Theses of the PhD dissertation entitled

Method development for the analysis of liquid and solid samples by laser-induced breakdown spectroscopy

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1. Introduction

The operation of laser-induced breakdown spectroscopy (LIBS) is based on the laser light – material interaction. LIBS spectrometers use a short duration, high intensity laser beam focused onto the surface of a solid sample or into a fluid sample to produce such a high power density in the focal spot that within ps-ns time, the laser light locally vaporizes, thermally atomizes, excites and ionizes the sample. A laser-induced microplasma (LIP) is generated, the light emission of which is evaluated according to the principles of atomic emission spectroscopy in order to gain analytical information about the sample composition.

LIBS spectroscopy has an advantageous, unique set of characteristics which makes it very competitive within atomic spectroscopy instruments. For example, any samples, regardless of their consistency, can be measured quickly, *in situ*. The method is microdestructive and requires less than a μg sample mass, with minimal sample preparation. The small dimensions of the LIP plasma allows the execution of spatially resolved measurements. LIBS spectroscopy provides highly characteristic, „fingerprint-like" spectra, which can be used for qualitative analysis efficiently. In-field measurements are also possible by using compact spectrometers. Recent results also proved that by using two or more laser pulses with very short interpulse delays, the analytical performance can be further enhanced (double- or multi-pulse LIBS, abbreviated as DP-LIBS and MP-LIBS).

In the past decades, optoelectronic devices and laser spectroscopy have developed at an amazing rate. Thanks to this, LIBS spectrocopy is also being used in more and more research and industrial applications. Every single year, several hundreds of scientific publications appear in the literature in this topic – this makes LIBS one of the hottest topics in the field of atomic spectroscopy. Our own research group has been actively working on the study of LIP plasmas and the development of LIBS analytical methods since 1999.

2. Research goals

Our research group was among the firsts to realize the analytical potential of MP-LIBS spectroscopy and started to pursue the development of related instrumentation and analytical methods. Former results of our group have conclusively documented the MP-LIBS figures of merit and provided explanation to their improvement over single-pulse LIBS. As a consequence, one of the goals of the experimental work leading to this dissertation was to assess the applicability of MP-LIBS spectroscopy to solve some challenging, quantitative analytical problems, which have a great practical importance.

Qualitative discriminant analysis is an important field within analytical applications (see e.g. quality control, provenance study). LIBS spectroscopy, due to its ability to produce information-rich, „fingerpint-like" spectra, very short measurement times and virtually non-destructive analysis, is a potent tool for this purpose. Because of this, we also set the goal of developing novel data evaluation methods for the purposes of LIBS qualitative discriminant analysis.

LIBS spectroscopy is primarily used for solid sample analysis, because there are a number of challenging conditions – related to beam handling and detection – when liquid sample analysis or the analysis of solids submerged in water are attempted. In spite of these challenges, and because of the numerous liquid sample applications which are in need of an analytical method that can provide what LIBS can offer, that is *in situ*, fast, multielemental and in-field measurements, liquid sampling analysis is at the forefront of LIBS research right now. Thus, we also looked into the possibilities of developing sample presentation methods and devices for the elemental analysis of small volume (μL) liquid samples.

3. Instrumentation, experimental methods and proceedings

In my experiments I used five, slightly different nanosecond LIBS systems and a laser ablation setup according to the needs of the applications.

The laser used in those experiments, where the aim was the development of an in-field executable sample preparation and measurement method, I used a commercially available, compact, portable LIBScan 25+ (Applied Photonics, GB) system. This system has a Q-switched Nd:YAG solid-state laser emitting max. 50 mJ pulses with ca. 4-6 ns pulse length at its fundamental wavelength (1064 nm) and its repetition rate is 1 Hz. The built-in fiber optic spectrometer can operate in the 238-353 and 360-455 nm spectral range. The light focusing and collection optics built in the proprietary, manual probe head of this system was employed.

In the experiments which required high pulse energies, I applied a laboratory-based, KYP-1QS/W type (Hefei Anhey Optic-Electronic Co., China), actively Q-switched Nd:YAG laser. The maximum available pulse energy was 300 mJ at 1064 nm, with a pulse length less than 8 ns. Spectroscopic data acquisition was done using a two-channel fiber optic CCD spectrometer (AvaSpec FT2048, Avantes, the Netherlands) operating in the UV (198–318 nm) and visible–near-infrared (345–888 nm) spectral ranges. Synchronization of the operation of the laser and the spectrometer was achieved using a fast fiber optic–coupled photodiode (DET10A, Thorlabs, USA) and a pulse delay generator (TGP-110, Thurlby Thundar Instruments, Huntingdon, GB). The pulse shapes were continuously monitored by a digital oscilloscope (TDS-1002, Tektronix, USA).

In MP-LIBS experiments I had to use a system capable of emitting multipulse laser pulses. This experimental setup was built around a Brunel SP80 microscope, and was based on a fast triggerable, 2048 pixel, fiber optic CCD spectrometer (AvaSpec 2048FT, Avantes, The Netherlands). The laser is equipped with a passively Q-switched, flashlamp-pumped, Nd:GGG solid-state laser (MP/G-Q-005, Technoorg-Linda, Hungary). The pulse structure of the train of pulses was monitored using the same photodiode and an oscilloscope (TDS-1002, Tektronix, USA).

For the underwater LIBS experiments, I used a special DP-LIBS system built in the laboratory of Prof. Dr. Laserna (Universidad de Malaga, Spain). The Quantel Twins B Brilliant type laser (Coherent Scientific, Australia) contains two Q-switched Nd:YAG laser heads (1064 and 532 nm, 10 Hz, 400 mJ/pulse, 5.5 ns pulse duration). In order to simulate the conditions typical of a real marine environment, the sample was placed inside a tank of 100 liter capacity (35 cm x 80 cm x 41 cm) filled with water. The laser beam was focused onto the sample surface by a fused silica lens (100, 200, 300, 500, 800 mm focal length). The spectroscopic data collection system consisted of a CCD spectrometer (AvaSpec-2048-2-USB2) and a fiber optic cable (2 m long, 600 µm diameter, NA=0,22) and was used in the 300-500 nm spectral range.

For the study of the changes induced by laser ablation in the PDMS polymer, a high pulse energy laser system was required, which is also capable of using different wavelengths. Several laser systems were employed during the ablation experiments. The Thunder Art Nd:YAG laser (Quanta Systems, Italy) was suitable for this purpose, because it is capable of emitting single laser pulses at the fundamental, second and fourth harmonic wavelengths (1064, 532 and 266 nm) with maximum useful pulse energies of 900, 500 and 220 mJ. The pulses were 7-9 ns in duration and could be released with a maximum repetition rate of 20 Hz.

In addition to the above instrumentation, I also used optical microscopy, contact profilometry and FTIR spectroscopy. The two optical microscopes employed were a Labophot-2 (Nikon, Japan) and an Optika B600-TiFL (Optika, Italy) microscopes, whereas the contact profilometry was performed by using a Dektak-8 (Veeco, USA) equipment. The FT-IR measurements were performed on a Bio-Rad FTS-65A/896 spectrometer (ATR, Harrick Meridian Split-PEA Diamond ATR). Reference elemental analyses were done using a JY-24 type ICP-AES (Jobin-Yvon, France), and a 7500ce type ICP-MS spectrometer (Agilent, USA) devices.

Spectroscopic data was recorded using the AvaSoft 7 (Avantes,the Netherlands) and LIBSoft V9.0.5 (Applied Photonics, GB) software. The data evaluation was done with Peax 2 (Systematix AB, Sweden), Origin 8.6 (OriginLab 8.6, Northampton, MA), Office Excel 2010 (Microsoft, USA) and

Matlab R2012b (MathWorks, USA) software. The microscope images were taken with the TSView (Fuzhou Tucsen Image Technology, China) software. The figures and other illustrations were made by Origin 8.6 (OriginLab, USA) and Xara X (Xara, GB).

All metals and other chemicals used in the experiments were of analytical purity. For the calibration purposes, I used ICP-AES and ICP-MS standard stock solutions. In the experiments concerning qualitative discriminant analysis I used commercially available soldering tin samples, five different mineral coals and high purity graphite, six different kind of papers (office, half wood-free, colour) and eight types of printers.

PDMS microfluidic chips were cast in cooperation with The Department of Inorganic and Analytical Chemistry, University of Debrecen, by the method of soft lithography technique and using the Sylgard 184 (Dow Corning, USA) kit.

4. A concise description of the achieved scientific results

1. I have shown, through the measurement of the Pb and Sn content of various soldering samples, that in quantitative analytical applications the performance of multi-pulse LIBS supersedes that of single-pulse LIBS. Due to favourable plasma conditions, the dynamic range of MP-LIBS is significantly broader. The measurable top concentration can be as large as 40-60 m/m% as opposed to the typical 2-3% value for SP-LIBS. Reference measurements by ICP-AES spectrometry proved that the accuracy of MP-LIBS results in this application is good (the measurement error is only 1-5%), and the precision is about 5%. These figures of merit make MP-LIBS spectrometry highly useful for carrying out localized and fast industrial analytical measurements.

2. I have proved, by testing the performance of several comparative and advanced statistical methods and measuring various sample types, that LIBS spectra can be used highly efficiently for the qualitative discrimination analysis of solid samples, if the proper statistical method is used for the data evaluation. The analysis usually requires only one laser pulse to be delivered, thus it is fast and microdestructive. These results can be advantageously exploited in industrial, archaeological or forensic applications.

2a) I have showed that alloy (soldering tin) samples can be efficiently discriminated based on their LIBS spectra and by employing the method of overlapping integrals also in cases when the composition of the samples are identical in their major components and are different only in their trace element composition.

2b) After studying the laser ablation behaviour of a total of 54 clean and printed papers I successfully demonstrated that both the paper and the printer types can be accurately identified based on their LIBS spectra and by employing the appropriate comparative or advanced statistical method for data evaluation. The best results were obtained by using the

method of multivariate alternating curve resolution combined with discriminant analysis (MCR-ALS/DA), which showed 96% accuracy in the identification of paper, and 83% in the identification of the printer type.

3. I have systematically assessed the performance of several sample presentation methods useful for liquid sample LIBS analysis. I also successfully designed and built two kinds of LIBS ablation cells, which can be used for the measurement of biologically and/or chemically hazardous samples analysis in a closed system. These ablation cells were designed to allow the analysis of small sample volumes (μL), quickly, also in the field. The applicability was demonstrated by using a portable LIBS instrument and via assessing the analytical figures of merit for the case of the measurement of cesium in human blood serum and urine samples. The achieved absolute limits of detection in the two matrices were 6 and 27 ng, respectively.

4. For the first time in the literature, I successfully realized the coupling of a LIBS detector to a polydimethylsiloxane (PDMS) microfluidic device. The developed device allows the field-applicable handling and chemical sample preparation of small volume liquid samples prior to elemental analysis.

4a) By employing various spectroscopy and microscopy instruments, I was the first to study and document the laser ablation behaviour of the PDMS polymer under the impact of single pulses as well as a train of multiple laser pulses characterized by very short (μs range) interpulse delays.

4b) I successfully carried out the speciation analysis of Cr(III) and Cr(VI) in an aqueous sample with the help of the developed microfluidic setup with LIBS detector. The separation of ions was achieved via ion-pair forming with tetrabutylammonium bromide on a C18 microcolumn. Using as little as 0.5 μL sample volume, the achieved absolute detection limit was 2 ng, and the recovery was over 90%.

5. I was the first to carry out systematic experiments in order to assess the applicability of collinear double-pulse LIBS spectroscopy for the analysis of solid samples immersed in water. I studied the effect of several experimental conditions (water temperature, length of underwater optical path, interpulse delay and gate delay) on the intensity of analytical signals. It was established that the optimal interpulse delay time significantly decreases with the increase of the length of the underwater optical path, whereas the water temperature has a signal decreasing effect. Signal intensity and ablated mass also decrease with the length of the underwater optical path. The optimal detection gate delay was found to be 700 ns in all cases. In addition to the fundamental purposes of this study, these results can also be employed in marine archaeology.

5. Scientific publications

Hungarian Scientific Bibliography (MTMT) identifier: 10037134

Publications related to the scientific topic of the dissertation:

1. G. Galbács, N. Jedlinszki, **A. Metzinger**: Analysis and discrimination of soldering tin samples by collinear multi-pulse laser induced breakdown spectrometry, supported by inductively coupled plasma optical emission and mass spectrometry, *Microchemical Journal*, 107 (2013) 17-24
   IF_{2013}= 3,583

2. **A. Metzinger**, É. Kovács-Széles, I. Almási, G. Galbács: An assessment of the potential of laser induced-breakdown spectrometry for the analysis of cesium in liquid samples of biological origin, *Applied Spectroscopy*, 68 (2014) 789-793
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3. Jedlinszki N., **Metzinger A.**, Galbács G.: Az analitikai teljesítőképesség javítása kísérleti és numerikus eljárásokkal a lézer indukált plazma spektrometriában, *Magyar Kémiai Folyóirat*, 120 (2014) 50-54
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4. **A. Metzinger**, R. Rajkó, G. Galbács: Discrimination of paper and print types based on their laser induced breakdown spectra, *Spectrochimica Acta Part B*, 94-95 (2014) 48-57
   IF_{2014}= 3,176

5. F. J. Fortes, S. Guirado, **A. Metzinger**, J. J. Laserna, A study of underwater stand-off laser-induced breakdown spectroscopy for chemical analysis of objects in the deep ocean, *Journal of Analytical Atomic Spectrometry*, 30 (2015) 1050-1056
   IF_{2014}= 3,466

6. **A. Metzinger**, A. Nagy, A. Gáspár, Zs. Márton, É. Kovács-Széles, A. Buzás, G. Galbács, On the feasibility of liquid sample microanalysis using polydimethylsiloxane microfluidic cships with in-channel and in-port laser-induced breakdown spectroscopy, *Journal of Analytical Atomic Spectrometry*, (2015) közlésre benyújtva
   IF_{2014}= 3,466

$\Sigma IF_{accepted}$ =12,100

Other publications:

1. Z. Csendes, G. Varga, N. V. Nagy, É. G. Bajnóczi, M. Sipiczki, S. Carlson, S. E. Canton, **A. Metzinger**, G. Galbács, P. Sipos, I. Palinko: Synthesis, structural characterisation, and catalytic activity of Mn(II)–protected amino acid complexes covalently immobilised on chloropropylated silica gel, *Catalysis Today,* 241 (2015) 264-269
   IF_{2014}= 3,309

2. G. Galbács, H. Szokolai, A. Kormányos, A. Metzinger, L. Szekeres, C. Marcu, F. Peter, C. Muntean, A. Negrea, M. Ciopec, A. Jancsó, „Cd(II) capture ability of an immobilized, fluorescent 4 hexapeptide", *Bulletin of the Chemical Society of Japan*, 89 (2016) 243-253
   IF_{2014}= 2,210

$\Sigma\Sigma IF_{accepted}$ = 17,619

Conference lectures and posters related to the scientific topic of the dissertation:

1. G. Galbács, N. Jedlinszki, **A. Metzinger**, K. Fintor: Use of complementary spectral information from micro-Raman and LIBS spectroscopy for discrimination between paper and printing ink types, *XIV. Hungarian-Italian Symposium on Spectrochemistry*, Hungary, Sümeg, 5-7 October, 2011

   (poster)

2. Galbács G., Jedlinszki N., **Metzinger A.**: Hasonló eredetű minták LIBS spektrumainak összehasonlítása a minták megkülönböztetése céljából, *55. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 9-11 July, 2012

   (oral lecture)

3. **Metzinger A.**, A. Kadenkin, Galbács G., I. Gornushkin, Gáspár A.: Folyadékminták LIBS mérésére szolgáló mintaelőkészítési módszerek összehasonlítása, *55. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 9-11 July, 2012

   (poster)

4. **Metzinger A.**, Galbács G.: Folyadékminták vizsgálata LIBS spektroszkópiával, *Kémiai Előadói Napok*, Hungary, Szeged, 29-31 October, 2012

   (oral lecture)

5. **Metzinger A.,** Palicskó K., Nagy A., Gáspár A., Márton Zs., Galbács G.: Poli(dimetil-sziloxán) anyagú mikrofluidikai eszközök optikai és lézer ablációs jellemzőinek vizsgálata, *"Környezetbarát anyagok és technológiák" konferencia és 56. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 1-3 July, 2013

(oral lecture)

6. **Metzinger A.,** Rajkó R., Galbács G.: Fejlett statisztikai adatkiértékelési módszerek alkalmazása papír- és nyomatminták megkülönböztetésére lézer indukált plazma spektrumaik alapján, *"Környezetbarát anyagok és technológiák" konferencia és 56. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 1-3 July, 2013

   (poster)

7. **Metzinger A.**: LIBS spektrumok nyomelemanalitikai információinak felhasználása minták diszkriminációjára, *XXXI. Országos Tudományos Diákköri Konferencia*, *Kémia és Vegyipari Szekció*, Hungary, Eger, 3-5 April, 2013

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8. **A. Metzinger**, É. Kovács-Széles, I. Almási, G. Galbács: An assessment of the potential of laser induced breakdown spectrometry for the analysis of cesium in liquid samples of biological origin, *Proceedings of the 19th International Symposium on Analytical and Environmental Problems*, Hungary, Szeged, 23 September, 2013

   (poster)

9. **Metzinger A.**, Nagy A., Gáspár A., Márton Zs., Galbács G.: PDMS elasztomer lézer ablációs jellemzőinek vizsgálata, *XXXVI. Kémiai Előadói Napok*, Hungary, Szeged, 28-30 October, 2013

   (oral lecture)

10. G. Galbács, **A. Metzinger**, N. Jedlinszki, R. Rajkó: Laser induced breakdown spectrometry using multiple collinear laser pulses, *European*

Symposium on Atomic Spectrometry, Czech Republic, Prague, 16-21 March, 2014

(oral lecture)

11. S. Guirado, F. J. Fortes, **A. Metzinger**, J. J. Laserna: Chemical analysis of archeological material underwater by laser-induced breakdown spectroscopy, *XIV. Reunión del Grupo Regional Andaluz de la Sociedad Española de Química Analítica*, Spain, Madrid, 26-27 June, 2014

(poster)

Analytical Methods Poster Award

12. **Metzinger A.**, S. Guirado, F. J. Fortes, J. J. Laserna, Galbács G.: Folyadékminták analitikai teljesítőképességének és szilárd minták víz alatti mérési lehetőségének vizsgálata lézer indukált plazma spektroszkópiával, *I. Vízkémiai és Technológiai Konferencia és 57. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 7-9 July, 2014

(oral lecture)

13. Nagy A., Baranyai E., **Metzinger A.**, Galbács G., Gáspár A.: Mikrofluidikai csipek fejlesztése atomspektrometriás detektorokhoz, *I. Vízkémiai és Technológiai Konferencia és 57. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 7-9 July, 2014

(oral lecture)

14. A. Nagy, E. Baranyai, **A. Metzinger**, G. Galbács, A. Gáspár: Miniaturization efforts for atomic spectrometry, *14th Symposium and Summer School on Bioanalysis*, Slovakia, Bratislava-Smolenice, June 18.- July 6, 2014

(oral lecture)

15. **A. Metzinger**, D. Palásti, A. Nagy, A. Gáspár, É. Kovács-Széles, T. Ajtai, Z. Bozóki, G. Galbács: Analysis of liquid and aerosol samples by laser-induced breakdown spectroscopy, *European Winter Conference on Plasma Spectrochemistry*, Germany, Münster, 22-26 February, 2015

(poster)

16. Palásti D., **Metzinger A.**, Rajkó R., Ajtai T., Kovács-Széles É., Galbács G.: Szénminták és az ezekből lézeres ablációval keltett aeroszolok vizsgálata lézer indukált plazma spetkroszkópiával, *XII. Magyar Aeroszol Konferencia*, Hungary, Szeged, 18-20 March, 2015

(poster)

17. **A. Metzinger**, É. Kovács-Széles, G. Galbács, Development of analytical methods for the determination of Cs, Th, and U in nuclear run-off liquid samples by LIBS, *European Symposium on Atomic Spectrometry*, Hungary, Eger, 31 March- 2 April, 2016

(reported oral lecture)

Other conference lectures and posters:

1. G. Galbács, N. Jedlinszki, Cs. Mezei, **A. Metzinger**: Signal normalization in multi-pulse laser induced breakdown spectrometry, *The International Symposium on Analytical and Environmental Problems, with Special Emphasis on Heavy Metal Ion as Contaminants*, Hungary, Szeged, 24 September, 2012

(poster)

2. Kohut A., **Metzinger A.**, Márton Zs., L. Ludvigsson, K. Deppert, Geretovszky Zs., Galbács G.: Plazmaspektroszkópiai megfigyelések egy szikrakisülési nanorészecske generátorban, *"Környezetbarát anyagok és technológiák" konferencia és 56. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 1-3 July, 2013

(oral lecture)

3. Kohut A., **Metzinger A.**, Márton Zs., Kopniczky J., Galbács G., Geretovszky Zs.: Nanorészecskék folyadékfázisú lézer ablációs előállítása és vizsgálata, *Proceedings of the 19th International Symposium on Analytical and Environmental Problems*, Hungary, Szeged, 23 September, 2013

   (oral lecture)

4. Kálomista I., **Metzinger A.**, Galbács G.: Arany nanoszolok méreteloszlásának vizsgálata SP-ICP-MS módszerrel, *Proceedings of the 19th International Symposium on Analytical and Environmental Problems*, Hungary, Szeged, 23 September, 2013

   (poster)

5. A. Kohut, **A. Metzinger,** G. Galbács, L. Ludvigsson, B. O. Meuller, M. E. Messing, Zs. Márton, K. Deppert, Zs. Geretovszky: Emission spectroscopic investigation of the spark discharge used for Cu nanoparticle production, *European Aerosol Conference,* Czech Republic, Prague, 1-6 September, 2013

   (poster)

6. Kálomista I., **Metzinger A.**, Galbács G.: Nanoszolok méreteloszlásának vizsgálata SP-ICP-MS módszerrel, *XXXVI. Kémiai Előadói Napok*, Hungary, Szeged, 28-30 October, 2013

   (oral lecture)

7. Kohut A., **Metzinger A**., Márton Zs., L. Ludvigsson, K. Deppert, Galbács G., Geretovszky Zs.: Szikrakisüléses nanorészecske generátor emissziós spektroszkópiai vizsgálata Cu nanorészecskék előállítása közben, *XI. Magyar Aeroszol Konferencia*, Hungary, Debrecen, 28-30 October, 2013

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8. Kálomista I., **Metzinger A.**, Galbács G.: Fém és fémoxid típusú nanorészecskék vizsgálata, *XV. Eötvös Konferencia*, Hungary, Budapest, 25 April, 2014

(oral lecture)

9. L. Ludvigsson, A. Kohut, **A. Metzinger**, G. Galbács, B. O. Meuller, M. E. Messing, Zs. Márton, K. Deppert, Zs. Geretovszky.: Spectroscopic investigation of fundamental spark properties during nanoparticle production, *Nordic Society for Aerosol Research - Aerosol Symposium 2014*, Sweden, Stockholm, 30-31 January, 2014

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10. Kálomista I., Horváth G., **Metzinger A.**, Geretovszky Zs., Galbács G.: Lézeres ablációval és kémiai eljárással vizes közegben készített nanorészecskék vizsgálata, *I. Vízkémiai és Technológiai Konferencia és 57. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 7-9 July, 2014

(poster)

11. Galbács G., **Metzinger A.**, Kálomista I.: Induktív csatolású plazma tömegspektrometriás mérések deutérium tartalmú vizes közegű mintákban, *I. Vízkémiai és Technológiai Konferencia és 57. Magyar Spektrokémiai Vándorgyűlés*, Hungary, Veszprém, 7-9 July, 2014

(poster)

12. I. Kálomista, G. Horváth, **A. Metzinger**, Zs. Geretovszky, G. Galbács: On the synthesis and characterization of metal and metal-oxide nanoparticles in aqeous medium, *6th Szeged International Workshop on Advances in Nanoscience*, Hungary, Szeged, 15-18 October, 2014

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13. A. Kohut, **A. Metzinger**, G. Galbács, L. Ludvigsson, B. Meuller, M. E. Messing, Zs. Márton, K. Deppert, Zs. Geretovszky: Au nanoparticle generation by spark discharge – An emission spectroscopic study, *6th Szeged International Workshop on Advances in Nanoscience*, Hungary, Szeged, 15-18 October, 2014

(poster)

14. I. Kálomista, **A. Metzinger**, G. Galbács: Rapid characterization of nanoparticles using single particle ICP-MS in cases complicated by spectral interferences, *European Winter Conference on Plasma Spectrochemistry*, Germany, Münster, 22-26 February, 2015

(poster)

15. A. Jancsó, S. Bálint, L. Szekeres, H. Szokolai, L. Rózsahegyi, G. Galbács, A. Kormányos, **A. Metzinger**, I. Kálomista: Peptides as potential receptors for sensing metal ions, *XIII. International Symposium on Inorganic Biochemistry*, Poland, Karpacz, 1-6 September, 2015

(poster)