M U N I

COMMENTARY TO HABILITATION THESIS[1]

LASER-MATTER INTERACTION AS A KEY PROCESS FOR SAMPLING BY LASER ABLATION

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This habilitation thesis contains 12 related publications, all focused on the use of laser ablation as a sampling method for inductively coupled plasma mass spectrometry. It presents the range of applications for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) technique and provides a detailed analysis of laser ablation parameters and their influence on laser-matter interaction and subsequent aerosol formation. The quality of this aerosol is crucial for the accuracy and precision of the analysis. Parameters such as wavelength, laser pulse duration, fluence or choice of ablation mode are discussed. The thesis also highlights the significance of the sample's physical, chemical, and surface properties. Additionally, it discusses various methods for studying the processes that occur during the interaction of the laser pulse with the sample. These methods include the study of ablation craters, the characterisation of the generated aerosol, in particular the determination of the particle size distribution and the time-resolved signal processing of the monitored isotopes.

The research included in the habilitation thesis shows that the use of shorter laser wavelengths, specifically the reduction from 266 nm to 193 nm, significantly limits the formation of particles larger than 150 nm during the ablation of metal samples. This finding underscores the potential for improved precision in particle size control during aerosol generation. The study further shows that the duration of the laser pulses significantly affects the thermal dynamics during ablation. Longer pulses in the nanosecond and picosecond range enhance non-stoichiometric ablation due to preferential evaporation of volatile components, resulting in significant material melting. This molten material mechanically interacts with the plasma, leading to the production of larger particles by hydrodynamic sputtering and thereby affecting the particle size distribution and composition of the aerosol. The use of femtosecond laser pulses has been shown to be helpful in mitigating microparticle formation - a prevalent problem with longer nanosecond pulses - by reducing thermal effects and minimizing material melting. This advance in pulsed laser ablation not only refines aerosol particle sizes, but also increases the analytical accuracy and precision of the LA-ICP-MS method.

In addition, adjustments in the fluence and ablation mode are shown to play a pivotal role. Higher fluences with nanosecond lasers reduce preferential evaporation of volatiles on metal samples, independent of surface topography. The findings also confirm that the setting of the ablation mode, especially the spot size in spot ablation or the scan speed in scanning ablation, significantly affects the particle size distribution and thus directly affects the analytical signal.

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[1] The commentary must correspond to standard expectations in the field and must include a brief characteristic of the investigated matter, objectives of the work, employed methodologies, obtained results and, in case of co-authored works, a passage characterising the applicant's contribution in terms of both quality and content.

This work further confirmed that matrix and sample surface modifications are key to optimizing the laser-matter interaction. Surface treatments such as roughening, or deposition of metal nanoparticles can significantly affect the amount and size of produced particles due to changes in the optical and thermal properties of the surface. These modifications not only enhance the analytical signal, but also substantially reduce the detection limits.

The work underlines the basic factors influencing the course of laser-matter interaction and the formation of sample aerosol using methods such as diagnostics of ablation craters, measurement of aerosol particle size and concentration, and analysis of analytical signals. Other parameters such as carrier gas type and flow rate, ablation cell geometry and laser repetition rate are certainly very important, and all these factors require thorough optimization for accurate and precise application of the LA-ICP-MS method.

The habilitation thesis not only collects a range of research findings but also places them in a wider scientific context, including references to the work of other research groups dealing with similar research topics. The primary focus of this work is on nanosecond laser ablation, in accordance with the capabilities of our laboratory, thus representing a specific subsection of the extensive domain of LA-ICP-MS.

[1][2] WERTICH, Vojtech, Martin KUBES, Jaromir LEICHMANN, **Marketa HOLA**, Jakub HAIFLER, Juraj MOZOLA, Pavla HRSELOVA a Michal JAROS. Trace element signatures of uraninite controlled by fluid-rock interactions: A case study from the Eastern Moldanubicum (Bohemian Massif). *Journal Of Geochemical Exploration* [online]. 2022, **243**, Article 107111. ISSN 1879-1689. Dostupné z: doi:10.1016/j.gexplo.2022.107111

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
30	10	20	20

[2] HOLA, Marketa, Jiri KALVODA, Hana NOVAKOVA, Radek SKODA a Viktor KANICKY. Possibilities of LA-ICP-MS technique for the spatial elemental analysis of the recent fish scales: Line scan vs. depth profiling. *Applied Surface Science* [online]. 2011, **257**(6), 1932–1940. ISSN 1873-5584. Dostupné z: doi:10.1016/j.apsusc.2010.09.029

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
50	60	40	30

[3] HOLA, Marketa, Karel NOVOTNY, Jan DOBES, Ivo KREMPL, Vojtech WERTICH, Juraj MOZOLA, Martin KUBES, Veronika FALTUSOVA, Jaromir LEICHMANN a Viktor KANICKY. Dual imaging of uranium ore by Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Laser Induced Breakdown Spectroscopy. *Spectrochimica Acta Part B-Atomic Spectroscopy* [online]. 2021, **186**, Article 106312. ISSN 1873-3565. Dostupné z: doi:10.1016/j.sab.2021.106312

[2] Bibliographic record of a published scientific result, which is part of the habilitation thesis.

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
30	50	30	50

[4] MOZNA, Veronika, Jorge PISONERO, **Marketa HOLA**, Viktor KANICKY a Detlef GUENTHER. Quantitative analysis of Fe-based samples using ultraviolet nanosecond and femtosecond laser ablation-ICP-MS. *Journal Of Analytical Atomic Spectrometry* [online]. 2006, **21**(11), 1194–1201. ISSN 1364-5544. Dostupné z: doi:10.1039/b606988f

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
-	30	15	20

[5] HOLA, Marketa, Zita SALAJKOVA, Ales HRDLICKA, Pavel PORIZKA, Karel NOVOTNY, Ladislav CELKO, Petr SPERKA, David PROCHAZKA, Jan NOVOTNY, Pavlina MODLITBOVA, Viktor KANICKY a Jozef KAISER. Feasibility of Nanoparticle-Enhanced Laser Ablation Inductively Coupled Plasma Mass Spectrometry. *Analytical Chemistry* [online]. 2018, **90**(20), 11820–11826. ISSN 1520-6882. Dostupné z: doi:10.1021/acs.analchem.8b01197

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
50	60	80	70

[6] SALAJKOVA, Zita, **Marketa HOLA**, David PROCHAZKA, Jakub ONDRACEK, David PAVLINAK, Ladislav CELKO, Filip GREGAR, Petr SPERKA, Pavel PORIZKA, Viktor KANICKY, Alessandro DE GIACOMO a Jozef KAISER. Influence of sample surface topography on laser ablation process. *Talanta* [online]. 2021, **222**, 121512. ISSN 1873-3573. Dostupné z: doi:10.1016/j.talanta.2020.121512

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
40	60	80	80

[7] NOVAKOVA, Hana, **Marketa HOLA*(corresponding author)***, Michal VOJTISEK-LOM, Jakub ONDRACEK a Viktor KANICKY. Online monitoring of nanoparticles formed during nanosecond laser ablation. *Spectrochimica Acta Part B-Atomic Spectroscopy* [online]. 2016, **125**, 52–60. ISSN 0584-8547. Dostupné z: doi:10.1016/j.sab.2016.09.017

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
50	80	70	90

[8] HOLA, Marketa*(corresponding author)*, Jakub ONDRACEK, Hana NOVAKOVA, Michal VOJTISEK-LOM, Romana HADRAVOVA a Viktor KANICKY. The influence of material properties on highly time resolved particle formation for nanosecond laser ablation. *Spectrochimica Acta Part B-Atomic Spectroscopy* [online]. 2018, **148**, 193–204. ISSN 0584-8547. Dostupné z: doi:10.1016/j.sab.2018.07.001

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
60	80	80	90

[9] HOLA, Marketa*(corresponding author)*, Veronika KONECNA, Pavel MIKUSKA, Jozef KAISER a Viktor KANICKY. Influence of physical properties and chemical composition of sample on formation of aerosol particles generated by nanosecond laser ablation at 213 nm. *Spectrochimica Acta Part B-Atomic Spectroscopy* [online]. 2010, **65**(1), 51–60. ISSN 0584-8547. Dostupné z: doi:10.1016/j.sab.2009.11.003

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
60	80	80	90

[10] HOLA, Marketa*(corresponding author)*, Veronika KONECNA, Pavel MIKUSKA, Jozef KAISER, Katerina PALENIKOVA, Stanislav PRUSA, Renata HANZLIKOVA a Viktor KANICKY. Study of aerosols generated by 213 nm laser ablation of cobalt-cemented hard metals. *Journal Of Analytical Atomic Spectrometry* [online]. 2008, **23**(10), 1341–1349. ISSN 1364-5544. Dostupné z: doi:10.1039/b802906g

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
60	80	80	90

[11] HOLA, Marketa*(corresponding author)*, Pavel MIKUSKA, Renata HANZLIKOVA, Jozef KAISER a Viktor KANICKY. Tungsten carbide precursors as an example for influence of a binder on the particle formation in the nanosecond laser ablation of powdered materials. *Talanta* [online]. 2010, **80**(5), 1862–1867. ISSN 1873-3573. Dostupné z: doi:10.1016/j.talanta.2009.10.035

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
70	80	80	80

[12] HOLA, Marketa, Zita SALAJKOVA, Ales HRDLICKA, Jakub ONDRACEK, Karel NOVOTNY, David PAVLINAK, Michal VOJTISEK-LOM, Ladislav CELKO, Pavel PORIZKA, Viktor KANICKY, David PROCHAZKA, Jan NOVOTNY a Jozef KAISER. The effect of nanoparticle presence on aerosol formation during nanoparticle-enhanced laser ablation inductively coupled plasma mass spectrometry. *Journal Of Analytical Atomic Spectrometry* [online]. 2020, **35**(12), 2893–2900. ISSN 1364-5544. Dostupné z: doi:10.1039/d0ja00324g

Experimental work (%)	Supervision (%)	Manuscript (%)	Research direction (%)
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