



**AGH UNIVERSITY OF KRAKOW**

Faculty of Metals Engineering and Industrial Computer Science  
al. A. Mickiewicza 30, 30-059 Kraków, Poland

**Electrospun Fibers Group**

<http://fibers.agh.edu.pl/>

**Prof. Urszula Stachewicz, PhD, DSc, MSc**

Phone: +48 12 617 52 30

E-mail: [ustachew@agh.edu.pl](mailto:ustachew@agh.edu.pl)

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Evaluation report of the PhD thesis of Radik Mametov entitled:

*'Novel approach for Low Molecular Weight Compounds analysis using nanomaterials-assisted Laser Desorption/Ionization Mass Spectrometry and Solid-Phase Microextractionstructure'*.

The dissertation was submitted to Nicolaus Copernicus University in Toruń, Centre for Modern Interdisciplinary Technologies, Faculty of Chemistry, Department of Inorganic and Coordination Chemistry Faculty of Chemical Technology and Engineering, under the supervision of dr. hab. Paweł Pomastowski, NCU Prof, and co-supervision of dr. hab. Aleksandra Radtke, NCU Prof

The aim of PhD study of Radik Mametov was to fabricate innovative analytical devices for analysis of volatile and non-volatile low molecular weight compounds and investigate potential of their complementary application for metabolic profiling of bacterial strains. Within his PhD thesis he covered the following tasks:

1. Synthesis, characterization and fabrication of solid-phase microextraction (SPME) fibers based on modification of the polypyrrole coating material with

metal organic frameworks zeolitic Imidazolate framework-8 (ZIF-8) for analysis of low molecular weight volatile organic compounds.

2. Synthesis, characterization and investigation of laser desorption/ionization mass spectrometry (LDI-MS) performance of gold anisotropic nanoparticles for analysis of low molecular weight analytes.
3. Synthesis, characterization and fabrication of silver nanostructured LDI-MS substrates for analysis of low molecular weight analytes.
4. Application of polypyrrole@ZIF-8 SPME fibers and silver nanostructured LDI-MS substrates for metabolic profiling of bacterial strains.

The PhD dissertation consists of four journal publications:

1. [P1] Mametov R.; Sagandykova G.; Monedeiro-Milanowski M.; Gabryś D.; Pomastowski P. 'Electropolymerized Polypyrrole-MOF Composite as a Coating Material for SPME Fiber for Extraction VOCs Liberated by Bacteria'. *Scientific Reports*. 2023, 13 (1), 1–10. IF = 4.6 MP = 140.
2. [P2] Sagandykova G., Pryshchepa O., Rafinska K., Mametov R., Madajski P., Pomastowski P. 'LDI-MS performance of gold nanostars as an inorganic matrix for low molecular weight analytes' *International Journal of Mass Spectrometry*, 478, 116872 (2022). IF = 1.934 MP = 70.
3. [P3] Sagandykova G.; Piszczek P.; Radtke A.; Mametov R.; Pryshchepa O.; Gabryś D.; Kolankowski M.; Pomastowski P. 'Silver Nanostructured Substrates in LDI-MS of Low Molecular Weight Compounds'. *Materials (Basel)*. 2022, 15 (13). IF = 3.748 MP = 140.

4. [P4] Mametov R.; Sagandykova G.; Monedeiro F.; Florkiewicz A.; Piszczek P.; Radtke A. and Pomastowski P. 'Metabolic Profiling of Bacteria with the Application of Polypyrrole-MOF SPME fibers and Plasmonic Nanostructured LDI-MS Substrates' Scientific Reports. 2024, 14, 5562. IF = 4.6 MP = 140.

Based on the co-author's declaration, the Author of this thesis was responsible for:

- In P1, the characterization of composite materials and fabrication of the SPME fibers for the concept and the design of the experiments and writing the publication.
- In P2, he synthesized gold nanostars, designed the experiments, and participated in writing and correcting the manuscript.
- In P3, he was responsible for sample preparation, designing experiments, and writing.
- In P4, he synthesized, fabricated, and characterization of the SPME fibers. Additionally, he participated in experiments related to bacteria growth. Designing experiments and writing and editing the manuscript were also his responsibilities.

Prior to including the publications in the thesis, in Chapter 3, entitled Research Problem, the following topics are listed:

1. Investigation of the effect of modification of polypyrrole coating material for SPME fibers by metal-organic frameworks (ZIF-8) on the efficiency of extraction of low molecular weight compounds.
2. Investigation of the performance of gold anisotropic nanoparticles in laser desorption/ionization mass spectrometry of low molecular weight compounds.

3. Investigation of the effect of mass of precursor on performance of silver nanostructured substrates in laser desorption/ionization mass spectrometry of low- low-molecular-weight compounds.
4. Investigate the potential of polypyrrole@ZIF-8 SPME fibers and silver nanostructured LDI-MS substrates for differentiating bacterial species and gaining insights into their metabolism with their complementary application.

The described research topic in Chapter 3 is followed by the publications listed in Chapter 4, which are the core of the PhD thesis.

At the end of the thesis, the summary in Polish is included, as well as the list of achievements, his education, publications, conferences, and projects. He was the PI of the Praeludium project founded by the National Science Center during his PhD study. He did 2 internships and received 2 Rector Awards. Apart from many publications, he is co-authoring the patent application. In the thesis, we can also find co-authors of the publication's statements, which is especially important for publications where the PhD candidate is not the first author.

As the publications have already gone through the revision process, I have the following questions and clarifications for the Author of this thesis.

**Comments to the discussion:**

For P1 entitled 'Electropolymerized Polypyrrole-MOF Composite as a Coating Material for SPME Fiber for Extraction VOCs Liberated by Bacteria'

1. The SEM parameters are missing, clarify how the samples were prepared for microscopy investigation.
2. What kind of distilled water was used in the analysis?
3. The equipment detail regarding the hot plate is missing.
4. Was the temperature of 30° C measured on the heating plate or inside the solution?



5. What type of UV lamp was used for sterilization?
6. You wrote: ' Since the film thickness of the coating may affect the extraction efficiency, the value of film thickness was estimated based on the SEM pictures and the well-known diameter of the stainless-steel substrate (Fig. 1c). The value of film thickness varied within the range between 65 and 72  $\mu\text{m}$ . ' So how many measurements were done and what was the statistical error? The correct data should be provided for the thickness if it is essential instead of giving just a range.
7. Did you measure the roughness of the coatings, as there should be some difference based on the images you presented in Figure 1?
8. How was the adhesion of the coating evaluated?

For P2, entitled – 'LDI-MS performance of gold nanostars as an inorganic matrix for low molecular weight analytes.'

1. Similarly, the settings and conditions of the micrographs taken with SEM and TEM are not considered as they are crucial to determining the values of working distance and voltage or current.
2. Any analysis of the size of the particles after imaging would be helpful in comparing the results of different syntheses.
3. The results from SEM measurements would be interesting to compare with the size distribution analysis obtained with other techniques.
4. You mentioned, 'we applied TEM analysis for interpretation of results on size distribution as a complementary analytical technique,' but it is not described in the methods; what are the statistics on that? As you mentioned in the discussion, the histograms would be very useful in showing the distribution, as there is a significant difference. Please provide the statistical analysis and the significance level of the methods used.

5. In Figures 5 and 6, a red star notation has been added, but it is not explained in the legend of the Figure caption; what does it mean?

For P3 entitled - 'Silver Nanostructured Substrates in LDI-MS of Low Molecular Weight Compounds'

1. SEM settings are missing with the parameter used to take micrographs.
2. Did you perform any wetting contact angle analysis on the coating, as it would be interesting to see the changes of surface free energy once the various coatings are applied?
3. As in the discussion in the section 3.3. *LDI-MS Performances of Silver Nanostructures for Lipids*, you have added the following description 'In contrast, plates AgPs0.11 and AgPs0.2, which showed higher intensities for PEs, consisted of microparticles with irregular shape.' How did you justify that? Was it based on SEM images? Did you perform any surface roughness analysis that would indicate the differences in the effective surface area?

For P4 entitled - 'Metabolic Profiling of Bacteria with the Application of Polypyrrole-MOF SPME fibers and Plasmonic Nanostructured LDI-MS Substrates'

1. What were the statistical methods used to analyze the data from microbial and bacteria growth?
2. In Figure 1 you have used ',' on the numbers provided on Y-axis.
3. What was the reason of the exponential bacterial growth phase observed between 10 and 16 h presented in Figure 1?
4. How was the cross-correlation matrix obtained (Figure 6)?

This PhD thesis aims are clear and logically presented with an up-to-date bibliography. Radik Mametov's thesis is an excellent example of fundamental chemistry studies, including synthesis and characterization studies with the optimization for antibacterial applications. The preceding comments are subject to debate as they contain editorial remarks. However, it's important to note that these remarks do not detract from the overall positive evaluation of the work. Instead, they serve as constructive guidelines to enhance the PhD student's scientific and research development.

Upon thoroughly examining the dissertation and carefully analyzing its outcomes, I am pleased to acknowledge the comprehensive and meticulous description and explanation of the research objectives. This thesis stands as a remarkable example of interdisciplinary research, seamlessly integrating chemical synthesis, fabrication, and characterization with antibacterial tests. Its significance lies in addressing pivotal topics directly relevant to practical applications stemming from the obtained results. Therefore, I am suggesting the distinction of this doctoral thesis.

The dissertation authored by Radik Mametov encapsulates invaluable research findings and their insightful discussion. From my perspective, this scholarly endeavor impeccably aligns with the criteria outlined for doctoral dissertations, as stipulated by the Law on Higher Education and Science. Therefore, I earnestly recommend the esteemed Council of Chemical Science Discipline at Nicolaus Copernicus University in Toruń to accept the dissertation and grant Radik Mametov the opportunity to defend his work publicly.



Urszula Stachewicz