

Doctoral (*Ph.D.*) theses

Characterization and analytical application of multi-pulse laser induced plasmas

Nikoletta Jedlinszki

Supervisor: Dr. Gábor Galbács

Associate professor

Chemistry Doctoral School

University of Szeged

Faculty of Sciences and Informatics

Department of Inorganic and Analytical Chemistry



2011

1. Introduction

Laser light has several properties that can be used to the benefit of atomic spectrometry. These properties include narrow bandwidth, high intensity and good directionality that can be used for the efficient and selective excitation of analyte species. Very high irradiance is available from lasers operating in pulse mode, which can break down and evaporate solid samples, thus providing a means of sample introduction with high spatial resolution. In addition to the above, there are lasers which are tunable too. Thanks to these and other features of laser sources, several new analytical atomic spectroscopy methods came into existence and the analytical performance of known methods enhanced significantly in the past couple of decades.

One novel laser atomic spectroscopy method is laser-induced breakdown spectroscopy (LIBS), which is based on the observation of the emission of a microplasma created on the sample surface. This method allows for the determination of the elemental composition of any condensed or gaseous samples without sample preparation also with spatial or depth resolution, even from a distance or in the field. The number of the LIBS analytical applications is increasing quickly due to these favorable properties and the rapid development of opto-electrical devices. LIBS is nowadays is applied in diverse fields such as in space research or in the pharmaceutical industry, investigation of the cultural heritage or environmental studies, just to name a few.

LIBS is also subject to intense physical and analytical research worldwide. LIBS research mainly aims at investigating ablation and excitation mechanisms taking place in laser-induced plasmas and at the development of the analytical performance. Since 2000, the laser- and plasma atomic spectroscopic research group working at our department is also active in the field of LIBS research. I joined the group in 2006. The objective of my research activity has been to investigate the physical and spectroscopic characteristics, as well as the analytical performance of plasmas induced by two or more collinear laser impulses.

2. Objectives

An improved analytical performance can be achieved in LIBS, if more than one laser pulses, rapidly following each other, are used for the generation of a laser-induced plasma. This has been convincingly documented by several studies in the literature, especially in the relatively easy-to-realize case of double-pulse LIBS (DP-LIBS), but also for triple- or multiple-pulse LIBS (TP-LIBS and MP-LIBS). However, it is not yet conclusively clarified yet, what fundamental processes are responsible for or contribute to the improvement of analytical performance. Contradicting observations and theories can also be found on the matter in the literature, which is so partly because LIBS setups used in studies are slightly different, and experimental conditions are known to have a significant effect on the processes taking place in the high temperature and very transient environment of LIB plasmas.

The above said things especially apply to collinear MP-LIBS, where plasma processes are even more complicated. Collinear MP-LIBS studies are also scarce in the literature, although the published data are generally very promising.

Based on this, the aim of the present series of investigations was to examine the characteristics of MP-LIB plasmas induced by collinear laser impulses and to assess the analytical performance of the method. In particular, my experimental work was centered around the following three areas:

- 1.) Construction and execution of temporally and spatially resolved spectroscopic measurements to pursue the causes of the improved analytical performance, experienced in former experiments,

- 2.) Extensive, systematic studying of the analytical figures of merit of collinear MP-LIBS,

- 3.) Development of analytical methods for the application of collinear MP-LIBS spectrometry to the determination of elemental composition of different solid samples. In this part my work, I paid special attention to the application of the novel calibration method (generalized linear correlation method, GLCM), introduced formerly by our research group.

3. Experimental

3.1. Materials

- **Analytical purity metals:** Al, Cu, Mg, Si and Zn sheets (Reanal, Hungary; BDH and Advent Material Research, Great Britain).
- **Gold alloys:** a nine-member, certified gold alloy series. The marking and gold content of the samples were the followings: 8K=334.1‰; 10K=412.7‰; 12K=506.3‰; 14K=586.8‰; 16K=674.2‰; 18K=756.8‰; 20K=838.1‰; 22K=912.2‰ and 24K=994.3‰, respectively. These certified concentration datas were determined by the standard cupellation method in two standard assay offices in Hungary. The ratio of the concentrations of the alloying elements was the same in all samples.
- **Steel samples:** a six-member, certified steel sample series (Research Institute for Ferrous Metallurgy, Budapest, Hungary). The marking and chromium content of the samples were A3=0.37%; A2=0.66%; A12=1.25%; A1=1.46%; A16=1.75% és A11=2.16%, respectively.
- **Aluminum alloy:** SM10 with a certified composition of 84.67% Al, 2.9% Si, 5.45% Zn, 2.8% Cu, 1.96% Fe, 1.08% Mg, 0.29% Mn, 0.24% Pb, 0.26% Sn (Apex Smelter Co., South-Africa).
- **Soldering tin samples:** commercially available alloys. The manufacturer, product number and composition of the samples were as follows: CFH 52340 No. 3 (Sn 97%, Cu 3%), CFH 52330 (Sn 40%, Pb 60%), Multicore 419590 (Sn 5%, Pb 93.5%, Ag 1.5%), Lux 539066 (Sn 30%, Pb 70%), Super Solder Wire (Sn 60%, Pb 40%).
- **Galvanized metal samples:** commercially available chromium-coated copper and nickel-coated zinc alloys.
- **Pyrolytic graphite:** highly oriented pyrolytic graphite (HOPG) flats (Advanced Ceramics Corporation, Lakewood, OH, USA).
- **Polytetrafluoroethylene (PTFE):** commercial, 80 µm thick, 12 mm wide filling tape (Schläfer, Germany).
- **Poliethylene (PE):** BCR CRM 680, a plastic standard material with certified elemental contents (Institute for Reference Materials and Measurements, Belgium)

No special sample preparation was performed on the samples prior to the measurements. The samples were simply fixed to microscope slides using double-sided adhesive tapes (Tesa, Germany) and their surface was wiped clean with analytical purity acetone or ethanol.

3.2. Instruments

The predominant part of the experiments was performed using the MP-LIBS system built in our laboratory. The system is centered around a metallurgical microscope (SP80, Brunel), which not only allows for the effective focusing of the laser light onto the sample surface, but also for the convenient moving and observation of the sample by a digital camera (Motic 350, Motic). The system includes a flashlamp-pumped, compact Nd:GGG laser, repetition rate is 1 Hz, equipped with a solid state passive Q-switch, and emitting at 1055 nm (MP/G-Q-005, Technoorg-Linda). The duration of the pulses is ≈ 10 ns and the number of the pulses can be directly controlled. The microplasma is observed using a two-channel fiber optic CCD spectrometer (AvaSpec 2048FT, Avantes) which allows for time- and space-integrated LIBS data collection both in the UV (198–318 nm; 0.09 nm optical resolution) and Vis (345–888 nm; 0.4 nm optical resolution) spectral ranges. The plasma light emission is collected and coupled into two, deep-UV resistant 200 μm diameter optical fiber by two collimating lenses placed at an angle of 45° . The synchronization of the spectrometer operation with the laser is done by means of a Si photodiode and a pulse delay generator (TGP-110, TTI). The pulse structure of the laser source is monitored using digital storage oscilloscopes (TDS-1002, Tektronix; DS1102E, Rigol). The delay time for spectral data collection was 3.4 μs and the integration time was 2 ms. All spectra were collected in ambient air.

Characteristics of the ablation craters was studied by means of light microscopy, scanning electron microscopy (Hitachi S-4700 SEM) and optical profilometry (Veeco Wyko 1000 NT). The temporal and spatial evolution of the plasma was studied with an iCCD camera (576-S/RB-E, Princeton Instruments) attached to an imaging spectrograph (SpectraPro-500i, Acton Research).

Hereby I would also like to clarify in what sense the expression „laser shot“ is used throughout this dissertation. One „laser shot“ means one „firing“ of the laser, that is releasing a laser burst consisting of the adjusted number of pulses. In spectroscopy experiments, one shot is also accompanied by the recording of an emission (UV and/or Vis) spectrum.

Since the reproducibility of the pulse structure is not prominently good by the used Q-switched lasers, hence to obtain consistent data we did all experiments in 20–50 repetitions along with the monitoring of the burst structure and then retained only those data that originated from laser bursts with very similar structure (within about 5% tolerance).

Spectral lines in LIBS spectra were assigned using a spectroscopy software (Peax v2.0, Systematix AB) based on the NIST (National Institute of Standards and Technology) database. All further data evaluation and presentation was done in Microsoft Office Excel 2003 (Microsoft) and in Origin 7.5 (OriginLab).

4. Summary of new scientific results

1. Study of the ablation, spatial and temporal characteristics of MP-LIB plasmas

- 1.a.** By means of profilometric and microscopic examination of ablation craters produced in pure copper and galvanized alloys I established that an interaction exists between the ablation processes induced by collinear laser pulses. The increase of the ablation depth with the number of pulses was found to be stronger than linear; for example, the amount of the material ablated by a four-pulse burst was found to be six times greater than that ablated by the same number of single pulses. Based on my results and literature data, the increase of the ablated material can be attributed to the decrease of the ablation threshold due to the pre-heating of the sample surface and/or the lower pressure zone above the sample surface produced by earlier pulses within the burst.
- 1.b.** I studied the temporal and spatial evolution of collinear MP-LIB plasmas and I established, that the luminosity, the maximum volume and the linear expansion rate of the plasma induced by the first laser pulse are lower than relevant data for later coming pulses and the SP-LIB plasma lifetime is the half. The shape of MP-LIB plasmas is similar to the shape of SP-LIB plasmas: it is basically globular with some elongation in the vertical direction. I also determined the temperature of MP-LIB plasmas using Saha-Boltzmann method and the intensity of Mg ionic lines and I found it to be 20000-25000K. The results indicate that the later coming pulses, with the exception of the second pulse, are not able to heat the plasma to a higher temperature than former pulses.
- 1.c.** I studied the temporal course of line and continuum emission by MP-LIB plasmas induced on Si, Zn, Cu and Al targets. The emission from spectral lines with high excitation potential and integrated background emission was found to be stepwise in time, while the emission from spectral lines with lower excitation energy (originating mainly from neutral species) ring off very slowly, with a duration of sometimes as much as several ms. I established that the time steps of the stepwise emission curves coincide with the interpulse time delays. These results suggest that for the excitation of species with high excitation energy, the conditions are only favorable for the short time in the lifetime of an MP-LIB plasma when a laser pulse rekindles the plasma and its temperature is the highest.

1.d. Based on the above presented results, I provided experimental evidence that the reproducible significant signal enhancement in collinear MP-LIBS spectroscopy with time integrated detection is mainly due to the effect of two mechanisms. The determining mechanism is the repetitive ablation caused by sequential laser pulses, which results in a higher total ablated mass, also increased by the decrease of the ablation threshold. The other mechanism is plasma reheating and the re-excitation of plasma species by sequential laser pulses.

2. Characterization of analytical performance

2.a. I studied the net and the pulse number (energy) normalized net signal intensity as a function of the number of pulses in a burst in metallic, polymer and graphite samples. In case of atomic spectral lines I established, that both the net and the energy normalized net intensities increase with the increase of the number of pulses. For ionic lines I found a different behavior; some lines (e.g. Mg (II) 448.1 nm and Si (II) 412.8 nm) behave analogously to neutral lines, but in case of other ionic lines (e.g. Au (II) 312.7 nm and Al (II) 422.7 nm) the normalized intensity curves are practically constant. This indicates that the net signal intensity for these lines which originate from high-lying excited levels, generated by each pulse is similar or increases only slightly. I established from numerous data, that using our experimental MP-LIBS system and six laser pulses the maximum signal enhancement can be found at spectral lines with 5-7 eV excitation potential. I showed, that the background signal generated by each pulse in the burst is short lived and its contribution is about the same from the second pulse on, hence the use of time integrated spectral data acquisition does not worsen the S/B ratio.

2.b. I experimentally studied the behavior of the net intensity of spectral lines of the same element in different matrices as a function of the number of laser pulses. I found that the influence of matrix is relatively low on the shape of intensity curves as a function of the number of pulses, however the relative net signal enhancement with the same pulse number is different for the same spectral line in different matrices.

2.c. I showed that the repeatability improves significantly with an increase of the number of pulses in a burst. Using six pulses in a burst, the relative standard

deviation on net intensities drops down to about 5%. This value means a multiple-time improvement compared to the repeatability of SP-LIBS signals.

2.d. I established that the linear dynamic range of MP-LIBS calibration curves is much wider than SP- or DP-LIBS calibration curves. The effect of self absorption - which restricts the upper concentration limit of the linear dynamic range for SP-LIBS - is advantageously suppressed, and the calibration curves show good linearity up to tens of percents concentration.

2.e. I demonstrated, that as a combined consequence of the improved repeatability and increased sensitivity is a significant improvement of the limits of detection. In our experimental system and for the studied spectral lines, MP-LIBS LOD data were 4.2-16.7 times better than DP-LIBS data.

3. Analytical applications

3.a. An analytical method was worked out for the accurate determination of the accurate composition of gold alloys. After a careful optimization of experimental parameters, using the advanced GLCM calibration method and by exploiting the improved analytical performances provided by collinear MP-LIBS it is feasible to perform a quantitative analysis of gold alloys with an accuracy and precision comparable to that of the cupellation method. The error and the precision of my results were only a few ‰.

5. Scientific publications

Publications related to the scientific topic of the dissertation

1. G. Galbács, **N. Jedlinszki**, G. Cseh, Z. Galbács, L. Túri: Accurate quantitative analysis of gold alloys using multi-pulse laser induced breakdown spectroscopy and a correlation-based calibration method, *Spectrochimica Acta Part B*, 63 (2008) 591-597.

IF₂₀₀₈=2,853

2. G. Galbács, **N. Jedlinszki**, K. Herreira, B. Lauly, N. Omenetto, J.D. Winefordner: A study of ablation, spatial and temporal characteristics of laser-induced plasmas generated by multiple collinear pulses, *Applied Spectroscopy*, 64 (2010) 91-102.

IF₂₀₀₉=1,564

3. **N. Jedlinszki**, G. Galbács: An evaluation of the analytical performance of collinear multi-pulse laser induced breakdown spectroscopy, *Microchemical Journal*, 97 (2011) 255-263.

IF₂₀₁₀=2,579

ΣIF=6,996

Other publications

1. G. Galbács, I. Kevei-Bárány, E. Szőke, **N. Jedlinszki**, I.B. Gornushkin, M.Z. Galbács: A study of stalagmite samples from Baradla Cave (Hungary) by laser induced plasma spectrometry with automatic signal correction, *Microchemical Journal*, közlésre benyújtva

Conference lectures and posters

1. Galbács G., Cseh G., Galbács Z., **Jedlinszki N.**: Műanyag minták RoHS megfelelési vizsgálata többszörös lézerimpulzusokkal indukált plazma spektroszkópiával, 49. Magyar Spektrokémiai Vándorgyűlés, 2006. július 10-12., Miskolc

Oral lecture

2. Galbács G., **Jedlinszki N.**, Cseh G.: Elemanalitikai mérések lézer- és röntgensugárzással működő korszerű spektrométerekkel, 13rd Symposium on Analytical and Environmental Problems, September 25, 2006, Szeged

Poster

3. **Jedlinszki N.**: Műanyag minták elemanalitikai célú vizsgálata spektroszkópiai módszerekkel, *XXVIII. Országos Tudományos Diákköri Konferencia*, 2007. április 2-4., Szeged

Oral lecture

4. Galbács G., Cseh G., **Jedlinszki N.**, Galbács Z.: A többszörös impulzusokkal kivitelezett lézer indukált plazma spektroszkópia analitikai alkalmazásai, *50. Centenárium Vegyészkonferencia*, 2007. május 29-június 1, Sopron

Oral lecture

5. **Jedlinszki N.**, Cseh G., Galbács G.: Aranyötvözetek pontos mennyiségi analízise lézer indukált plazma spektrométerrel, *14th Symposium on Analytical and Environmental Problems*, September 24, 2007, Szeged

Poster

6. G. Galbács, **N. Jedlinszki**, G. Cseh, Z. Galbács, L. Túri: Accurate quantitative analysis of gold alloys using multi-pulse laser induced breakdown spectroscopy and a correlation-based calibration method, *2008 Pittsburgh Conference*, March 2-8, 2008, New Orleans, USA

Poster

7. **N. Jedlinszki**, G. Cseh, G. Galbács: Application of laser induced breakdown spectroscopy to the qualitative analysis of samples related to the human health, *10th DKMT Conf. on Cross-border Bioecology and Public Health*, May 16-17, 2008, Arad, Romania

Poster

8. **N. Jedlinszki**, G. Galbács, B. Lauly: Spatially and temporally resolved studies on LIB plasmas induced by multiple laser pulses, *5th International Conference on LIBS (LIBS 2008)*, 2008, September 22-26, Berlin, Germany

Poster

9. **N. Jedlinszki**, G. Cseh, G. Galbács: Evaluation of the analytical performance of multi-pulse laser-induced breakdown spectroscopy (MP-LIBS), *Colloquium Spectroscopicum Internationale XXXVI*, August 30-September 3, 2009, Budapest

Oral lecture

10. A. Buzás, Zs. Geretovszky, **N. Jedlinszki**, G. Galbács: On the role of the elevated temperature of the target in the enhanced emission signal in multi-pulse laser-

induced breakdown plasma (MP-LIBS) spectroscopy, *Colloquium Spectroscopicum Internationale XXXVI*, August 30-September 3, 2009, Budapest

Oral lecture

11. **Jedlinszki N.**, Galbács G.: A többimpulzusos lézer indukált plazma spektroszkópia (MP-LIBS) analitikai teljesítőképességének vizsgálata, *XXXII. Kémiai Előadói Napok Tudományos Szimpózium*, 2009. október 26-28., Szeged

Oral lecture

12. Galbács G., **Jedlinszki N.**, Geretovszky Zs.: Az analitikai jellemzők javítása a lézer indukált plazmaspektroszkópiában, MKE Analitikai Napok, 2010. január 28-29., Budapest

Oral lecture

13. **Jedlinszki N.**, Kukovecz Á., Galbács G.: Többimpulzusos lézer ablációs kráterek morfológiai és kémiai jellemzőinek tanulmányozása, *Vegyészkonferencia és 53. Magyar Spektrokémiai Vándorgyűlés*, 2010. június 30-július 2., Hajdúszoboszló

Oral lecture

14. G. Galbács, **N. Jedlinszki**: A comparative evaluation of the efficiency of signal normalization methods in SP-LIBS and MP-LIBS, *XIV. Hungarian-Italian Symposium on Spectrochemistry*, 2011. október 5-7., Sümeg, Hungary

Reported oral lecture

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

Reported oral lecture