ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD)
in the educational program "8D05301 – Chemistry"

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Development of comprehensive methods for organic compounds determination in water.

Characterization of the work. This study aimed to develop reproducible, robust, and sensitive methods for accurate determination of prevalent biogenic volatile organic compounds using dynamic headspace extraction with sorbent tubes coupled with gas chromatography-mass spectrometry.

The relevance and degree of development of the research topic. Biogenic volatile organic compounds (BVOCs) are the dominant source of atmospheric volatile organic compounds (VOCs), accounting for 75-90% of global VOC emissions. Due to their high reactivity and abundance, BVOCs are fundamental drivers of atmospheric chemistry, affecting photochemical oxidation, ozone production, and secondary organic aerosol (SOA) formation. As precursors to aerosol particles and cloud condensation nuclei (CCN), they influence radiative forcing, cloud characteristics, and the Earth's energy balance. Therefore, accurate quantification of BVOCs is critical for understanding air quality, the atmospheric oxidative capacity, and global climate patterns. Within the broad range of BVOCs, specific subgroups play distinct biogeochemical roles. Sulfur-containing compounds, particularly dimethyl sulfide (DMS) and its precursor dimethylsulfoniopropionate (DMSP), hold a unique place in the marine sulfur cycle and climate regulation. DMS is the most abundant biogenic sulfur compound in the atmosphere and constitutes a significant pathway for transporting sulfur from aquatic systems to the atmosphere.

In addition to sulfur compounds, BVOCs such as 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal serve as important indicators of biological and biogeochemical processes, reflecting microbial and plant activity, the marine halogen cycle, and the formation of secondary organic aerosols that affect atmospheric chemistry, climate, and air quality. Despite their environmental relevance, the development of methods for the determination of 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, nonanal, DMS and DMSP remains a challenge. Their low levels, high reactivity, and tendency to degrade require sensitive, reliable analytical methods. Conventional techniques such as liquid-liquid extraction and solid-phase extraction are often labor-intensive, solvent-consuming, and unsuitable for high-throughput environmental monitoring. Analysis of water samples faces additional challenges due to matrix effects,

including dissolved organic matter (DOM) and ionic strength.

BVOCs have been studied in atmospheric chemistry, with a focus on their detection in air and water using GC-MS coupled with various sampling techniques. Headspace solid-phase microextraction was established as a green approach for the analysis of volatile compounds in aqueous matrices, which was later widely adopted for BVOCs in water. Using HS-SPME, several research groups successfully quantified sulfur-containing and oxygenated BVOCs, including DMS and DMSP, mainly in seawater, achieving high sensitivity but also demonstrating strong matrix and salinity effects. Purge-and-trap-based methods were developed to improve detection limits for marine BVOCs; however, these methods required large sample volumes and complex instrumentation. Conventional static headspace approaches were applied to BVOCs in water, but their relatively low sensitivity limits trace-level analysis.

Dynamic headspace extraction combined with gas chromatography-mass spectrometry (DHS-GC-MS) offers a high sensitivity, automation capability, enhanced preconcentration efficiency, and reduced matrix effects. DHS enables continuous purging of VOCs from the sample headspace onto a sorbent tube, thereby increasing analytical throughput and minimizing manual sample handling. However, despite the method's advantages, fully optimized DHS-GC-MS protocols designed for 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, nonanal, DMS, and DMSP detection in water samples do not exist.

Considering the global significance of BVOCs in atmospheric chemistry and climate regulation and the persistent analytical challenges associated with their quantification, there is an urgent need for a robust and sensitive methods for BVOCs determination. The development and optimization of DHS–GC–MS methods capable of accurately determining 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, nonanal, DMS, and DMSP in complex water samples would substantially enhance biogeochemical monitoring, improve the representation of BVOC and sulfur fluxes in climate models, and provide more reliable tools for evaluating environmental processes. The significance of this work is therefore driven by both fundamental scientific needs and practical challenges in monitoring key atmospheric and marine components within the framework of environmental analytical chemistry.

The aim of the study: Development of new methods for the determination of volatile organic compounds in water samples using the dynamic headspace technique combined with gas chromatography-mass spectrometry.

The tasks of the study:

1. To develop and validate a method for the determination of 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal in water samples using dynamic headspace extraction coupled with gas chromatography-mass spectrometry (DHS-GC-MS), and to apply the developed technique to environmental water samples.
2. To develop and validate a DHS-GC-MS method for the determination of dimethyl

sulfide and indirect quantification of dimethylsulfoniopropionate in environmental water samples.

3. Application of the developed method of dimethyl sulfide and indirect quantification of dimethylsulfoniopropionate for investigating the emissions of dimethyl sulfide during microalgae aerosolization in water.

Objects of the study: Methods for quantification of biogenic volatile organic compounds in water samples using dynamic headspace extraction with gas chromatography–mass spectrometry.

The subject of the research: Optimization of DHS-GC-MS methods for the determination of biogenic volatile organic compounds in environmental water.

The methods of the research: During this dissertation work, scientific and engineering methods were employed to formulate hypotheses, design experiments, and evaluate analytical performance. The following methods were used: dynamic headspace extraction of BVOCs from the gas phase onto sorbent tubes, followed by separation and detection by gas chromatography with mass spectrometric detection.

The scientific novelty of the research

1. For the first time, a DHS-GC-MS method for the determination of BVOCs in water was developed and applied to quantify 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal in model water samples.

2. A new DHS-GC-MS method was developed for the first time for the determination of dimethyl sulfide and indirect quantification of dimethylsulfoniopropionate in environmental water.

3. The emissions of dimethyl sulfide during microalgae aerosolization were studied for the first time using a new method for the determination of dimethyl sulfide and the indirect quantification of dimethylsulfoniopropionate in water.

The validity and reliability of the obtained results

The obtained results are valid and reliable, as all experiments used one or two independent variables, with the other variables held constant. Dependent variables reflected the main parameters of the methods, including accuracy, recovery, analyte response, limits of detection and quantification, and reproducibility. All measurements were carried out in at least three replicates. For sensitive and selective identification and separation of BVOCs, gas chromatography with mass spectrometric detection was used.

Theoretical and practical significance of the dissertation.

This work improved the theoretical and practical background of methodologies for dynamic headspace-based analysis of volatile organic compounds in water. The established relationships between trapping and drying parameters, analyte enrichment, and water building in sorbent tubes provide valuable insights into the fundamentals and challenges of DHS applied to water samples. The DHS-based method developed for indirect quantification of DMSP broadens the applicability of green sample preparation methods in combination with gas chromatography-mass spectrometry in the analysis of biogenic

compounds.

Two new analytical methods for quantification of BVOCs, namely, 2-pentanone, dibromomethane, α-pinene, Δ3-carene, nonanal, dimethyl sulfide, and dimethylsulfoniopropionate in water, were developed by systematic optimization of parameters of dynamic headspace sampling. The developed methods overcome the challenges of BVOCs quantification in water related to matrix interferences, sensitivity, robustness, automation, and sample throughput, thereby strengthening the theoretical and practical foundations of trace-level BVOCs analysis in complex aqueous matrices. Environmental laboratories can use the developed methods for determining BVOCs in water for monitoring, pollution mapping, and studying the influence of biogenic volatile organic compounds on cloud formation and climate change.

The main provisions to be defended

1) Dynamic headspace extraction coupled with gas chromatography-mass spectrometry (5977A) for the determination of 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal in 5 mL water samples, under optimized parameters including a trapping gas volume of 500 mL at 30 °C and a drying gas volume of 500 mL at 40 °C, provides detection limits of 0.05-0.31 μg L^{-1}, a coefficient of determination in the concentration range 1-200 μg L^{-1} of $R^2 \geq 0.998$, and recoveries of 100-122%.

2) Indirect determination of dimethylsulfoniopropionate via its alkaline hydrolysis product, dimethyl sulfide, using dynamic headspace extraction coupled with gas chromatography-mass spectrometry (5977A) in 5 mL water samples at the optimized parameters, including incubation temperature 30 °C, trapping gas volume 250 mL, drying gas flow rate 100 mL min^{-1}, and drying gas volume 300 mL, allows to achieve a limit of detection of 0.014 μg L^{-1}, determination coefficients of $R^2 \geq 0.998$ over the concentration range 10 - 1000 μg L^{-1}, and relative standard deviations ≤ 8.5%.

3) Determination of dimethylsulfoniopropionate via derivatization to dimethyl sulfide combined with optimized dynamic headspace extraction yields a 34-53-fold increase in analytical response relative to a static headspace-based method, at a concentration range of 10 - 1000 μg L^{-1}, lowering the limit of quantification from 7.4 μg L^{-1} to 0.048 μg L^{-1}.

Main research results.

The fully automated DHS-GC-MS method for 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal in water was proposed based on systematic optimization of analyte trapping and sorbent drying parameters. Increasing the trapping temperature above 30°C led to water accumulation in the sorbent tube and the GC column. Increasing the trapping gas volume from 500 to 1500 mL increased the standard deviation of the responses without significantly affecting peak areas. Increasing the drying temperature of the sorbent tube above 40 °C resulted in breakthrough of BVOCs from the sorbent. Sea salt addition did not cause a statistically significant change in responses for 2-pentanone, dibromomethane, α-pinene, Δ^3-carene, and nonanal ($p > 0.05$), confirming matrix robustness. In contrast, high dissolved-organic-matter (DOM) levels suppressed the signals

of dibromomethane and α-pinene by 18 % and 41 %, respectively, indicating DOM-related adsorption effects.

For dimethyl sulfide (DMS), Carbopack B sorbent tubes provided > 34-fold higher peak areas than Tenax TA, establishing Carbopack B as the optimal sorbent. The optimized DHS-GC-MS protocol for DMS and DMSP achieved the spike recoveries of 100-107 %. Alkaline hydrolysis performed by the addition of 500 µL of 10 M NaOH solution to a 5mL water sample allowed conversion of DMSP into DMS with a consistent efficiency of 19±3 % across a concentration range from 0.05 µg L^{-1} to 10.1 µg L^{-1}.

Connection of the dissertation with research and state programs.

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Publications.

The main results of this research were published in international peer-reviewed papers, including:

– 1 article in "Microchemical journal", Web of Science - Q1, Impact Factor 5.1; Scopus - 80th percentile, CiteScore 7.2 according to 2024 data. https://doi.org/10.1016/j.microc.2025.113989

– 1 article in journal "Nature portfolio journal: Climate and atmospheric science", Web of Science - Q1, Impact Factor 8.4; Scopus – 94th percentile, CiteScore 8.7 according to 2024 data. https://doi.org/10.5281/zenodo.18078207

– 1 abstract at the EAC 2025 foreign international conference (Lecce, Italy).

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

In the article "Advanced determination of biogenic volatile organic compounds in environmental water using dynamic headspace extraction" (Microchemical Journal, 2025), Bektassov M. is the first author, who made a significant contribution to the conceptualization of the study, as well as the development and validation of the methodology. He conducted experimental research, managed data processing, prepared the initial draft of the manuscript, and contributed to its revision following peer review.

In the article "Aerosolisation of microalgae: Unveiling dimethyl-sulfide emissions during bubbling" (Nature portfolio journal: climate and atmospheric science, 2026), Bektassov M. performed the DMSP analyses of DMSP and prepared the initial draft of the manuscript. He also participated in its revision following peer review.