Theses of the doctoral (Ph.D.) dissertation

Signal formation and the optimization of parameters in single particle ICP-MS

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INTRODUCTION

Nowadays, nanotechnology is one of the most dynamically developing fields. This discipline deals with the synthesis, modification, characterization and application of nanomaterials. Nanomaterials (nanoparticles) have found their way to many application fields due to their exceptional and versatile physical and chemical properties. Most relevant application fields include (micro)electronics, materials science and biomedicine, but catalysis and energy sectors also greatly benefit from nanomaterials.

The advancements in the application, impact assessment and synthesis of nanomaterials also require the continuous development of the detection techniques. This is partly due to the increased need of monitoring the synthesis or the presence of nanoparticles in the environment, in products, etc., but also due to the development of measurement technologies and data evaluation procedures. As a result, the availability, flexibility and performance of the characterization methods are rapidly growing.

One of the new nanoparticle characterization tools, which has recently been brought into the spotlight, is the so-called single particle inductively coupled plasma mass spectrometry (single particle ICP-MS or spICP-MS) technique. In my doctoral thesis, I have carried out research in this field, with the primary interest in studying the details of signal formation processes, interferences and the optimization of analytical performance of the spICP-MS. My thesis is the first in this topic in Hungary.

The spICP-MS method takes advantage of the analytical properties of the ICP-MS (ppt level detection limits, multi-component analysis, high selectivity,

reliability, robustness, etc.) and uses these to tackle the challenges presented by the goal of characterizing nanoparticles dispersed in liquid or gas media. spICP-MS is generally used under conditions when nanodispersions are introduced into the instrument in a highly diluted way, optimally one after the other, in sequential fashion. The decomposition of each individual nanoparticle in the plasma produces ion clouds, which will then generate a signal spike, which can be recorded as a signal time profile. The time resolution is around a few milliseconds or, in newer instruments, ca. 10 microseconds. The intensity of signal peaks depends on the number of atoms present in the nanoparticles (which is proportional to the mass or volume), whereas the number of detection events is proportional to the particle concentration. As results in my dissertation show, the utilization of the selectivity of ICP-MS measurements and in-depth examination of high-resolution signal profiles also allow for the determination of other particle modalities. The main attraction of the spICP-MS method is that it is versatile, it offers a fast analysis with a good statistical quality, and requires only a small volume of sample (small number of nanoparticles).

OBJECTIVES

The main objective of my research was to develop spICP-MS analytical methods with enhanced analytical performance and reliability, as well as to expand the applicability of this technique. In particular, my research focused on how the experimental parameters influence the analytical signal, on the optimization of sample preparation, as well as the data mining of high-time resolution signal profiles.

My investigations were carried out using nanoparticles of different size, shape and structure. In terms of composition, the particles were made of metals (*e.g.*: Au, Ag) and metal oxides (*e.g.*: ZnO, Fe_2O_3, Cr_2O_3). All nanoparticles were measured in the form of aqueous nanodispersions and were introduced into the ICP-MS by a pneumatic nebulizer.

I carried out experiments to reveal which stabilizers are best suited for spICP-MS measurements and I also assessed the advantages and dangers of the sonication of dispersions prior to measurements. I have studied the effect of measurement parameters (e.g. integration time, particle size and concentration, plasma RF power, plasma sampling depth, gas flow rates, etc.) on the signal intensity, as well as on particle size detection limits, size resolution and accuracy. My experiments also addressed the problem of potential spectral interferences that may be present during spICP-MS measurements and I attempted to suggest means to eliminate or reduce these interferences. Last but not least, I also intended to explore the relationship between high resolution time-dependent signal profiles and the structure and shape of the particles.

RESULTS

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

1.) Using the standard nanodispersions with different sizes of spherical gold and silver nanoparticles, I studied the effect of the main experimental parameters on the analytical performance of the spICP-MS measurements and found that [1, 2, 3]:

1a.) By examining the relationship between integration time, size, concentration and measurement time, I determined that these parameters need to be coordinated to optimize the sensitivity and the number of detected particles. Using high-resolution (μs) measurement data, I also showed that the transit time of ion clouds are changing linearly with the particle size in the range of 20-100 nm, but the actual value for a given particle also depends on its quality (dissociation energy, ionic energy and atomic mass). For example, gold particles gave rise to 66% longer transit times, than same size silver particles.

1b.) A minimum of 1300-1500 W plasma RF power is required for the efficient ionization and detection of nanoparticles above 20 nm in diameter. Signal intensities as well as the number of detection events were found to increase monotonously with the plasma RF power. This trend is attributed to the increase of plasma temperature.

1c.) By optimizing the plasma sampling depth, not only the size detection limits can be reduced significantly (by 25-30%), but also the size resolution (separation of the different size particles in the size distribution chart). Optimal plasma sampling depth values do not differ significantly for solutions and nanodispersions. The optimum value is slightly dependent on the particle size, plasma power, analyte ionization potential, and atomic mass. In case of gold and silver, the optimum is 4-5 mm.

1d.) I studied the combined effect of the carrier gas and the aerosol dilution gas (HMI gas) using a MicroMist microconcentric nebulizer, and found that substantial performance improvements can not be achieved. The potential use of HMI gas flow as an aerosol dilution device is very limited (a max. two-fold dilution), because the nebulizer gas flow needs to be proportionally reduced if HMI is used, and this condition reduces the sensitivity and the number of detection events.

1e.) It was proved that the use of a helium gas collision cell with kinetic energy discrimination for the reduction of spectral interferences does not significantly reduce the performance of the spICP-MS method and also does not significantly affect the optimal value of the instrumental parameters. In my experiments, the helium collision cell did not cause a significant change in the ion cloud transit time either and did not increase the standard deviation of the measurements (3-5% RSD), even if the intensity of the measured

signals was very low (down to 50 counts), due to the good signal statistics.

1f.) Through the optimization of the measurement parameters, I achieved the best size detection limits (Au 13 nm, Ag 26 nm, Pt 17 nm, ZnO 18 nm, Fe_2O_3 15 nm, Cr_2O_3 39 nm) described in the literature.

2.) I identified five different potential sources of spectral interferents in spICP-MS measurements. By using metallic and oxide nanoparticle dispersions, I demonstrated that these contributions come from *i)* the dissolved analyte, *ii)* the plasma gas, solvent and air, *iii)* residues of synthesis reagents, *iv)* stabilizers, v) specific particle components (for multi-component particles). For each type, I described approaches along which these interferences can be eliminated or reduced. These approaches are based on the combined use of sample dilution, collision cell technology and a proper data evaluation [1].

3.) I have elaborated a data evaluation procedure and a computer program for the management and analysis of the high resolution signal time profiles produced by high-resolution (HR-)spICP-MS measurements. The program can identify and filter the particle detection events, it can determine the transit time of the ion clouds, the shape of the signal profile and it makes the statistical analysis of the data significantly easier [3, 4].

4.) I found characteristic differences between the high resolution signal time profiles of rod-shaped and spherical nanoparticles, which is dueto the free rotation of the nanoparticles while entering the plasma. By the statistical evaluation of the data, I developed a new analytical method to determine the volume, shape and dimension of the particles. I have demonstrated the

applicability and accuracy of this method by determining the size and the aspect ratio of several nanorod standards. The resulting values showed only a 6% deviation from the reference TEM data [3].

5.) I demonstrated, that information about the structure of nanoparticles can be extracted using high resolution time-dependent signal profiles. Based on the measurement of pure Ag, Au and Ag-Au alloy particles, I showed that HR-spICP-MS data is useful for determining whether the nanoparticles are mono- or bimetallic nanoparticles and what is their structure (homogenous alloy or core-shell). In the case of core-shell particles, the composition, the thickness of the shell and the core diameter can also be determined [4].

5. LIST OF PUBLICATIONS

ID in the Hungarian Collection of Scientific Publications (MTMT):10049434

Publications that are fundamentally relevant to my dissertation

[1] **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,
J. Anal. At. Spectrom. 31, 1112-1122, 2016
DOI: 10.1039/C5JA00501A
Q1, IF: 3.38

[2] **I. Kálomista**, A. Kéri, G. Galbács: Optimization of plasma sampling depth and aerosol gas flow rates for single nanoparticle analysis by inductively coupled plasma mass spectrometry,
Talanta, 172, 147-154, 2017
DOI: 10.1016/j.talanta.2017.05.051
Q1, IF: 4.16

[3] **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,
J. Anal. At. Spectrom. 32, 2455-2462, 2017
DOI: 10.1039/C7JA00306D
Q1, IF: 3.38

[4] A. Kéri, **I. Kálomista**, Á. Bélteki, D. Ungor, 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
Q1, IF: 4.16

ΣIF: 15.08

Additional publications related to the dissertation

[5] A. Sápi, D. G. Dobó, D. Sebők, Gy. Halasi, K. L. Juhász, Á. Szamosvölgyi, P. Pusztai, E. Varga, **I. Kálomista**, G. Galbács, Á. Kukovecz, Z. Kónya: Silica-based catalyst supports are inert, aren't they? – Striking differences in ethanol decomposition reaction originated from meso- & surface fine structure evidenced by small angle X-ray scattering
*J. Phys. Chem. C,*121, 5130-5136, 2017
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[6] A. Sápi, A. Kéri, **I. Kálomista**, D. G. 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
J. Anal. At. Spectrom. 32, 996-1003, 2017
Q1, IF: 3.38

[7] R. Geczy, N. J. Christensen, K. K. Rasmussen, **I. Kálomista**, M. K. Tiwari, P. Shah, S. W. Yang, M. J. Bjerrum, P. W. Thulstrup: Formation of fluorescent silver nanoclusters at interfacial binding sites facilitate DNA oligomerization,
Under submission to J. Am. Chem. Soc.

Further publications:

[8] K. Sárközi, A. Papp, E. Horváth, Z. Máté, E. Hermesz, G. Kozma, Z. P. Zomborszki, **I. Kálomista**, G. Galbács, A. Szabó: Protective effect of green tea against neuro-functional alterations in rats treated with MnO_2 nanoparticles
J. Sci. Food Agric., 97, 1717–1724, 2017
Q1, IF: 2.38

[9] N. Jedlinszki, **I. Kálomista**, G. Galbács, D. Csupor: Silybum marianum (milk thistle) products in Wilson's disease: a treatment or a threat?
J. Herb. Med., 6, 157-159, 2016
Q2, IF: 1.69

[10] T. Horváth, A. Szabó, A. Lukács, G. Oszlánczi, G. Kozma, D. Kovács, **I. Kálomista**, T. Vezér: A. Papp: Titán-dioxid nanorészecskék szubakut neurotoxicitásának vizsgálata patkány modellben
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[11] T. Horváth, A. Papp, G. Kozma, D. Kovács, **I. Kálomista**, T. Vezér: Electrophysiological alterations and general toxic signs obtained by subacute administration of titanium dioxide nanoparticles to the airways of rats,
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[12] T. Horváth, A. Papp, G. Kozma, M. Kiricsi, N. Igaz, **I. Kálomista**, T. Vezér: General and nervous system toxicity of titanium dioxide nanoparticles investigated by in vivo and in vitro methods, *Népegészségügy*, 95, 160-16, 2017

[13] Balogh Cs., Balázs J., **Kálomista I.**, Galbács G.: Előzetes nyomelemmérési eredmények Orosháza, Bónum, Faluhely régészeti lelőhelyről
Mozaikok Orosháza és vidéke múltjából,13, 58-63, 2015

[14] D. Szunyogh, R.M.L. McFadden, V.L. Karner, A.Ch. Chatzichristos T. Day Goodacre, M. Dehn, L. Formenti, D. Fujimoto, A. Gottberg, E. Kallenberg, **I. Kálomista**, R.F. Kiefl, F.H. Larsen, J. Lassen, C.D.P. Levy, R. Li, W.A. MacFarlane, I. McKenzie, G.D. Morris, S. Pallada, M.R. Pearson, S.P.A. Sauer, P. Schaffer, P.W. Thulstrup, L. Hemmingsen, M. Stachura: Direct observation of Mg^{2+} complexes in ionic liquid solutions by ^{31}Mg β-NMR spectroscopy
Dalton Transactions, in press
Q1, IF: 4.10

ΣΣIF: 32,80

Presentations at national and international conferences (author/co-author)

1. **Kálomista Ildikó**, Metzinger Anikó, Galbács Gábor: Arany nanoszolok méreteloszlásának vizsgálata SP-ICP-MS módszerrel,
   Proceedings of the 19th International Symposium on Analytical and Environmental Problems,
   Szeged, 2013

2. **Kálomista Ildikó**, Metzinger Anikó, Galbács Gábor: Nanoszolok méreteloszlásának vizsgálata SP-ICP-MS módszerrel,
   XXXVI. Kémiai Előadói Napok,
   Szeged, 2013

3. **Kálomista Ildikó**, Metzinger Anikó, Galbács Gábor: Fém- és fém-oxid típusú nanorészecskék vizsgálata SP-ICP-MS módszerrel,
   XV. Eötvös Konferencia,
   Budapest, 2014

4. **Kálomista Ildikó**, Horváth Gábor, Metzinger Anikó, Geretovszky Zsolt, Galbács Gábor: Lézeres ablációval és kémiai eljárással vizes közegben készített nanorészecskék vizsgálata,
   57. Magyar Spektrokémiai Vándorgyűlés,
   Veszprém, 2014

5. Galbács Gábor, Metzinger Anikó, **Kálomista Ildikó**: ICP-MS mérések deutérium tartalmú vizes közegű mintákban
   57. Magyar Spektrokémiai Vándorgyűlés,
   Veszprém, 2014

6. **Ildikó Kálomista**, Gábor Horváth, Anikó Metzinger, Zsolt Geretovszky, Gábor Galbács: On the synthesis and characterization of metal and metal-oxide nanoparticles in aqueous medium,
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7. **Ildikó Kálomista**, Anikó Metzinger, Gábor Galbács: Rapid characterization of nanoparticles using single particle ICP-MS in cases complicated by spectral interferences,
European Winter Conference of Plasma Spectroscopy,
Münster, Germany, 2015

8. **Ildikó Kálomista**, Albert Kéri, Gábor 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 (SP-ICP-MS) Measurements,
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9. Ildikó Kálomista, Albert Kéri, Gábor Galbács: Optimization of ICP-MS instrumental parameters for single nanoparticle analysis,
European Symposium on Atomic Spectrometry,
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10. Gábor Galbács, **Ildikó Kálomista**, Sára Bálint: On the possibility of the determination of deuterium by ICP-MS,
European Symposium on Atomic Spectrometry,
Eger, 2016

11. **Ildikó Kálomista**, Albert Kéri, Ditta Ungor, Edit Csapó, Imre Dékány, Gábor Galbács: Extending the applicability of the single particle ICP-MS technique to the investigation of nanorods and nanoalloys
IX Euro-Mediterranean Symposium on Laser Induced Breakdown Spectroscopy
Pisa, Italy, 2017