of UDMH TPs in soils contaminated with the rocket fuel

Before quantitative analyses, a faster and simpler screening of analytes in collected soil samples was conducted using Vac-HSSPME (without any additives) to disclose contaminated samples. In samples 1_1-1_3 and 1_7-1_10, DMF (except samples 1_2 and 1_3) and MTA (except sample 1_1) were the most frequently detected analytes. Higher signals were observed for MTA, with the highest chromatographic peak area (711 mV) detected in sample 1_10. The greatest number of analytes (all except 1-MPA) was detected in sample 1_7, however, their responses were slightly higher than the noise level (Table 24). On Site 2, only MTA was detected in samples 2_1, 2_3 and 2_5 out of the five samples analyzed. The highest MTA signal (190 mV s) was detected for sample 2_5, exceeding the signals of samples 2_1 and 2_3 by 9 and 15 times, respectively. At Site 3, only MTA (*S/N* 6-37) was detected in five of the eight collected samples. Because of the higher detected responses of the analytes, Site 1 was chosen for quantitation using the developed method.

Table 24 – Screening results of analytes in soil samples contaminated with the rocket fuel collected from fall places of first stages of Proton-M carrier rockets (Ulytau region, Kazakhstan) obtained on-site using GC-NPD

Sample	Signal-to-noise ratios of analytes detected in soil samples							
	Pyrazine	1-MPA	NDMA	DMF	MTA	MFA	1*H*-Pyrazole	3-MPA
	Site 1							
1_1	-	-	-	4.6	-	-	-	-
1_3	-	-	-	-	8.7	-	-	-
1_6	-	-	-	-	-	-	-	-
1_7	12	-	8	15	12	17	10	6
1_8	-	-	-	11	20	-	-	-
1_9	-	-	-	7.8	18	4.8	-	-
1_10	-	9.8	-	11	200	-	-	-
	Site 2							
2_1	-	-	-	-	4.9	-	-	-
2_3	-	-	-	-	19	-	-	-
2_5	-	-	-	-	176	-	-	-
	Site 3							
3_50_2	-	-	-	-	37	-	-	-
3_100_2	-	-	-	-	7	-	-	-
3_50_3	-	-	-	-	19	-	-	-
3_50_4	-	-	-	-	10	-	-	-
3_100_4	-	-	-	-	6	-	-	-
Note: - not detected.								

4.3.3 On-site quantitation of UDMH TPs in soil

During on-site measurements, control samples were monitored on three different days (interday), and multiple analyses were performed on the same day (intraday). The relative standard deviations (RSD) for analytes were 3.9-25% and 2.9-14%, respectively, indicating adequate precision. Potential interferences were checked by analyzing blank matrix samples from uncontaminated sites, and no interfering peaks were detected at the retention times of the analytes.

The developed method was applied for the quantitation of analytes in six soil samples (1_7-1_12). The concentrations of detected analytes were calculated from the slopes of the calibration plots obtained using standards prepared with the extract from a similar uncontaminated (according to the screening) soil 1_6 from the same Site 1 (Table 25). All analytes (except NDMA) were detected in samples 1_11 and 1_12 at concentrations (except MFA) 9.2-75 and 18-139 µg/kg, respectively. In sample 1_10, the highest concentration of a single analyte was determined – MTA at 8500 µg/kg. Among other analytes, only 1-MPA was detected in this sample at 23 µg/kg. 1-MPA was detected in all samples at 6.9-37 µg/kg. Pyrazine (7.5 µg/kg) and DMF (150 µg/kg) were detected only in samples 1_7 and 1_9, respectively.

To account for possible interferences on the chromatograms, LODs were estimated using results obtained for real samples with lowest determined

concentrations. Determined LODs ranged from 3 (1-MPA) to 60 (MFA) µg/kg (Table 25). LODs determined in the laboratory using chromatograms of calibration standards with the lowest concentrations were 1.3 (for 3-MPA and MTA), 2.3, 3.3, 13 and 15 times (for 1*H*-pyrazole, MFA, NDMA and pyrazine, respectively) lower compared to the LODs determined in the field using real samples. This difference could be caused by the greater noise level when analyzing real samples in field conditions. For 1-MPA and DMF, LODs determined in the laboratory were 1.7 and 1.5 times higher, respectively, than in the field.

LODs determined in the laboratory for aqueous standards were 3.3, 11.4, 11.6, 12.5, 22, 23 and 33 times lower for 1*H*-pyrazole, MTA DMF, pyrazine, MFA, 3-MPA and NDMA, respectively, than reported in our previous article on the development of the method for on-site quantification of UDMH TPs in water [129]. This was probably achieved due to a more accurate air flow adjustment in the NPD using an external mass flow meter. The GC manufacturer recommended 2 psi for air flow 100 mL/min, but the step size on the control panel is only 1 psi, causing major uncertainties in the flow rate. At the same time, LOD for 1-MPA increased 2.5 times, which could be caused by the negative impact of the increased (from ~70 to 100 mL/min) air flow rate on its ionization effectiveness.

4.3.4 Quantitation of UDMH TPs in collected soils in laboratory using GC-MS

For the quantitation of the analytes, calibration plots in the concentration range 1.2-32,700 µg/kg with determination coefficients of 0.809-0.993 were obtained. Concentrations of the detected UDMH TPs were calculated using the slopes presented in Table 26. Only two analytes were detected and quantified: pyrazine in sample 1_8 with a concentration of 1.7 µg/kg (equal to its LOD), and MTA in sample 1_10 at 6200 µg/kg (1.4 times lower than the concentration detected on-site). The difference in MTA concentrations determined using on-site GC-NPD and in-laboratory GC-MS in sample 1_10 is in the range of standard deviations. Other observed differences could be caused by the different selectivity and sensitivity of these instruments to different compounds.

Table 25 – Concentrations of analytes in soil samples determined on-site using the developed method

Analyte	Linear range (mg/kg)	R^2	Slope (mV s kg/µg)	LOD (µg/kg)	LOQ (µg/kg)	Analyte concentration (µg/kg) in soil samples					
						17	1_8	1_9	1_10	1_11	1_12
Pyrazine	0.21-2.1	0.9791	2.7	6	20	7.5	-	-	-	9.2	18
1-MPA	0.20-2.0	0.9693	4.5	3	11	15	7.6	6.9	23	18	37
NDMA	1.03-10.3	0.9880	0.055	27	91	-	-	-	-	-	139
DMF	0.96-9.6	0.9827	0.089	10	33	-	-	150	-	75	89
MTA	1.13-11.3	0.9780	0.12	9	29	-	-	-	8500	28	81
MFA	5.2-52	0.9629	0.018	60	190	-	-	-	-	400	3600
1*H*-Pyrazole	1.03-10.3	0.9921	0.15	14	47	-	-	-	-	44	131
3-MPA	1.3-10.3	0.9936	0.27	4	13	-	-	-	-	23	64
Note: - not detected											

Table 26 – Slopes of analytes obtained using external standard calibration in laboratory by GC-MS

Analyte	Linear range (µg/kg)	R^2	Slope
Pyrazine	1.2-250	0.9903	64958
1-MPA	1.2-230	0.8090	27518
NDMA	30-5940	0.9754	3592
DMF	140-27800	0.9728	988
MTA	160-32700	0.9774	1426
MFA	30-29700	0.9167	491
1*H*-Pyrazole	6-5940	0.9795	6343
3-MPA	30-5940	0.9930	15771

4.3.5 Spike recoveries of the analytes from different types of soil

The goal of this experiment was to study the recovery of the analytes during aqueous extraction from different types of soil collected in the field and estimate the matrix effect. Spike recoveries of the analytes during the experiment varied from 82±8% for pyrazine to 123±17% for MFA (Table 27) indicating their high extraction effectiveness from the studied soils to water. Highest spike recoveries were 181% and 146% for MFA in sample 1 and DMF for sample 4, which could be caused by overlapping matrix peaks. These two data points were considered as outliers and were not included in calculations for the mean values and standard deviations. RSDs between different soil samples were from 5% (for 3-MPA) to 16% (for DMF and MTA) (Figure 18). These results prove that the proposed approach based on the preliminary extraction with water and matrix matched calibration provide an effective minimization and control of the matrix effects.

Table 27 – Recoveries (%) of analytes from soil samples during aqueous extraction

Code	Recovery (%)							
	Pyrazine	1-MPA	NDMA	DMF	MTA	MFA	1*H*-Pyrazole	3-MPA
1	96	91	95	119	118	181*	97	97
2	84	91	90	92	90	117	88	91
3	79	80	83	92	115	140	94	94
4	81	83	83	146*	82	112	83	85
5	71	81	83	90	81	99	83	87
6	80	77	73	129	112	146	88	94
Mean	82	84	85	104	100	123	89	91
SD	8	5	7	16	16	17	5	4
* Outlier								

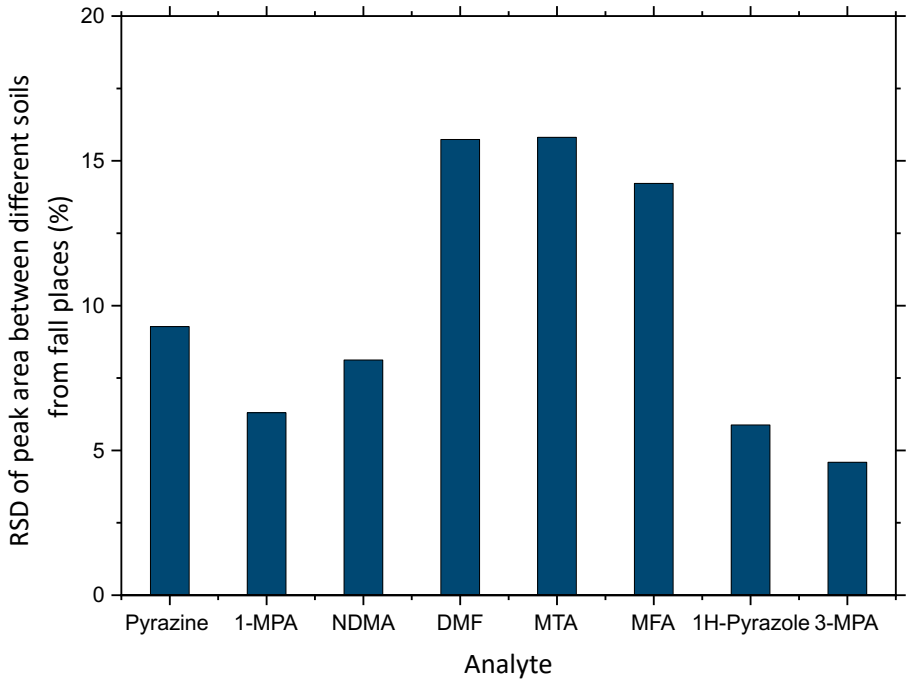


Figure 18 – Relative standard deviations of UDMH TPs peak areas obtained after Vac-HSSPME of aqueous extracts from six different soils collected from fall places of first stage of Proton-M carrier rockets (Ulytau region, Kazakhstan)

4.3.6 Greenness evaluation of the analytical method

The greenness of analytical methods is an important factor to consider during environmental monitoring. The greenness of a method aims at reducing chemical waste, lowering energy consumption, and assessment of overall environmental impact of the method. In this study, the developed method was assessed using AGREE [60] and AGREEPrep [130] metrics. According to the AGREE and AGREEPrep calculations, the method scores were 0.59 and 0.56, respectively, demonstrating moderate greenness. While these scores are promising, they highlight specific areas for improvement such as automation and throughput increase of sample preparation and analysis. The use of portable GC and SPME as a sample preparation tool brings a significant effect on the greenness of method.

The relatively high scores across these metrics confirm that the developed method is a greener alternative compared to traditional laboratory-based approaches, since it doesn't use high energy consumption equipment which requires a powerful vacuum pump. On-site application significantly reduces the need for sample transport and storage, which are major contributors to the environmental footprint of conventional methods. The combination of vacuum-assisted solid-phase microextraction (Vac-HSSPME) and portable gas chromatography (GC-NPD) not only meets the analytical requirements but also aligns well with the principles of green analytical chemistry.

Compared to other available methods, only the developed method has been optimized for a portable instrument and tested for on-site quantification of UDMH TPs in soil. The method of Zhubatov et al. [110] for quick quantitation of MTA was

recommended by authors for on-site application, but the developed method is greener because it does not require toxic organic solvents for extraction and allows simultaneous quantitation of multiple analytes (including MTA). In addition, the developed method provides two orders of magnitude lower LODs for MTA. LODs for the developed method are comparable to the LODs for the method based on HSSPME-GC-MS [117] (except NDMA). The Vac-HSSPME-GC-MS method for sand samples [119] provides lower LODs, but this can be caused by the higher extraction effectiveness of analytes from sand. Preliminary aqueous extraction of analytes from soil makes the LODs less dependent on the properties of analyzed samples because the method becomes less susceptible to matrix effects caused by different SPME effectiveness for different samples.

4 Chapter conclusion

In this study, a new green analytical method was developed for accurate on-site quantitation of eight main unsymmetrical dimethylhydrazine transformation products in soil using Vac-HSSPME and portable GC-NPD. To minimize matrix effects and improve accuracy, prior to Vac-HSSPME, aqueous extracts from soils were obtained, centrifuged, and NaCl was added. Vac-HSSPME of analytes from aqueous extracts demonstrated a lower variability in extraction effectiveness of analytes and matrix effect compared to extracts obtained using 1M HCl and 1M 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 developed method can be recommended for on-site quantitation of main UDMH TPs when results are quickly required, particularly, after accidents with rockets resulting in major fuel spills. According to AGREE [60] and AGREEPrep [130] metrics, the developed method is a greener alternative compared to traditional laboratory-based approaches. 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 analysed 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, improvements can be realized by incorporating commercially available

portable GC-MS instruments, which promise improved selectivity, lower detection limits and faster separation.

It has been the first time when Vac-HSSPME was used for the on-site quantitation of environmental pollutants in soil. On-site application of Vac-HSSPME did not represent additional technical challenges, only a vacuum pump had to be transported to the field.

5 AUTOMATION POSSIBILITIES AND PROPOSAL OF METHODOLOGICAL RECOMMENDATIONS FOR THE DEVELOPMENT OF ANALYTICAL METHODS FOR ON-SITE DETERMINATION OF ENVIRONMENTAL POLLUTANTS

The development of simple and accurate methods for on-site determination of VOCs requires not only methodological optimization of SPME parameters, but also systematic automation of the entire analytical chain. The automation of methods is crucial because it ensures metrological stability, kinetic precision, data integrity, operator safety, and scalability of environmental monitoring systems. Automation improves the accuracy of analyses by minimizing human-induced variability, thereby ensuring greater consistency and repeatability of results. Additional errors can be caused by fluctuating on-site conditions during manual sampling, but this risk can also be reduced by automated systems, as data acquisition processes can be standardised.

The baseline instrument used in this study is the SRI 8610C GC (Figure 3), which is a highly flexible gas chromatograph, ideal for VOCs analysis in environmental and industrial applications. Its modular design allows for customization, including the ability to handle various detectors, such as PID, NPD and FID.

Automation of analysis with HSSPME or Vac-HSSPME and SRI GC is possible by conversion of SRI 8610C GC to 8610V configuration and integration with HTA Autosampler. To enable automated field operation, the system can be converted to a vertical-oven configuration (8610V), which allows for the mechanical integration of an autosampler module. The integration of the HTA autosampler with the SRI GC can be achieved through straightforward hardware connections and software interfacing. The vertical oven allows to connect and use GC system with autosampler as a whole instrument.

The modernization will include: 1) replacement of the horizontal oven with a vertically configured one; 2) installation of a rigid autosampler mounting frame; 3) integration of electronic start/ready synchronisation signals between the GC and the autosampler; and 4) stabilisation of the inlet and detector control modules for unattended operation.

The HTA autosampler communicates with the SRI GC through a control interface, allowing synchronized operation between sample injection and chromatographic analysis. The autosampler is physically connected to the SRI GC directly into the GC injection port to which headspace sample is delivered. SRI 8610V GC and HTA autosampler doesn’t need a temperature-controlled transfer line to prevent sample loss, due to immediate injection into inlet. The autosampler's vial tray holds the samples and vials are picked up by the autosampler gripper and placed in the oven where they are simultaneously incubated and agitated in order for headspace extraction. The HTA autosampler is controlled via GC software, allowing for full automation of the headspace sampling process. Parameters such as

incubation time, agitation speed, and programmed into the autosampler software, ensuring precise and consistent operation for each sample.

Sample conditioning prior to extraction represents a significant source of analytical variability in manual workflows. For classical headspace SPME (HSSPME), typical process of automation (using 20-mL crimp-top glass vials and aluminium caps with PTFE/silicone septa) includes:

– precise control of fiber exposure time;

– temperature control during extraction;

– reproducible agitation regimes;

– automated desorption timing in the GC inlet.

However, in the case of vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME), additional automation measures are indispensable due to the requirement to maintain a highly hermetic and pressure-stable microenvironment inside the vial. Unlike conventional HSSPME, the extraction efficiency in Vac-HSSPME is directly governed by the absolute pressure within the system; therefore, even minor pressure deviations may alter analyte diffusion rates, phase equilibrium, and overall extraction kinetics.

To enable reliable automation of Vac-HSSPME, the following parameters must be carefully optimized and integrated into the automated workflow:

– implementation of vacuum-compatible, gas-tight vial caps ensuring long-term hermetic integrity;

– continuous or pre-extraction monitoring of reduced-pressure conditions within the vial;

– automated leak detection prior to fiber exposure;

– precise synchronization of extraction time and GC injection under controlled and reproducible pressure conditions.

The magnetic properties of the metallic body of the cap allow easy use with an autosampler, without use of magnetic caps.

Because mass transfer in Vac-HSSPME is highly sensitive to pressure fluctuations, uncontrolled manual handling may lead to significant variability in extracted analyte mass. The incorporation of automated pressure control and leak diagnostics ensures stabilization of the analyte extraction, enhances kinetic reproducibility, and substantially reduces the relative standard deviation of field measurements.

Thus, automation in Vac-HSSPME is a crucial requirement for achieving metrologically reliable and reproducible on-site quantitative analysis.

Results obtained during implementation of the study allowed to develop the following **recommendations for the development of analytical methods for on-site quantification of environmental pollutants:**

1) Sample preparation for an on-site method should be simple and fast because of the limited time and more difficult conditions compared to a laboratory.

2) Sample preparation should provide a high preconcentration factor of analytes because of the lower sensitivity of portable instruments.

3) Solid-phase microextraction provides the required level of simplicity, speed and preconcentration for on-site quantification of environmental pollutants.

4) Vacuum-assisted headspace solid-phase microextraction of environmental pollutants from samples of water and soil can be conducted on-site for lower limits of detection at lower extraction times.

5) For greater accuracy, calibration can be conducted on-site using matrix-matched external standards or standard addition.

6) GC columns with a narrower internal diameter provide narrower peaks, faster separation and lower consumption of carrier gas, and can be recommended for on-site quantitation of environmental pollutants.

7) For faster method development, similar existing methods can be adapted to on-site application with a portable instrument.

8) To save time and other resources, before quantitative analyses, screening can be conducted at parameters providing the highest responses of analytes. Only samples where analytes were detected, can be analyzed quantitatively. If analytes are not detected, quantitative analyses can be avoided to save resources.

9) For more efficient method development, modeling (e.g., in COMSOL Multiphysics®) should be used.

10) For faster and more accurate measurements, portable gas chromatograph should be equipped with mass spectrometric (MS) detector.

11) Laptop should be connected to Internet to avoid remote instrument control and data processing, particularly when field personnel has limited time and/or qualification for this purpose. Starlink internet can be used at remote locations where mobile networks are not available.

12) If electric power generator uses gasoline or diesel, they should be located at a longest possible distance from the sampling location to avoid contamination of samples with VOCs. In addition, the fuel should be stored in air-tight containers.

13) Sensitivity (determined using signal-to-noise ratio) of a portable instrument should be checked after transportation and regularly during on-site measurements using, e.g., control sample. GC should be constantly checked for leaks using a suitable leak detector.

14) During a method validation, results of quantitation should be compared with results obtained using existing analytical methods.

15) A developed method should be tested on-site on real samples, which should allow disclosing its drawbacks. The results of such testing will be important for improvement of the method to make it more reliable and accurate.

The analytical methods developed and adapted in this dissertation for the quantification of VOCs in environmental matrices were specifically designed for on-site application using solid-phase microextraction and portable gas chromatography. The methods include:

1) On-site quantification of benzene, toluene, ethylbenzene, xylenes in atmospheric air using SPME-GC-PID (Chapter 2);

2) On-site determination of unsymmetrical dimethylhydrazine transformation products in water using vacuum-assisted headspace SPME coupled with GC-NPD (Chapter 3);

3) On-site screening and quantification of unsymmetrical dimethylhydrazine transformation products in soil using vacuum-assisted headspace SPME coupled with GC-NPD (Chapter 4);

The principal objective of field implementation is to reduce the time between sampling and analytical reporting from several days (typical laboratory workflow) to several hours, thereby enabling rapid environmental risk assessment and evidence-based decision-making.

Based on the implemented analytical methods the operational workflow for field measurements was organized. The workflow integrates sampling, extraction, chromatographic analysis, calibration, data processing, and reporting into a single continuous field procedure performed using a mobile analytical materials.

Stage 1 – Arrival and setup (time will depend on the accident location) – includes:

– a briefing is conducted with field personel to define sampling objectives,

– the portable GC system is installed (vehicle trunk or temporary field laboratory),

– leak testing and detector sensitivity verification are performed,

– SPME fiber preconditioning is carried out,

– calibration standards are prepared or verified.

This preparatory phase typically requires 20-30 minutes and ensures analytical stability before sample processing.

Stage 2 – Sampling and SPME procedure combines:

– ambient air is pumped into four 250 mL calibrated gas bulbs (15 min),

– water samples are collected directly to the vials (2-5 min per sample),

– soil samples are collected using augers at defined depths (5-10 min per sample),

– HSPME is conducted for air using 85 μm Car/PDMS fiber (15 min),

– Vac-HSSPME is conducted for water using 85 μm Car/PDMS fiber (30 min),

– preliminary aqueous extraction (15 min stirring + 5 min centrifugation), followed by Vac-HSSPME using 85 μm Car/PDMS fiber from aqueous extract (30 min).

Sampling and extraction procedures can be performed in one time and completed within 30-60 minutes depending on the number of points.

Stage 3 – Gas-chromatographic analysis of samples and standards, and data processing:

– thermal desorption of analytes is performed in the modified GC inlet and chromatographic separation (35-40 min per sample + 5-10 min for oven cooling),

– peak identifications and their processing (10-15 min per chromatogram).

Consequently, the stage 3 may take around 4-5 hours depending on the number of samples.

Stage 4 – Reporting and decision support:

– preliminary verbal results: within 1-2 hours after arrival,
– complete written field report: within 5-6 hours after arrival.

As a result, the written report will include sampling description, chromatograms, calibration plots, quantified concentrations, LOD/LOQ values, interpretation relative to regulatory thresholds. This relative rapid reporting framework supports operational environmental management decisions, including restriction measures, contamination mapping, and remediation planning.

CONCLUSION

Within the framework of dissertation three analytical methods based on solid-phase microextraction and gas chromatography have been tested for quantification of:

– benzene, toluene, ethylbenzene and *o*-/*m*-/*p*-xylene (BTEX) in air;

– eight main transformation products (TPs) of unsymmetrical dimethylhydrazine (UDMH) in water;

– eight main UDMH TPs in soil.

As a result of the research, the following conclusions were made:

1. For quantification of BTEX in air, solid-phase microextraction (SPME) and gas chromatography with photoionization detector (GC-PID) were used. Quantitation was conducted using standard addition calibration on four replicate air samples in 250 mL calibrated gas bulbs, one of which was spiked with BTEX standard. Optimal extraction time for detecting lower concentrations of ethylbenzene and xylenes was 15 min. In Talgar, benzene concentrations 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. For quantification of transformation products of UDMH TPs in water, vacuum-assisted headspace solid-phase microextraction (Vac-HSSPME) and gas chromatograph with nitrogen-phosphorous detector (GC-NPD) were used. Compared to the known method based on Vac-HSSPME-GC-MS, the method based on GC-NPD provided 133-700 times higher LODs, most probably, due to a lower selectivity and higher noise of the NPD compared to the MS detector in selected ion monitoring (SIM) mode. 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). External standard calibration using standards of analytes prepared in distilled water can be used for accurate quantitation of all UDMH TPs (except DMF) in water samples providing spike recoveries 73.3% - 90.0% from different types of water.

3. For quantification of UDMH TPs in soil, Vac-HSSPME and GC-NPD were used. To minimize matrix effects and improve accuracy, prior to Vac-HSSPME, aqueous extracts from soils were obtained, centrifuged, and NaCl was added. Vac-HSSPME of analytes from aqueous extracts demonstrated a lower variability in extraction effectiveness of analytes and matrix effect compared to extracts obtained using 1M HCl and 1M 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 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.

The methods for on-site quantification of UDMH TPs in soil and water can be recommended for application on fresh places of UDMH spill, particularly after major accidents with carrier rockets. The method for on-site quantification of BTEX in air can be recommended for application at remote locations when long transportation of samples can result in losses of analytes and poor accuracy. In the future, the developed methods can be improved by using a portable GC-MS instead of a GC-NPD. In addition, the development of the portable GC or GC-MS optimized for automated on-site SPME seems prospective and is considered by our research group as the potential topic for the future research project.

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ANNEX A

Location of atmospheric air sampling point in Talgar (Almaty region, Kazakhstan)



The satellite image was taken from Google Earth.

ANNEX B

Map of soil sampling locations in the Ulytau region (Kazakhstan)



The satellite image was taken from Google Earth.