Theses of the doctoral (Ph.D.) dissertation

ICP-MS based analytical method development for the investigation of multi-component nanoparticles

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1. INTRODUCTION

One of the most rapidly developing and impactful field of science of the latest decades is nanotechnology. Size distribution, shape, composition, porosity, etc. of nanoparticles (NPs) greatly affects their application potential, thus, the fine-tuning of particle properties and their characterization is an important task.

A wide set of methods is available for the investigation of particle characteristics. It is worth emphasizing though that there is no universal method that would be capable of a full characterization of NPs, hence several methods needs to be combined. The calibration and validation of measurements is often challenging (due to that e.g. NP standards are still not widely available, sample amount is typically very small, etc.), thus the expectable accuracy and relative standard deviation are quite limited (e.g. 10-20%). These needs and difficulties, especially in the fields of analytical and materials science, create a constant need to develop new NP characterization methods.

One of the most widely used analytical method for the quantitative analysis of multi-component NPs is inductively coupled plasma mass spectrometry (ICP-MS). This is enabled by the outstanding absolute detection limits (as low as attograms), as well as the high matrix tolerance of ICP-MS, which can be well utilized in e.g. for environmental or nanotoxicology investigations in biological/natural media.

Single particle ICP-MS (spICP-MS) is a novel characterization method which was developed for the individual analysis of nano- and submicron particles in dispersions. Beside the determination of elemental and isotopic

composition, it is also capable of the direct analysis of size distribution and particle concentration, and can also provide structure- and shape-related information. In the last decade, this technique has been attracting an increasing attention in the scientific literature, with the signal formation, calibration approaches and application possibilities in the spotlight.

spICP-MS is a major research direction within our laser and plasma spectroscopy research group since 2012. Some of our previous results were disseminated in the doctoral dissertation of Ildikó Kálomista, a former member of the group, in 2018. She studied the signal formation and optimization of experimental parameters of spICP-MS for the case of the analysis of single-component (mostly metallic) NPs. My research continued her work and focused on spICP-MS and solution mode ICP-MS method development for the analysis of multi-component and porous NPs.

2. OBJECTIVES

spICP-MS is mostly used for the analysis of one-component, compact NPs in the scientific literature. At the same time, multi-component and porous particles possess great practical significance, thus, their characterization is an important task too.

For these reasons the main objective of my research was the extension of the analytical possibilities of spICP-MS for the determination of the composition and other properties (e.g. porosity, density) of multi-component NPs with different structures. To reach the analytical goal the investigation of the effect of experimental parameters and features of the signal time profiles

of multi-component NPs is also needed. I also intended to assess the analytical performance of the newly developed methods and make a detailed comparison with the alternative particle characterization methods (e.g. SEM-EDX, TEM, XPS, SAXS, etc.). The analyzed NPs were always dispersed and stabilized in aqueous media, and were partly commercially obtained, and partly synthesized specifically for my measurements by partner laboratories.

Currently the literature lacks a systematic assessment and comparison of the available ICP-MS based different characterization techniques. Therefore, one of my further aims was to perform such a study involving solution-mode ICP-MS analysis performed via direct particle nebulization or following the acid dissolution of the particles, as well as spICP-MS.

Last but not least, I also intended to demonstrate the applicability of the developed analytical methods in different scientific fields. Among these, particular attention was paid to the analysis of binary and tertiary NPs synthesized in a spark discharge generator (SDG) which results can shed light on the particle formation pathways and possibilities for composition fine-tuning. In addition to this, I also describe successful analytical applications on nanocatalysts and biological samples.

3. RESULTS

My research produced the new scientific results listed below, which form the basis of my dissertation. The numbers indicated in brackets refer to the number of the related reference in my list of publications:

1.) I developed single particle ICP-MS (spICP-MS) analytical methods for the quantitative determination of the composition of two-component nanoparticles (containing Au, Ag, Pt or Si) with different structures (e.g. random alloy, core-shell, composite) dispersed in an aqueous medium. The analytical performance of spICP-MS was compared to that of other particle characterization methods (e.g. XPS, SEM-EDX, geometric based TEM). My results revealed that by using standard particles for the size calibration of the technique, and after an optimization of experimental parameters and using a proper statistical evaluation, 1-9% relative accuracy and 0,8-2,6% precision (RSD) is obtainable for the studied nanoparticles and elements. These values are not only comparable but, in most cases, superior to those of alternative characterization methods [1, 2].

2.) I developed a novel spICP-MS based analytical method for the determination of the porosity of nano- and submicron particles. The applicability of the method was demonstrated by the analysis of particles with different structure, composition and size (Au-Ag core-shell, hollow Au, mesoporous SiO_2). The obtained relative accuracy and precision were in the range of 1-4% in all cases, which values are comparable to the analytical performance of alternative porosity determination techniques (e.g. BET gas adsorption, SAXS). I showed that the dynamic range of the method in terms of porosity (which is affected by the particle size, the isotopic abundance and the ionization energy) is about two orders of magnitude: it spans from a few percents to up to 99%. The main advantages of the new spICP-MS method

include that the result considers both open and closed pores, it can be used in the whole mesoporous range (2-50 nm), there is no need to evacuate the pores prior to the measurements and it only requires a very small amount of particulate sample (micrograms). The developed method also enables the determination of the density of the investigated particles [3].

3.) I identified the limitations of solution-mode analysis both via direct particle nebulization and after the acid dissolution of the particles. Through the analysis of different nanoparticles (e.g. Au-Ag, Pt/SiO_2), I proved that these analytical approaches can only provide accurate results only in the absence of a significant amount of dissolved analyte content. When direct particle nebulization is performed, preliminary time-resolved ICP-MS measurements are also needed to verify that the dilution of the nanodispersions is appropriate for the dynamic range of the detector [1, 2].

4.) I also performed a detailed study of the effect of experimental parameters related to the optimization of the analytical performance of spICP-MS by normal and high time resolution instruments on the analysis of multi-component and porous nanoparticles. Among others, I studied the effect of collision cell helium gas flow rate and stabilizing agent concentration on the signal intensity of nanoparticles as well as the transit time of the ion cloud, the effect of plasma sampling depth on the particle size detection limits and the utilization of time resolved data on the identification of qualitative particle composition. As a result, for example, I could decrease the size detection limit value for compact

SiO_2 particles from 306 nm to 232 nm, and for Au/Ag alloy NPs (molar ratio 1:1) from 39 nm to 31 nm [2, 3].

5.) Novel ICP-MS based methods (also including sample preparation) were developed and successfully applied to the determination and monitoring of the composition of multi-component NPs synthesized in spark discharge generators. Results from these measurements enable the optimization of the experimental parameters of the generator for the fine control of particle composition and the assessment of particle formation processes. The analytical applicability of the developed methods was successfully demonstrated by the measurement of different, Au, Ag, Co, W, La, Fe or Si containing two- and three-component nanoparticles [4, 5].

4. LIST OF PUBLICATIONS

My ID in the Hungarian Collection of Scientific Publications (MTMT) is 10058030.

Journal publications defining the basis of the dissertation:

[1] A. Sápi, **A. Kéri**, I. Kálomista, D. Dobó, Á. Szamosvölgyi, K. Juhász, Á. Kukovecz, Z. Kónya, G. Galbács: Determination of the platinum concentration of a Pt/silica nanocomposite decorated with ultra small Pt nanoparticles using single particle inductively coupled plasma mass spectrometry
Journal of Analytical Atomic Spectrometry, 32, 996-1003, 2017
DOI: 10.1039/C7JA00039A **IF: 3,61**

[2] **A. Kéri**, I. Kálomista, D. Ungor, Á. Bélteki, E. Csapó, I. Dékány, T. Prohaska, G. Galbács: Determination of the structure and composition of Au-Ag bimetallic spherical nanoparticles using single particle ICP-MS measurements performed with normal and high temporal resolution
Talanta, 179, 193-199, 2018
DOI: 10.1016/j.talanta.2017.10.056 **IF: 4,92**

[3] **A. Kéri**, A. Sápi, D. Ungor, D. Sebők, E. Csapó, Z. Kónya, G. Galbács: Porosity determination of nano- and sub-micron particles by single particle inductively coupled plasma mass spectrometry
Journal of Analytical Atomic Spectrometry, 2020, in press
DOI: 10.1039/D0JA00020E **IF (2018): 3,65**

[4] J. Feng, R. Geutjens, N. V. Thang, J. Li, X. Guo, **A. Kéri**, S. Basak, G. Galbács, G. Biskos, H. Nirschl, H. W. Zandbergen, E. Brück, A. Schmidt-Ott: Magnetic phase transition in spark-produced ternary LaFeSi nanoalloys
ACS Applied Materials & Interfaces, 10, 6073-6078, 2018
DOI: 10.1021/acsami.7b15441 **IF: 8,46**

[5] A. Kohut, **A. Kéri**, V. Horváth, J. Kopniczky, T. Ajtai, B. Hopp, G. Galbács, Zs. Geretovszky: Facile and versatile fabrication of SERS-active Au/Ag substrates for Raman sensing by spark discharge nanoparticle generation
Applied Surface Science, 2020, submitted (under review)

Σ IF: 20,64

Additional journal publications also related to the topic of dissertation:

6. I. Kálomista, **A. Kéri**, G. Galbács: On the applicability and performance of the single particle ICP-MS nano-dispersion characterization method in cases complicated by spectral interferences
Journal of Analytical Atomic Spectrometry, 31, 1112-1122, 2016
IF: 3,38

7. I. Kálomista, **A. Kéri**, G. Galbács: Optimization of plasma sampling depth and aerosol gas flow rates for single particle inductively coupled plasma mass spectrometry analysis
Talanta, 172, 147-154, 2017
IF: 4,24

8. I. Kálomista, **A. Kéri**, D. Ungor, E. Csapó, I. Dékány, T. Prohaska, G. Galbács: Dimensional characterization of gold nanorods by combining millisecond and microsecond temporal resolution single particle ICP-MS measurements
Journal of Analytical Atomic Spectrometry, 32, 2455-2462, 2017
IF: 3,61

9. M. Mészáros, G. Porkoláb, L. Kiss, A.-M. Pilbat, Z. Kóta, Z. Kupihár, **A. Kéri**, G. Galbács, L. Siklós, A. Tóth, L. Fülöp, M. Csete, Á. Sipos, P. Hülper, P. Sipos, T. Páli, G. Rákhely, P. Szabó-Révész, M. A. Deli, Sz. Veszelka: Niosomes decorated with dual ligands targeting brain endothelial transporters increase cargo penetration across the blood-brain barrier
European Journal of Pharmaceutical Sciences, 123, 228–240, 2018
IF: 3,53

10. A. Sápi, Gy. Halasi, A. Grósz, J. Kiss, **A. Kéri**, G. Ballai, G. Galbács, Á. Kukovecz, Z. Kónya: Designed Pt promoted 3D mesoporous Co_3O_4 catalyst in CO_2 hydrogenation
Journal of Nanoscience and Nanotechnology, 19, 436-441, 2019
IF (2018): 1,09

11. M. Mohl, Á. Dombóvári, M. Szabó, T. Järvinen, O. Pitkänen, A. Sápi, K. L. Juhász, **A. Kéri**, G. Galbács, Á. Kukovecz, Z. Kónya, K. Kordas: Size-dependent H_2 sensing over supported Pt nanoparticles
Journal of Nanoscience and Nanotechnology, 19, 459-464, 2019
IF (2018): 1,09

12. K. Bodó, Y. Hayashi, G. Gerencsér, Z. László, **A. Kéri**, G. Galbács, E. Telek, M. Mészáros, M. A. Deli, G. Tolnai, B. Kokhanyuk, P. Németh, P. Engelmann: Species-specific sensitivity towards noble metal nanoparticles: a multiparameter in vitro study of OECD standard soil sentinels
Environmental Science: Nano, 2020, submitted (under review)

Further journal publications:

13. G. Galbács, **A. Kéri**, I. Kálomista, É. Széles-Kovács, I. B. Gornushkin: Deuterium analysis by inductively coupled plasma mass spectrometry using polyatomic species: An experimental study supported by plasma chemistry modeling
Analytica Chimica Acta, 1104, 28-37, 2020
IF (2018): 5,26

14. H. A. H. Abd Elhameed, B. Hajdu, A. Jancsó, **A. Kéri**, G. Galbács, É. Hunyadi-Gulyás, B. Gyurcsik: Modulation of the catalytic activity of a metallonuclease by tagging with oligohistidine
Journal of Inorganic Biochemistry, 206, 111013, 2020
IF (2018): 3,22

ΣΣ IF: 46,06

Oral and poster presentations related to the topic of dissertation:

1. I. Kálomista, **A. Kéri**, G. Galbács: The effect of the plasma sampling depth and the flow rate of the aerosol dilution gas on the performance of single particle inductively coupled plasma mass spectrometry (spICP-MS) measurements
21st International Symposium on Analytical and Environmental Problems, Szeged, 2015

2. I. Kálomista, **A. Kéri**, G. Galbács: Optimization of ICP-MS instrumental parameters for single nanoparticle analysis
European Symposium on Atomic Spectrometry, Eger, 2016

3. I. Kálomista, **A. Kéri**, Á. Szamosvölgyi, D. Dobó, L. K. Juhász, A. Sápi, G. Galbács, Á. Kukovecz, Z. Kónya: Optimization of SP-ICP-MS instrumental parameters for the measurement of surface modified nanoparticles
7th Szeged International Workshop on Advances in Nanoscience, Szeged, 2016

4. **A. Kéri**, I. Kálomista, Á. Szamosvölgyi, D. Dobó, L. K. Juhász, A. Sápi, G. Galbács, Á. Kukovecz, Z. Kónya: Investigation of Pt/SiO_2 nanoparticles by solution and single particle mode ICP-MS
22nd International Symposium on Analytical and Environmental Problems, Szeged, 2016

5. **A. Kéri**, I. Kálomista, D. Dobó, L. K. Juhász, A. Sápi, G. Galbács: A comparison of the performance of spICP-MS with TEM, SEM-EDX, XPS and solution mode ICP-MS used for the investigation of surface-modified oxide nanoparticles
European Winter Conference on Plasma Spectrochemistry, Sankt Anton, Austria, 2017

6. I. Kálomista, **A. Kéri**, D. Ungor, E. Csapó, I. Dékány, T. Prohaska, G. Galbács: Extending the applicability of the Single Particle ICP-MS technique to the investigation of nanorods and nanoalloys
Colloquium Spectroscopicum Internationale XL, Pisa, Italy, 2017

7. I. Kálomista, **A. Kéri**, Á. Bélteki, G. Galbács: Nanorészecskék vizsgálata individuális részecske ICP-MS módszerrel
60. Magyar Spektrokémiai Vándorgyűlés, Debrecen, 2017

8. D. Fuderer, T. Dudás, **A. Kéri**, I. Pfeiffer, G. Galbács: Investigation of the chemical durability and effectiveness of textile products with silver coating
23rd International Symposium on Analytical and Environmental Problems, Szeged, 2017

9. **A. Kéri**, I. Kálomista, D. Ungor, Á. Bélteki, E. Csapó, I. Dékány, T. Prohaska, G. Galbács: Feasibility study of spICP-MS for the determination of the structure and composition of bimetallic nanoparticles
23rd International Symposium on Analytical and Environmental Problems, Szeged, 2017

10. B. Henrik, **A. Kéri**, A. Kohut, L. P. Villy, Á. Bélteki, Zs. Geretovszky, G. Galbács: Study of the composition and size distribution of gold-containing bimetallic nanoparticles synthesized in a spark discharge generator
24th International Symposium on Analytical and Environmental Problems, Szeged, 2018

11. K. Bodó, G. Gerencsér, **A. Kéri**, G. Galbács, E. Telek, M. Mészáros, G. Tolnai, B. Kokhanyuk, P. Németh, P. Engelmann: Unravelling the hazards of metal nanomaterials: comparative observations on invertebrate phagocytes
47th Annual Meeting of the Hungarian Society for Immunology, Bükfürdő, 2018

12. **A. Kéri**, A. Kohut, D. Ungor, Zs. Geretovszky, E. Csapó, G. Galbács: Quantitative ICP-MS analysis of nanoparticles synthesized by physical and chemical methods
XVI Hungarian - Italian Symposium on Spectrochemistry, Budapest, 2018

13. **A. Kéri**, H. Bali, L. P. Villy, A. Kohut, T. Ajtai, Z. Bozóki, Zs. Geretovszky, G. Galbács: Composition and morphology analysis of bimetallic nanoparticles generated in a spark discharge plasma
European Winter Conference on Plasma Spectrochemistry, Pau, France, 2019

14. **A. Kéri**, I. Kálomista, A. Sápi, D. Ungor, E. Csapó, T. Prohaska, G. Galbács: Analytical method development for nanoparticle characterization by spICP-MS: beyond monometallic spherical particles
European Winter Conference on Plasma Spectrochemistry, Pau, France, 2019

15. D. Palásti, **A. Kéri**, L. P. Villy, T. Biros, Á. Bélteki, B. Leits, P. Janovszky, A. Kohut, É. Kovács-Széles, Zs. Geretovszky, Z. Galbács, G. Galbács: Nanoparticle analysis by LIBS and ICP-MS in industrial and environmental samples
10th Euro-Mediterranean Symposium on Laser-Induced Breakdown Spectroscopy, Brno, Czech Republic, 2019

16. L. P. Villy, A. Kohut, **A. Kéri**, Á. Bélteki, G. Galbács, Zs. Geretovszky: Kétkomponensű nanorészecskék előállítása és összetételük változtatása szikrakisüléses nanorészecske generátorban
XIV. Magyar Aeroszol Konferencia, Visegrád, 2019

17. D. Palásti, **A. Kéri**, L. P. Villy, T. Biros, Á. Bélteki, B. Leits, P. Janovszky, A. Kohut, Z. Galbács, É. Kovács-Széles, Zs. Geretovszky, G. Galbács: Assessment of the usefulness of LIBS and ICP-MS for the characterization of nanoparticles in industrial and environmental samples
25th International Symposium on Analytical and Environmental Problems, Szeged, 2019

18. K. Bodó, Y. Hayashi, Z. László, G. Gerencsér, **A. Kéri**, G. Galbács, E. Telek, M. Mészáros, B. Kokhanyuk, M. A. Deli, P. Németh, P. Engelmann: Evolúciósan konzervált stressz és immuntoxikológiai folyamatok: ezüst és arany nanopartikulumok in vitro kölcsönhatásának vizsgálata gerinctelen immunsejteken
TOX'2019 Tudományos Konferencia, Szeged, 2019

19. **A. Kéri**, A. Sápi, D. Sebők, D. Ungor, E. Csapó, G. Galbács: Nanorészecskék porozitásának és sűrűségének vizsgálata spICP-MS technikával
62. Magyar Spektrokémiai Vándorgyűlés, Balatonszárszó, 2019

Further oral and poster presentations:

20. **A. Kéri**, L. Zs. Kiss, Zs. László: Investigation of membrane separation combined with UV radiation and heterogeneous photocatalysis *International Conference on Science and Technique based on Applied and Fundamental Research*, Szeged, 2014

21. **A. Kéri**, L. Zs. Kiss, Zs. László: Investigation of membrane separation combined with UV radiation and heterogeneous photocatalysis *Student's Scientific Symposium,* Hunedoara, Romania, 2015

22. J. Balázs, Gy. Pálfi, I. Szikossy, Á. Braun, **A. Kéri**, G. Galbács: LA-ICP-MS examination of mummy hair strands from the archeological artifacts found in the Dominican Church in Vác, Hungary *Colloquium Spectroscopicum Internationale XL*, Pisa, Italy, 2017

23. P. Janovszky, **A. Kéri**, L. Brunnbauer, A. Limbeck, G. Galbács: Quantitative multielemental mapping of biological samples by laser-induced breakdown spectroscopy: a case study of pig tissues *European Winter Conference on Plasma Spectrochemistry*, Pau, France, 2019