SPEKTROSKOPIE LASEREM BUZENÉHO PLAZMATU

LIBS

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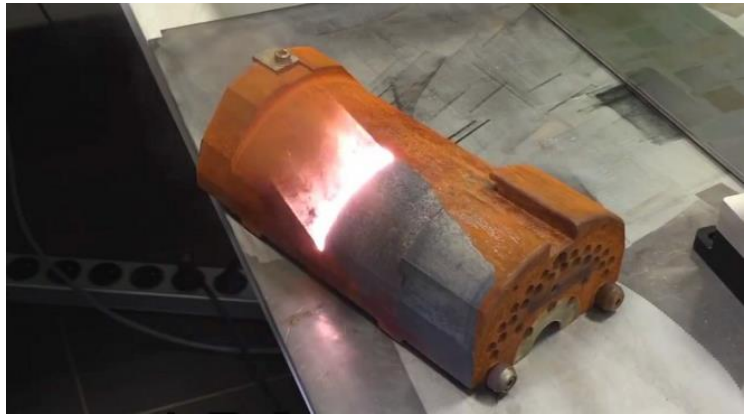
PřF UK na Albertově
28. března 2023

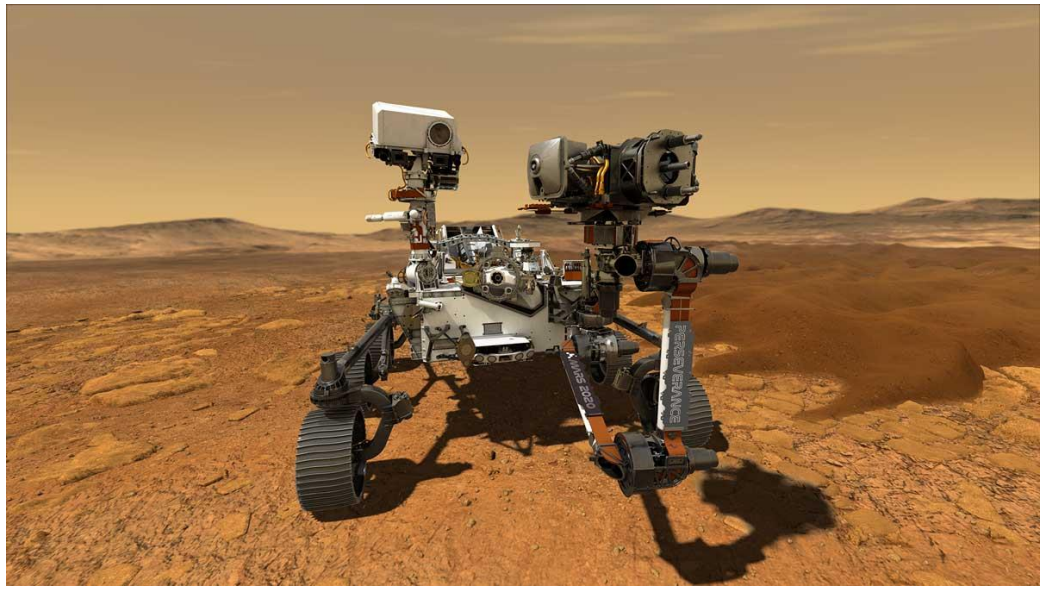
MUNI SCI

Science fiction recently, the reality today ...



Surface cleaning, welding, drilling

ELI BEAMLINES – advanced research



Space exploration

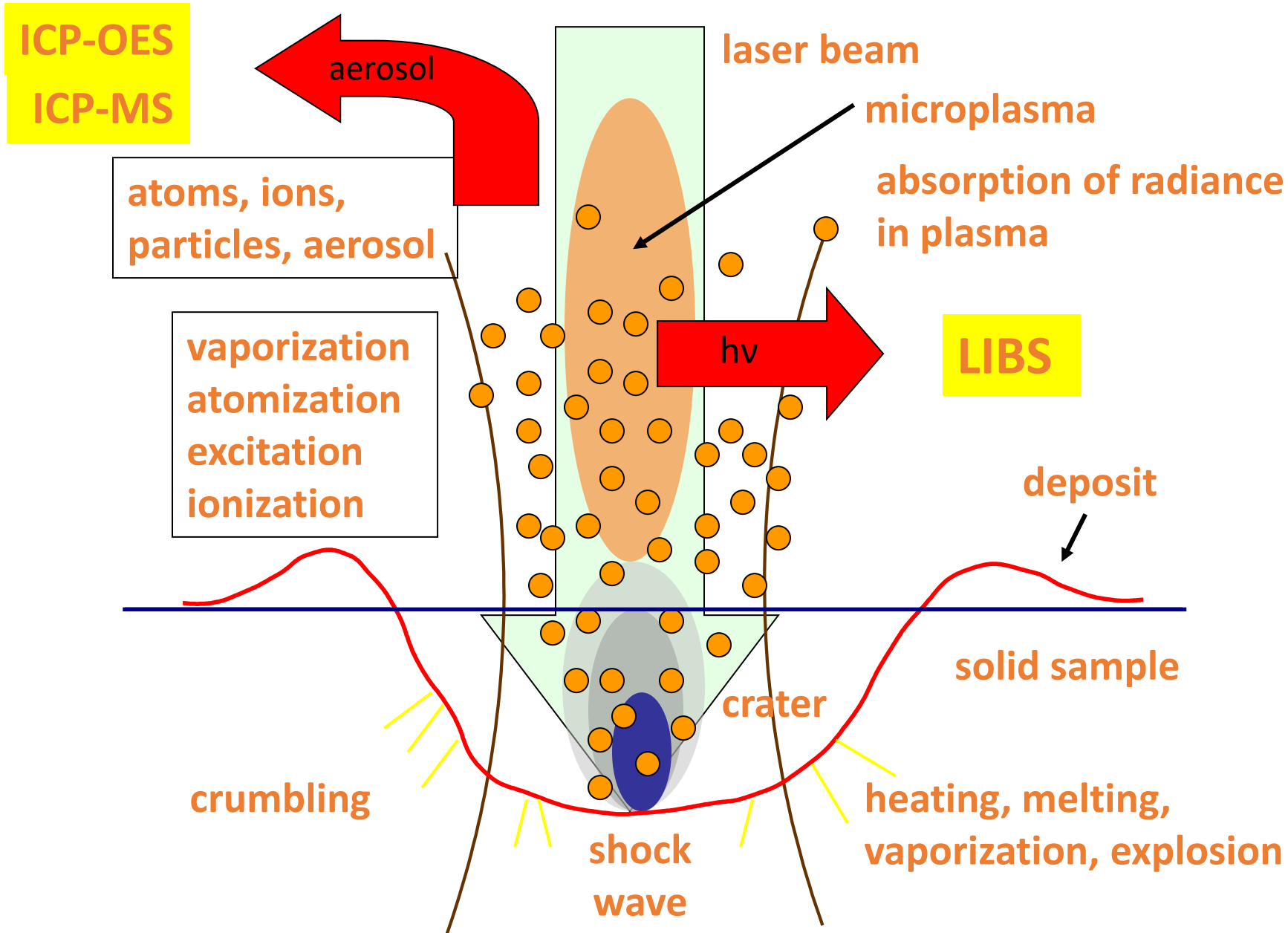
LIBS

(Laser-Induced Breakdown Spectroscopy)

High energy laser pulse - sample interaction:
three steps in dependence on laser energy

- damage threshold – **surface modification**
  (observable in an optical microscope)
- ablation threshold – **material removal**
  (LA-ICP-OES/MS signal starts to occur)
- plasma threshold – **optical breakdown of the vapour phase**
  (plasma ignition - LIBS signal)

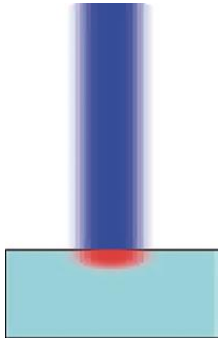
Laser beam - solid sample interaction



Laser beam - solid sample interaction

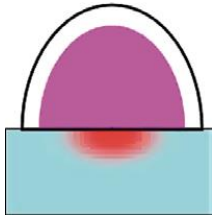
Plasma ignition: **ns laser (10^7 – 10^{11} W/cm^2)**
fs laser (10^{12} – 10^{17} W/cm^2)

Thermal vaporization (10^{-9} – 10^{-8} s)
Non-thermal ablation (10^{-9} – 10^{-8} s)
Plasma shielding (10^{-9} – 10^{-8} s)



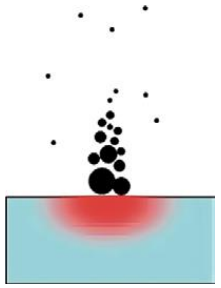
Plasma expansion and cooling:

Shockwave propagation
Plasma expansion (10^{-11} – 10^{-6} s)
Plasma radiation cooling (10^{-6} – 10^{-4} s)

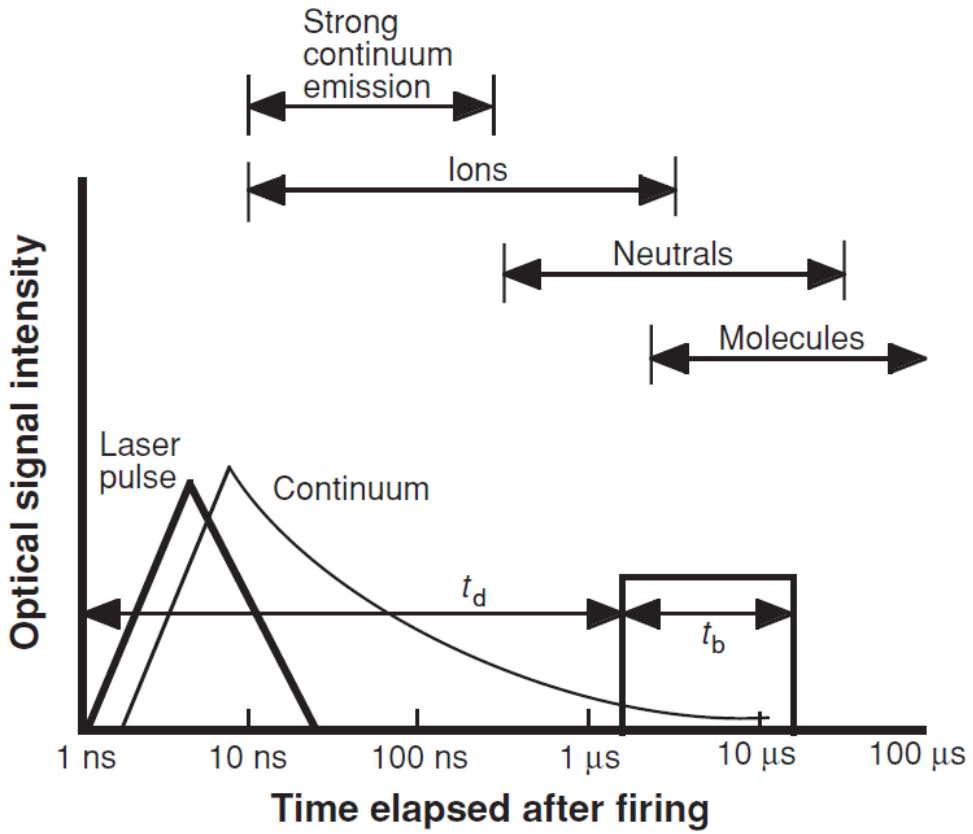


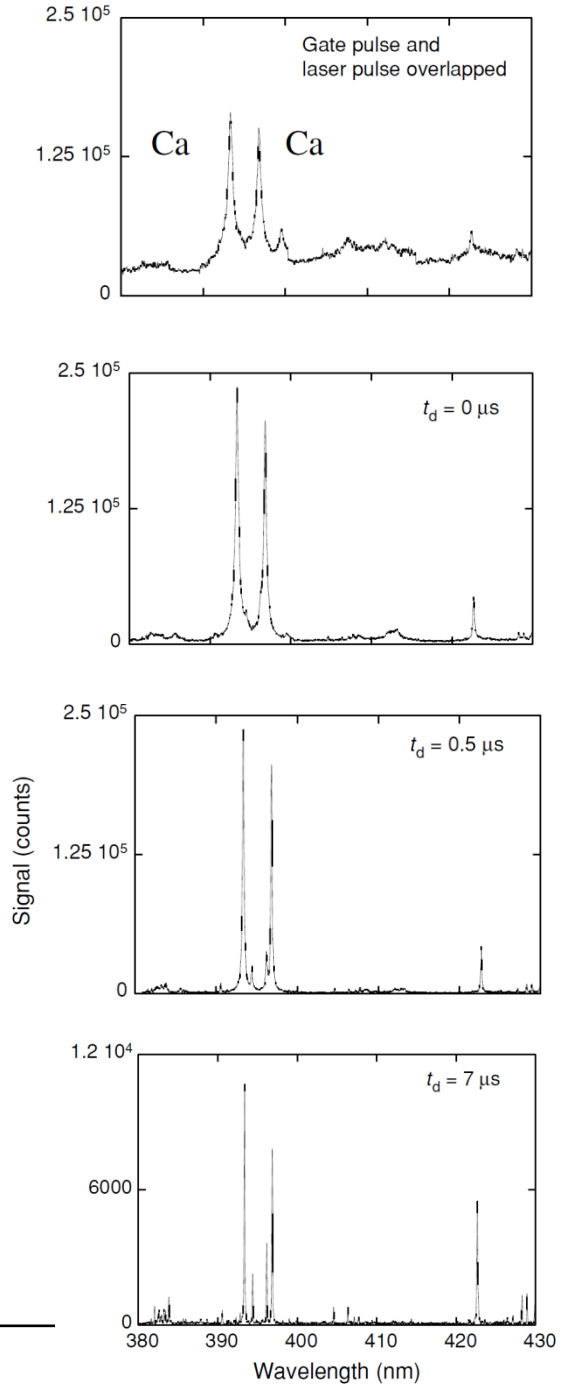
Particle ejection and condensation:

Ejection of liquid droplet (10^{-8} – 10^{-6} s)
Solid exfoliation (10^{-8} – 10^{-6} s)
Nano particles formation (10^{-4} – 10^{-3} s)



Important time periods after plasma formation





t_d - delay time, t_b – gate pulse width

LIBS

(Laser-Induced Breakdown Spectroscopy)

LAS – laser ablation spectrometry

LSS – laser spark spectrometry

-interaction of the sample with a laser beam of high radiation density (~ 0.1 – 10 $GWcm^{-2}$ - laser ablation), pulsed lasers

-rapid heating of the sample surface, evaporation, release of material in the form of aerosols and vapors

- microplasma formation, **emission of electromagnetic radiation**

- optical detection (**time-resolved spectrometry**)

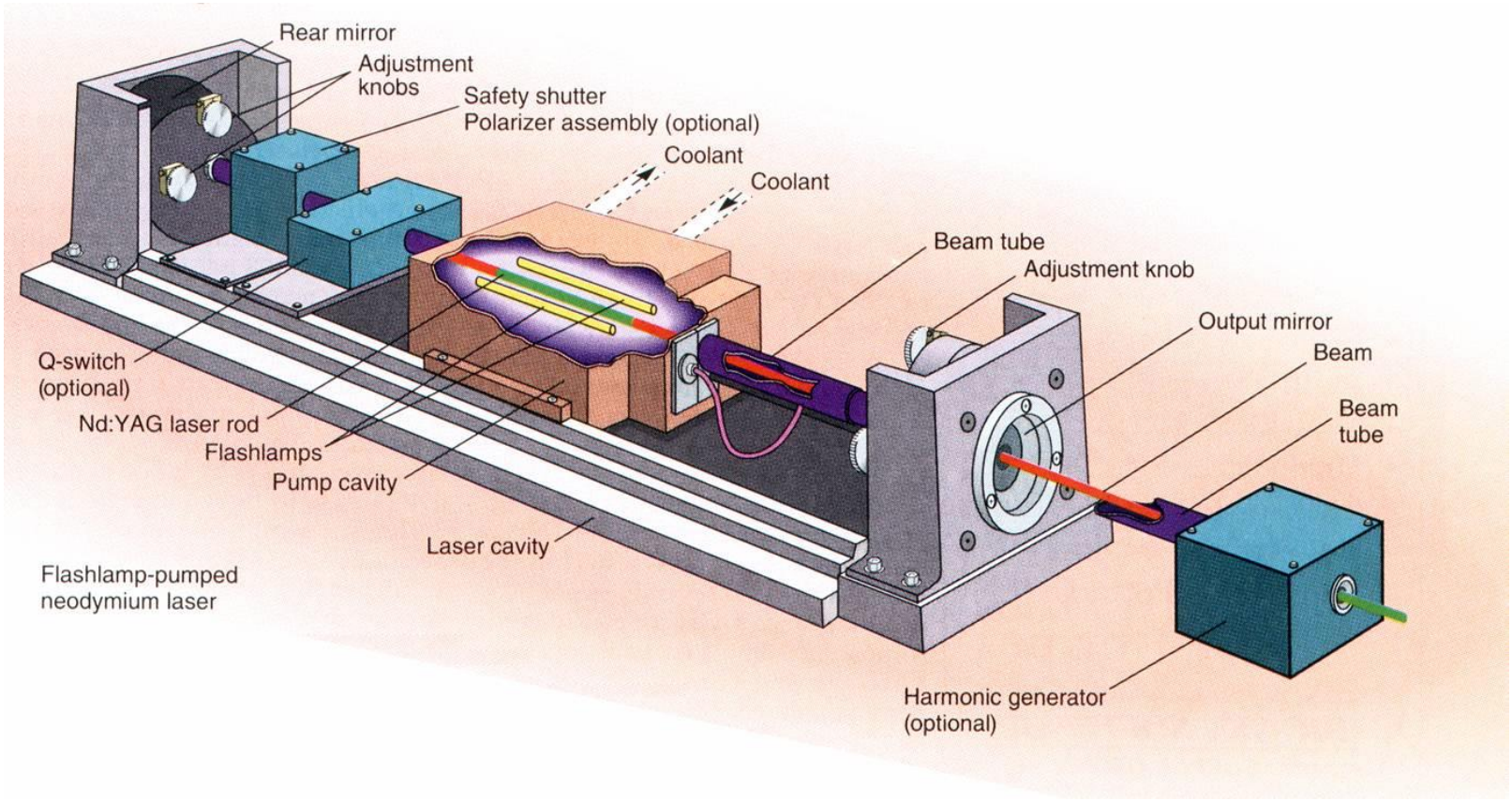
Pulsed laser typically used for LIBS

Type	Wavelength (nm)	Pulse width (ns)	Rep. rate (Hz)	Comments related to LIBS applications
Nd:YAG (s)	Fundamental: 1064	6–15	ss to 20	(1) Fundamental wavelength easily shifted to provide harmonic wavelengths (2) Available in very compact form for small instrumentation (3) Good beam quality possible (4) Dual-pulse capabilities in single unit (5) Flashlamp or diode-pumped available
	Harmonics: 532, 355, 266	4–8		
Excimer (g)	XeCl: 308	20 ns	ss to 200	(1) Requires periodic change of gases (2) Beam quality less than Nd:YAG laser (3) Provides UV wavelengths only
	KrF: 248			
	ArF: 194			
CO_2 (g)	10 600	200 (with 1000 ns trailing edge)	ss to 200	(1) Requires periodic change of gases or gas flow (2) Does not couple well into many metals (3) Beam quality less than Nd:YAG laser
Microchip	1064	<1 ns	1–10 k	(1) Good mode and beam quality (2) High shot-to-shot pulse stability
Ti:sapphire: femtosecond (s)	~800 ($\Delta\lambda$ ~ 10 nm)	20–200 fs	$10–10^3$	
Fiber laser (s)	Nd^{+3} 900 Pr^{+3} 1060 Er^{+3} 1540	<50	25–500 k	

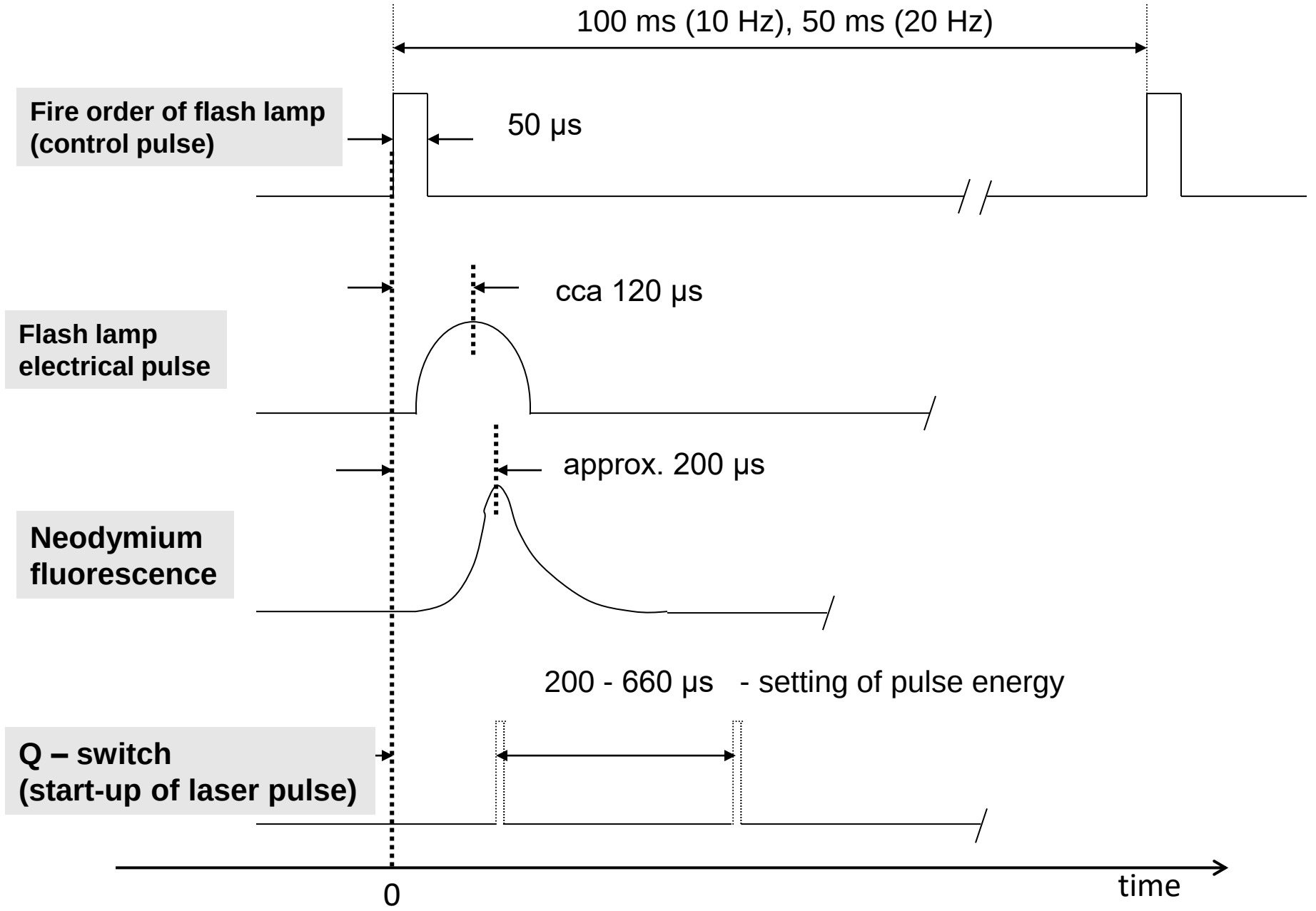
Notes: (s) = solid state laser; (g) = gas laser; ss = single shot.

Handbook of Laser-Induced Breakdown Spectroscopy D. Cremers and L. Radziemski

Nd:YAG laser used for LIBS



Overall timing diagram

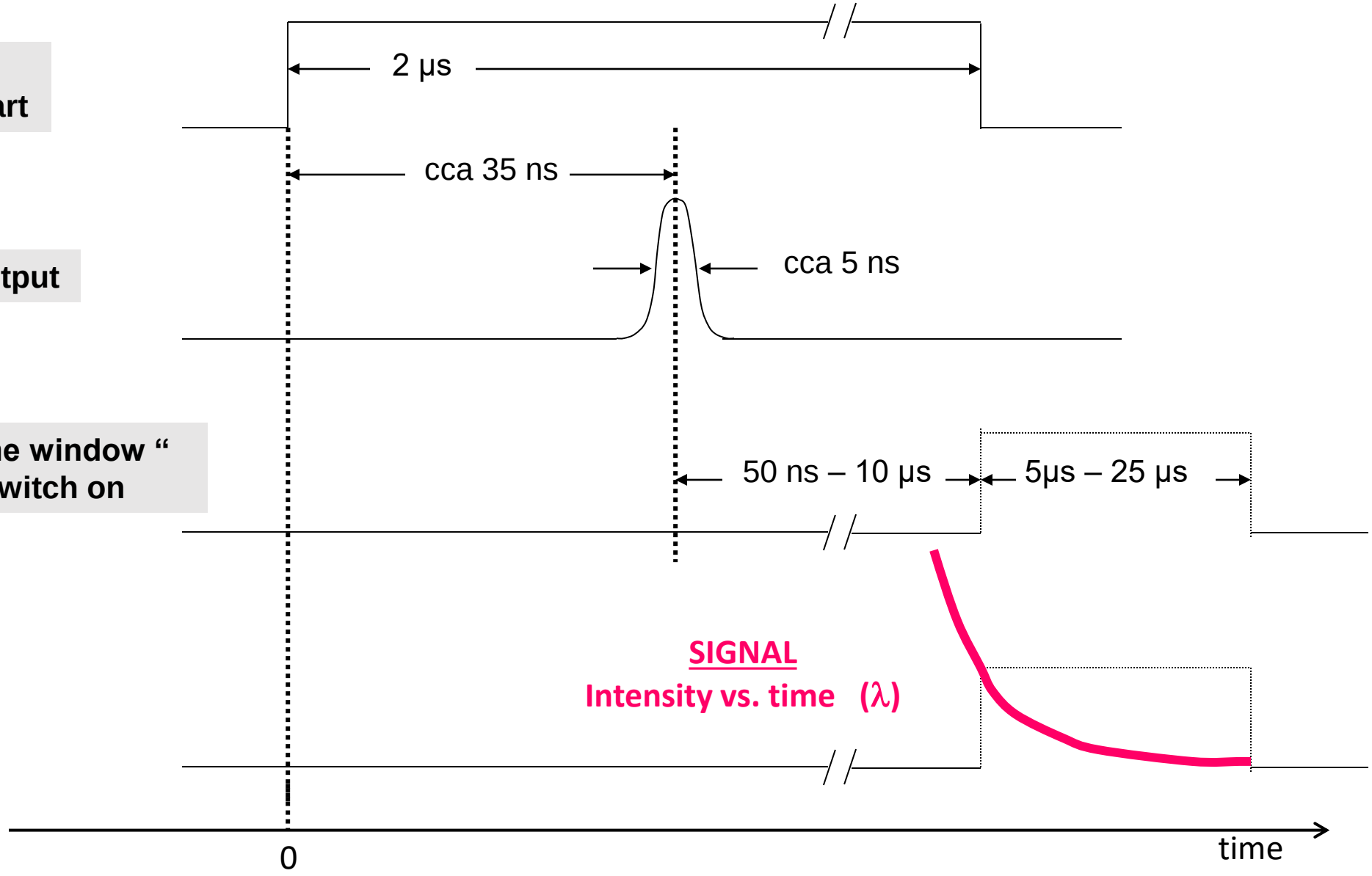


Overall timing diagram

Q – switch
laser pulse start

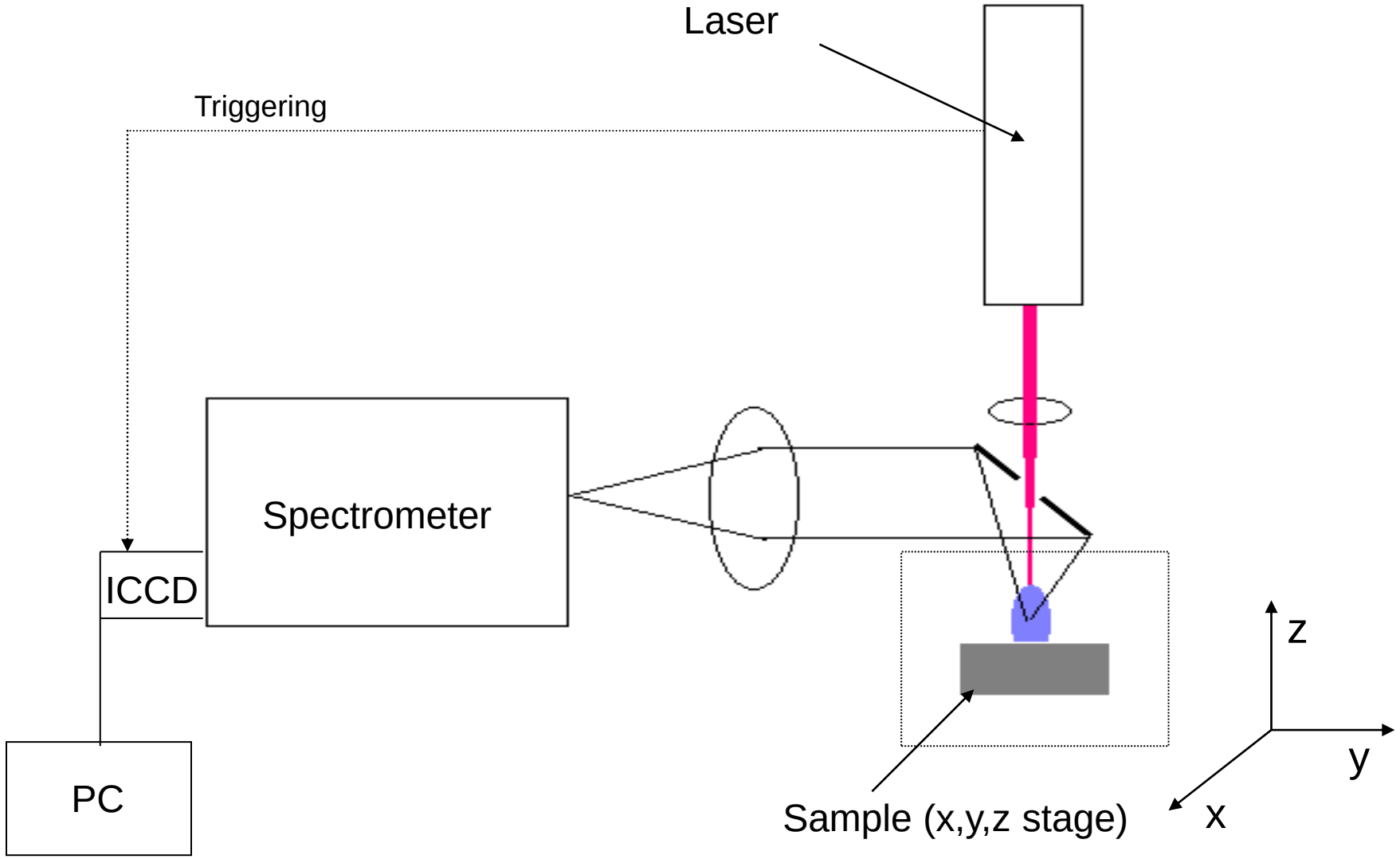
Laser pulse output

Detection „ time window “
ICCD or PMT switch on

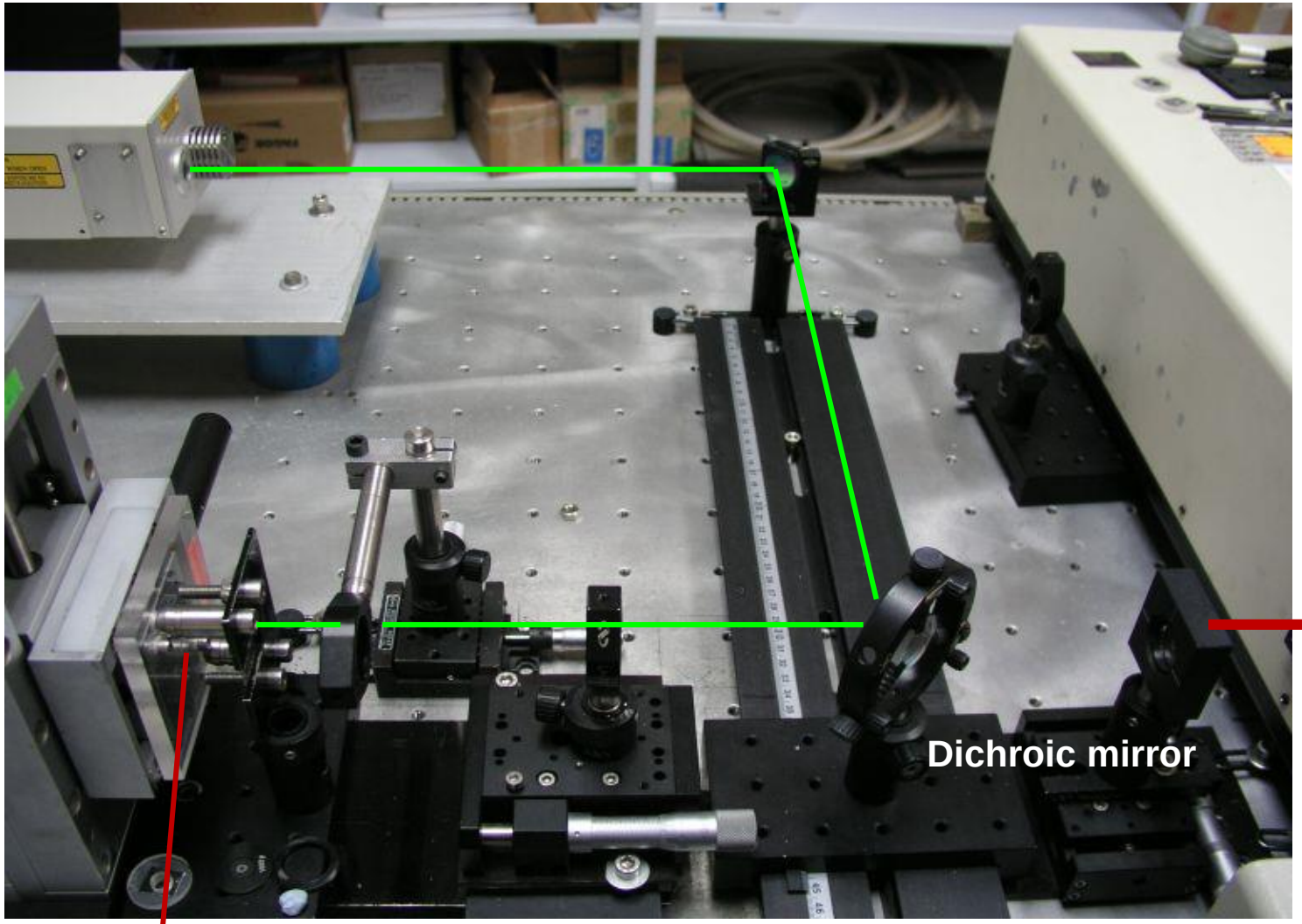


Basic configurations

1. Experimental setup with pierced mirror

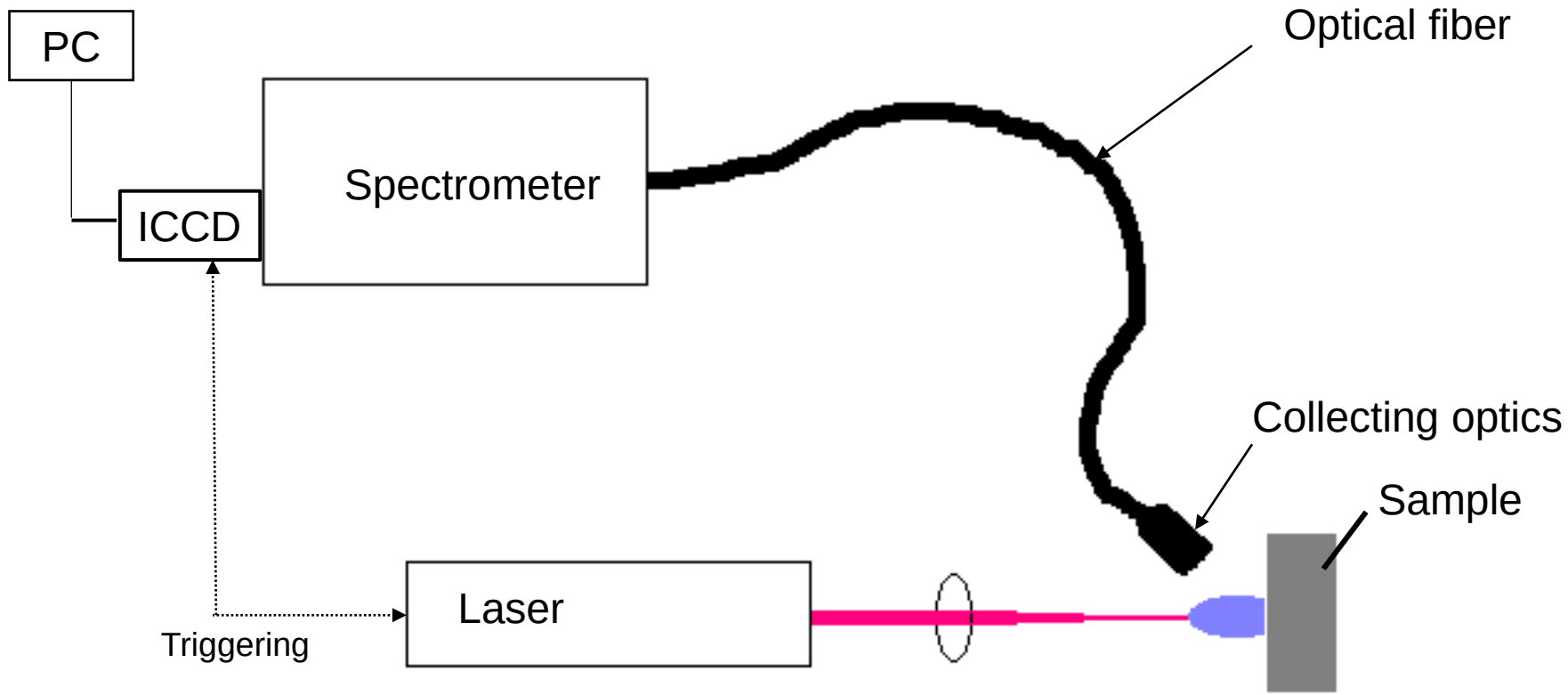


Basic configurations

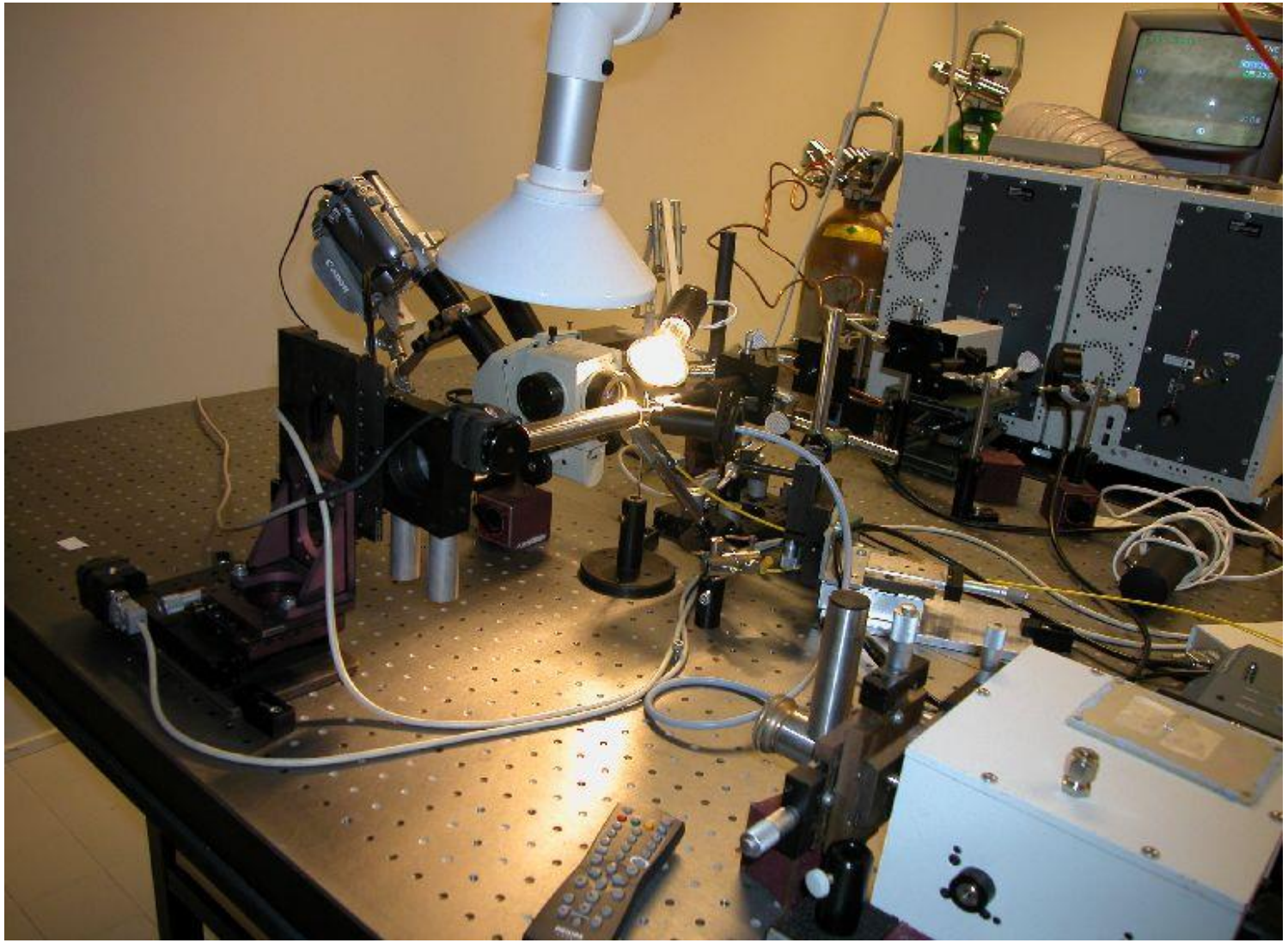


Basic configurations

2. Experimental setup with optical fiber



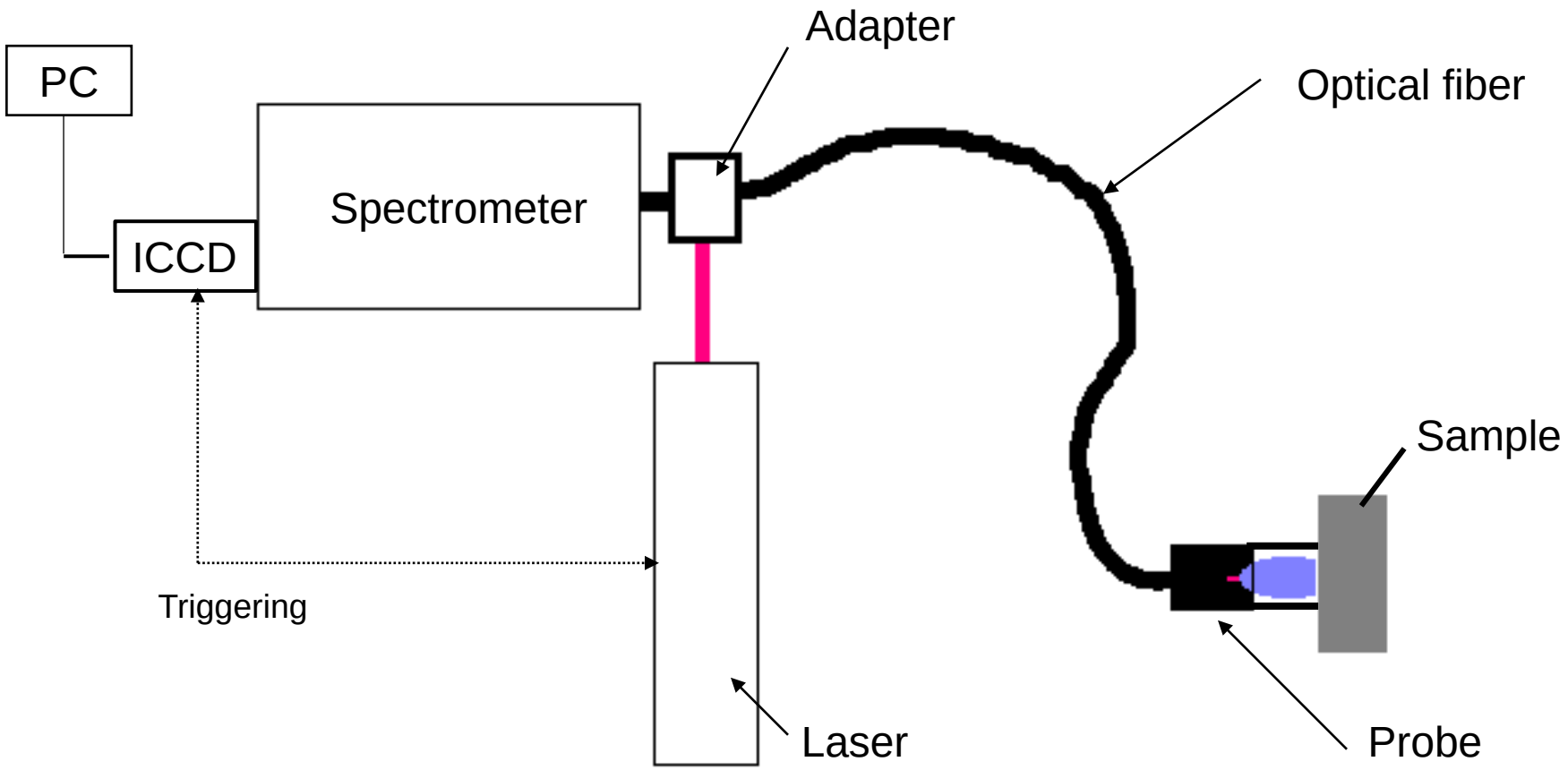
Basic configurations



Basic configurations

3. Experimental setup with optical fiber

(portable LIBS, underwater measurements)



Underwater measurements

(a) Remote LIBS instrument on the research vessel

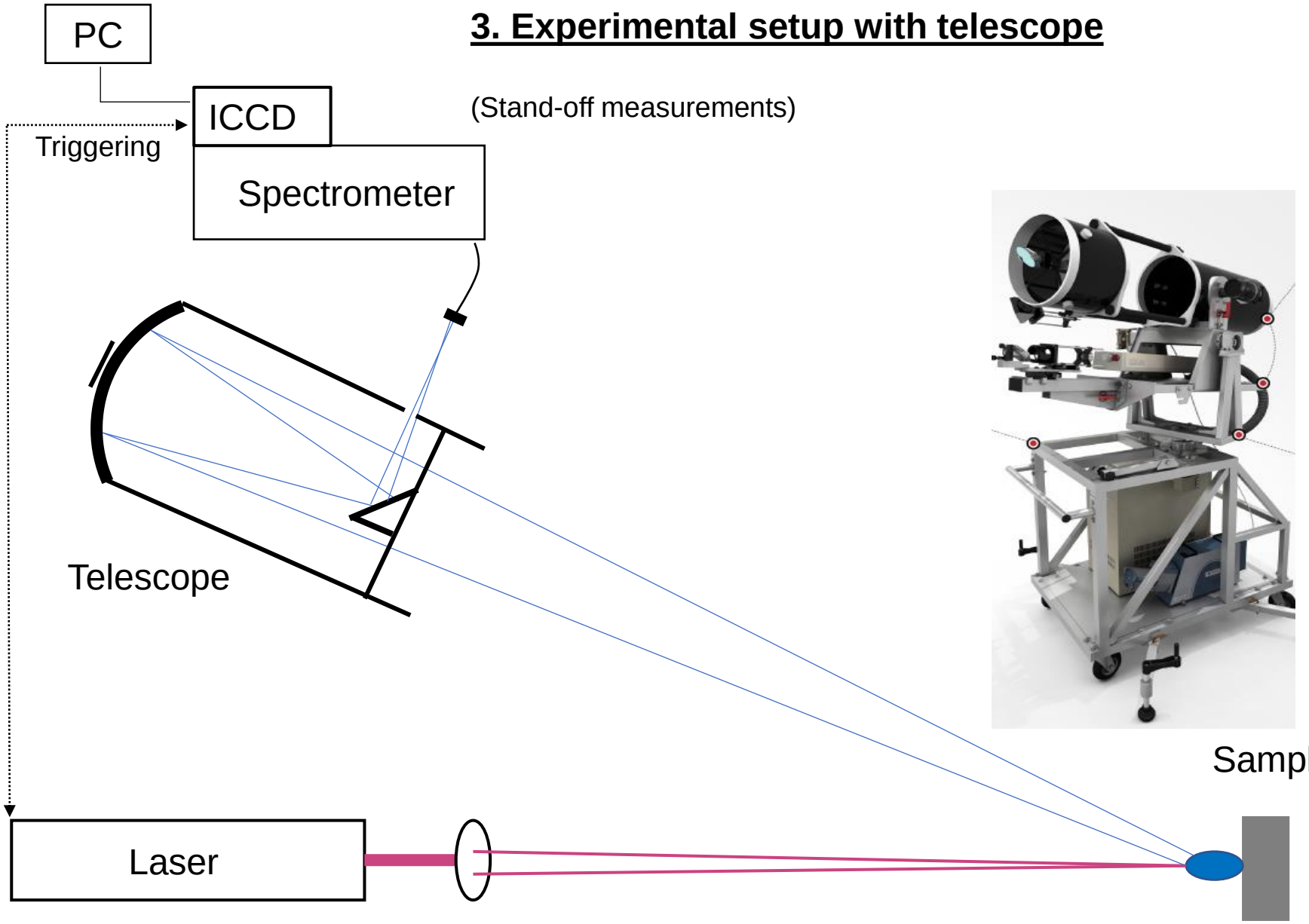
(b) Diver working at a 30 m depth

S. Guirado, F.J. Fortes, V. Lazic, J.J. Laserna, Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea, Spectrochimica Acta Part B: Atomic Spectroscopy, Volumes 74–75, 2012, Pages 137-143,

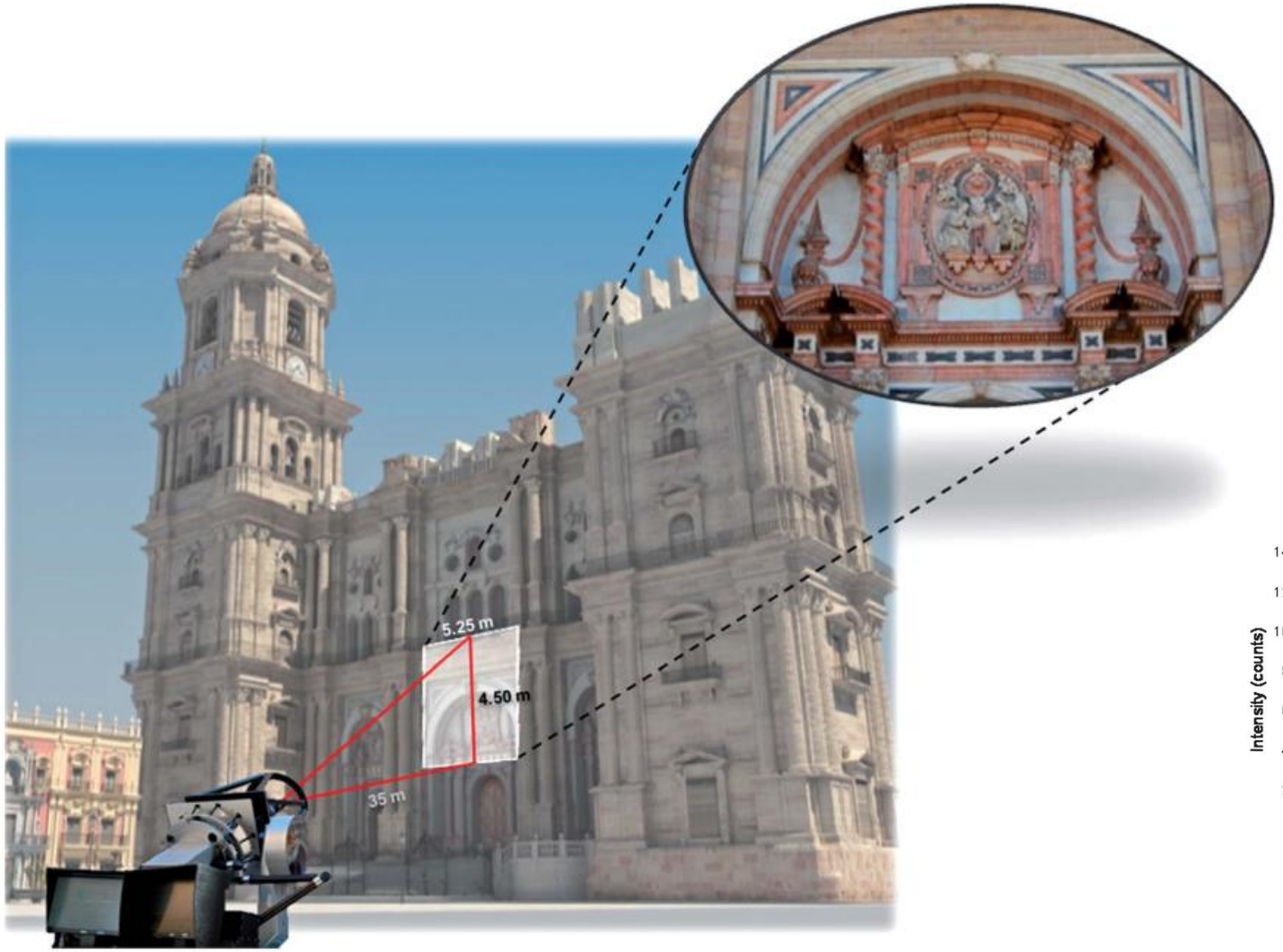
Basic configurations

3. Experimental setup with telescope

(Stand-off measurements)



Stand-off measurements



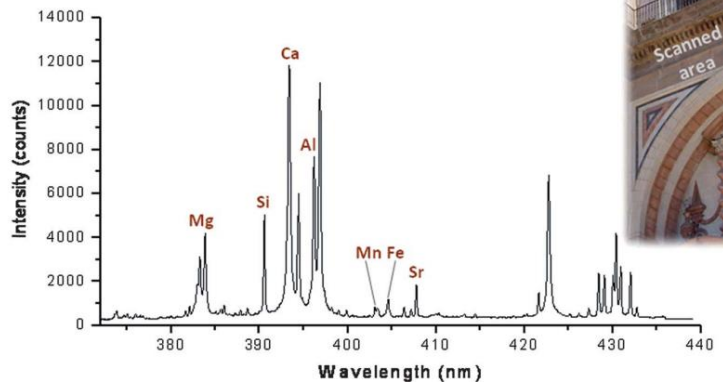


Fig. 1 Descriptive scheme on the working scenario. The emplacement of the LIBS platform, and section investigated, are highlighted.

I. Gaona, P. Lucena, J. Moros, F. J. Fortes, S. Guirado, J. Serrano and J. J. Laserna: Evaluating the use of standoff LIBS in architectural heritage: surveying the Cathedral of Málaga J. Anal. At. Spectrom., 2013, 28, 810

Basic configurations

Handheld LIBS Analyzers from Sciaps

Portable LIBS Laser OES from QuantoLux

Development of LIBS instrumentation on MU - history

1st generation

- Nd: YAG laser Brilliant (1064, 532 or 266 nm)
- monochromator Jobin Yvon TRIAX 320 (f=320 mm, three gratings – 1200, 2400 and 3600 g/mm)
- photomultiplier Hamamatsu gated by a laboratory-built control unit
- time resolved emission signal at given wavelength
- laboratory-made aluminum ablation chamber - different ablation atmosphere
  - connection to ICP OES

2nd generation

- ICCD camera Jobin Yvon Horiba (iStar Andor)

3rd generation

- orthogonal double pulse configuration
- laser ablation system New Wave UP 266 MACRO
- ablation chamber for simultaneous DP-LIBS and double pulse LA-ICP-OES
- sample surface monitoring by the internal CCD camera
- easy settings of all laser and detection parameters
- programmable sample moving
  - depth profiling, line scanning or raster scanning for bulk or surface analysis
- single or double pulse experiments
- detection by PMT or ICCD

SIMULTANEOUS DP-LIBS AND LASER ABLATION ICP-OES SYSTEM

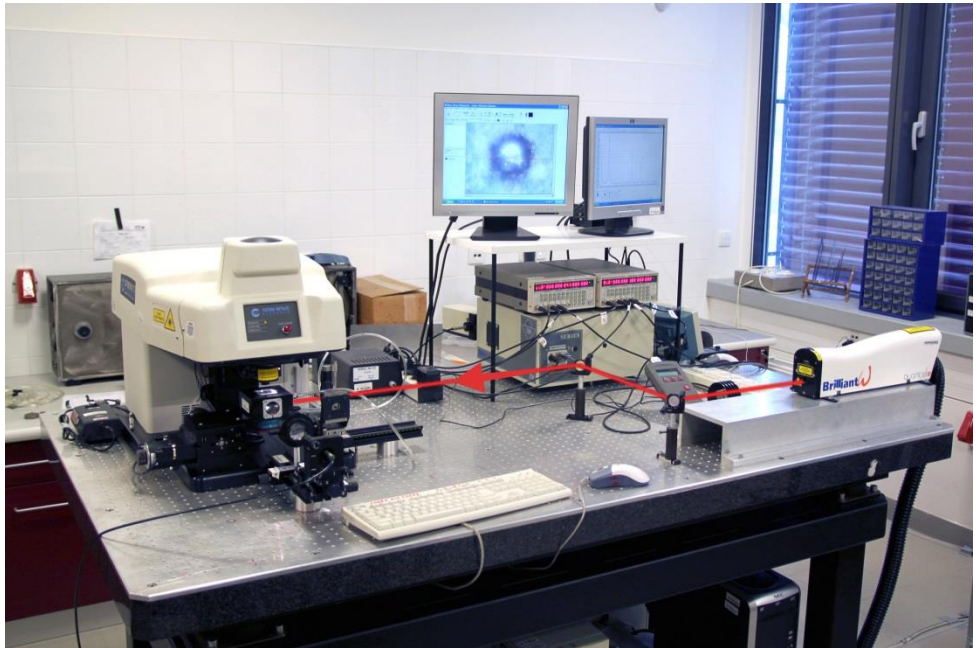
designed by utilizing a modified commercially available laser ablation system (New Wave, UP 266 MACRO)

- no modification of the original optics - possible to use all advantages of the original arrangement
- spot ablation for depth profiling, line scanning for lateral analysis and raster scanning for bulk or surface analysis.
- second re-heating laser pulse (Quantel Brilliant) is delivered orthogonally
  (periscope arrangement allowing precise laser beam positioning)

- two digital delay generators DG 645
- collection optics for emission transport to the monochromator Triax 320 (Jobin-Yvon)
- ICCD Princeton Instruments PI MAX-3
- sample holders
  (different size and shape)

For LA-ICP-OES experiments the original ablation chamber was replaced with a special laboratory made chamber

- window for entering the second orthogonal laser pulse
- window for collection of LIP emission
- stage for sample height alignment

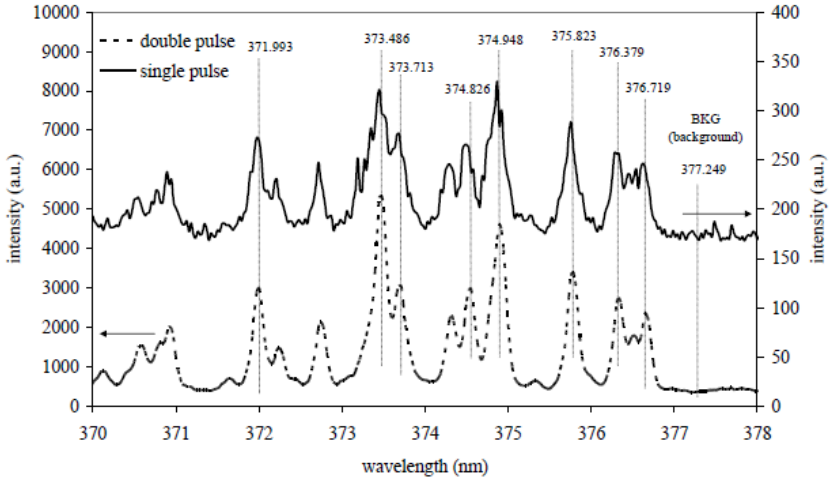


Double pulse technique (DP-LIBS)

Emission enhancement

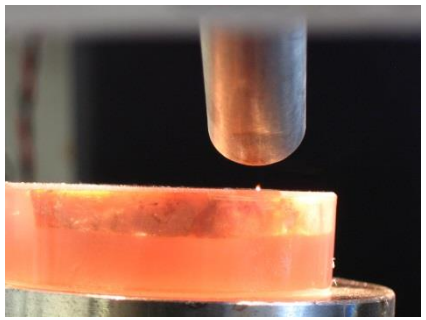
- plasma volume increasing
- higher temperature
- longer decay time
- S/N enhancement

Decreasing of LOD up to two orders of magnitude

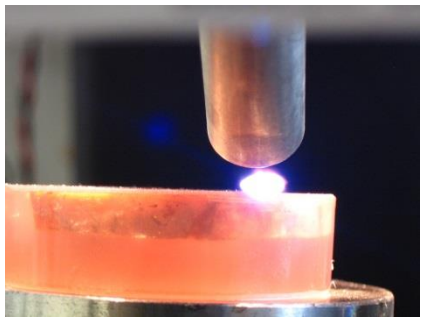


Comparison of the single and double-pulse signals in spectral region of selected iron lines

New Wave, UP 266 MACRO
Nd:YAG laser @ 266 nm (4-th harmonic frequency)
Second laser pulse Nd:YAG (Quantel Brilliant) @1064 nm



Single Pulse

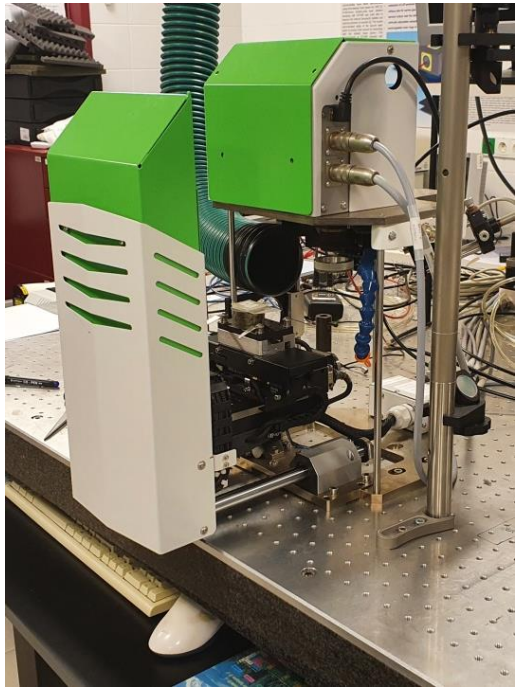


Double Pulse

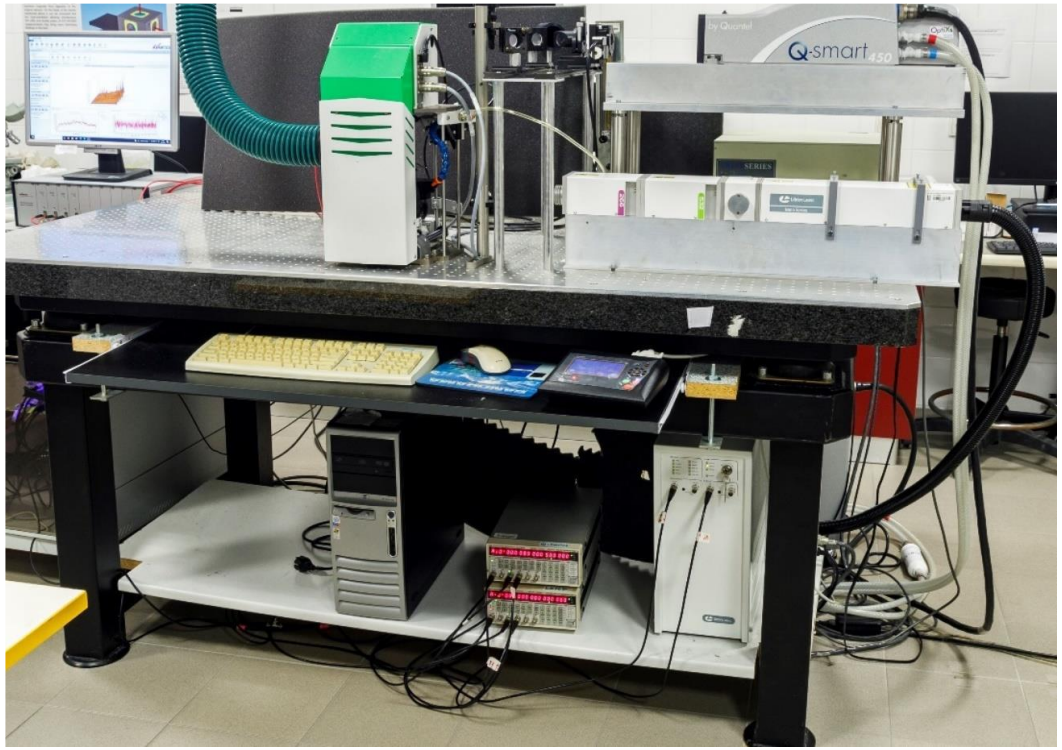
Novotny, K.; Lutzky, F.; Galiova, M.; Kaiser, J.; Malina, R.; Kanicky, V.; Otruba, V., Double pulse laser ablation and plasma: time resolved spectral measurements. *Chemicke Listy* 2008, 102, S1399-S1402.

Design, construction and testing of new instrumental configurations:

- double pulse arrangement
- fast imaging
- acoustic signal recording
- setup for laser ablation synthesis



Current experimental LIBS arrangement

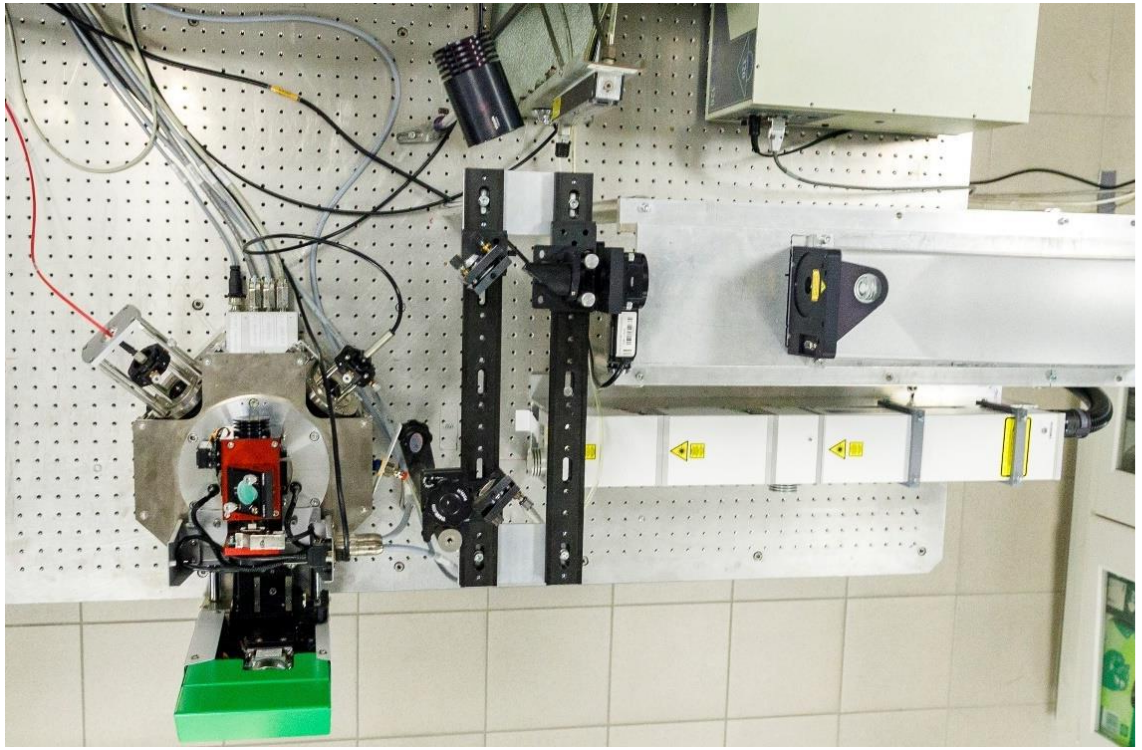


Lasers:

- Quantel Q-smart 450 – **1064 nm, 20 Hz**
- Litron Nano LG 200-20 – **266 nm, 20 Hz**

Focusing optics

- Sill Optics (1064)
- Thorlabs µ-Spot (266 nm)
- Edmund Optics ReflX Objective (DP LIBS)



Cage LIBS system (CEITEC BUT):

- x,y,z translation stages (Standa)
- collection optics (Thorlabs)

Spectrometers:

- AvaSpec-ULS4096CL-EVO-RM (Avantes)
- Triax 320 (Jobin Yvon)
- ICCD PI-MAX 4 (Teledyne Princeton Instruments)

Spatially resolved LIBS analysis

Parameters of spatially resolved LIBS analysis:

lateral resolution
depth resolution
sensitivity

	LIBS	LA-ICP-MS	EDX	SIMS	ICP-OES
lateral resolution	10 – 1000 µm	5 – 100 µm	> 0,5 µm	> 1 µm	X
depth resolution	0,1 – 10 µm	0,1 – 10 µm	1-10 nm	1-10 nm	X
limit of detection	0,1 – 10 ppm	10 – 100 ppb	0,1 % - ppm	ppm-ppt	0,1 – 10 ppb

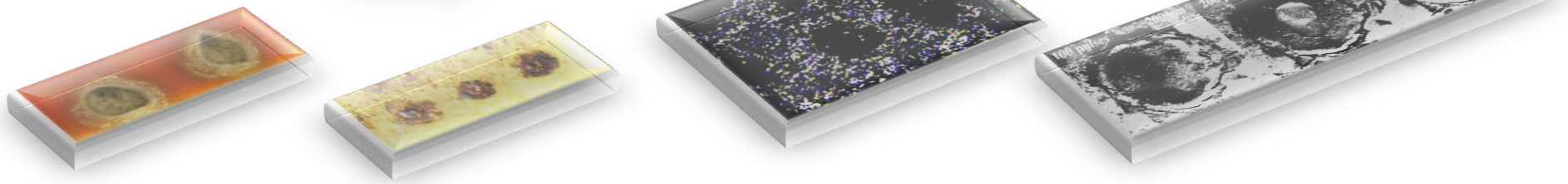
Ablation craters **:** **diameter**
depth
shape (cross section, redeposition)

ceramic tile

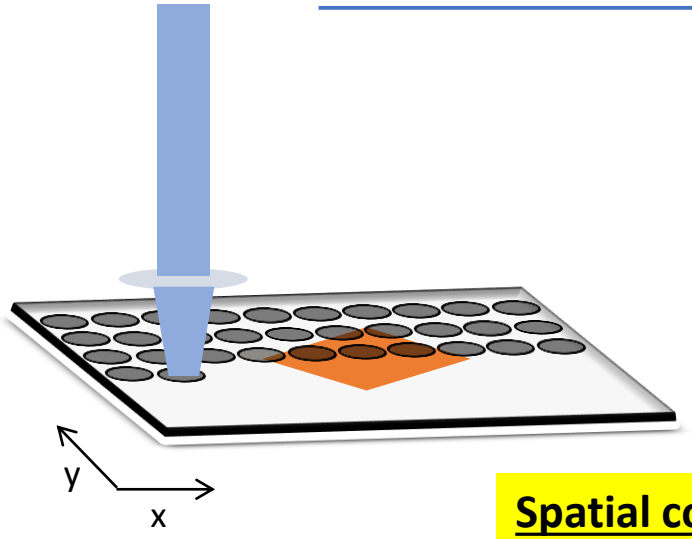
nanotextiles with coating

granite

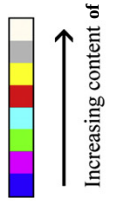
galvanized sheet



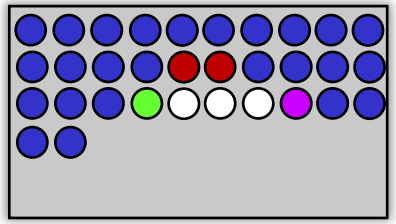
Two-dimensional chemical imaging



low resolution

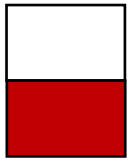


Chemical Map B



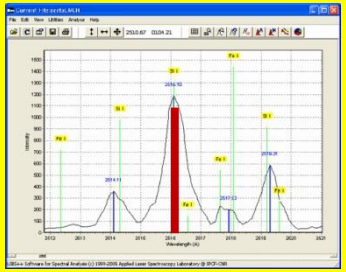
element A

element B



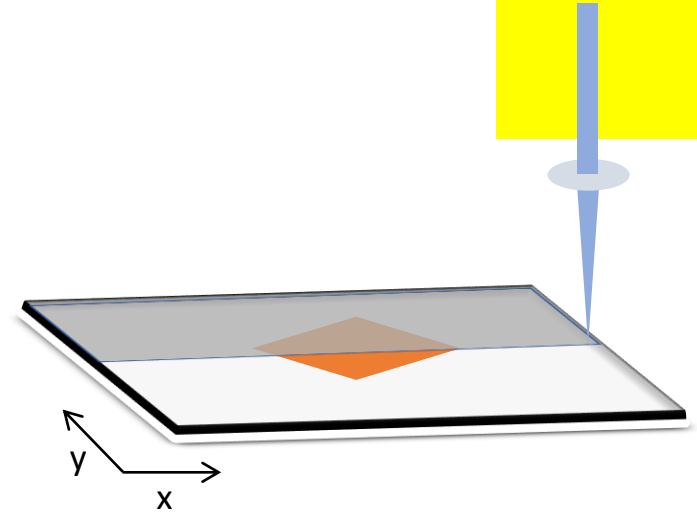
Spatial coordinates **LIBS spectra**

(x,y) +

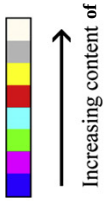


emission line
(element B)

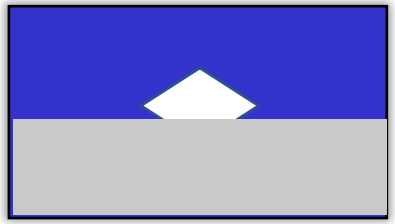
Surface distribution of element B



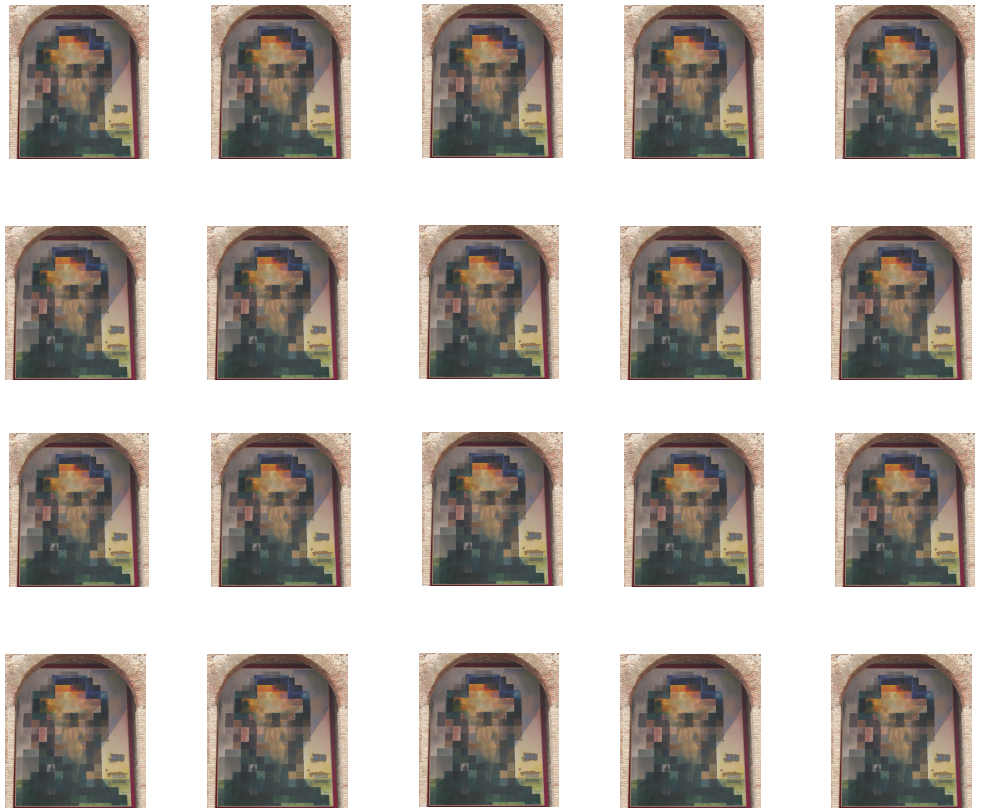
high resolution



Chemical Map A



Spatially resolved parameters must be set according to the size of the imaged structures



Salvador Dali • Painting, 1975

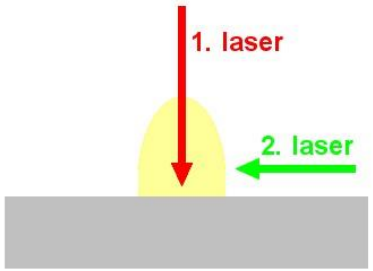
Two-dimensional chemical mapping

lateral and depth resolution X **surface sensitivity**

crater **diameter** and **depth** (one pulse) **excitation efficiency** in plasma

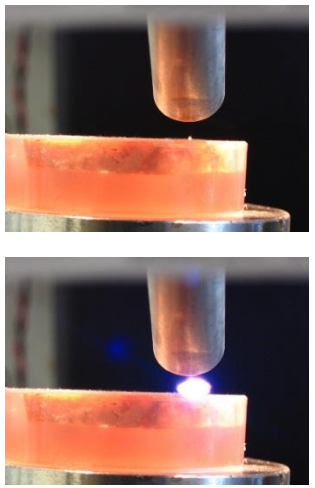
Double pulse technique (DP-LIBS)

orthogonal configuration

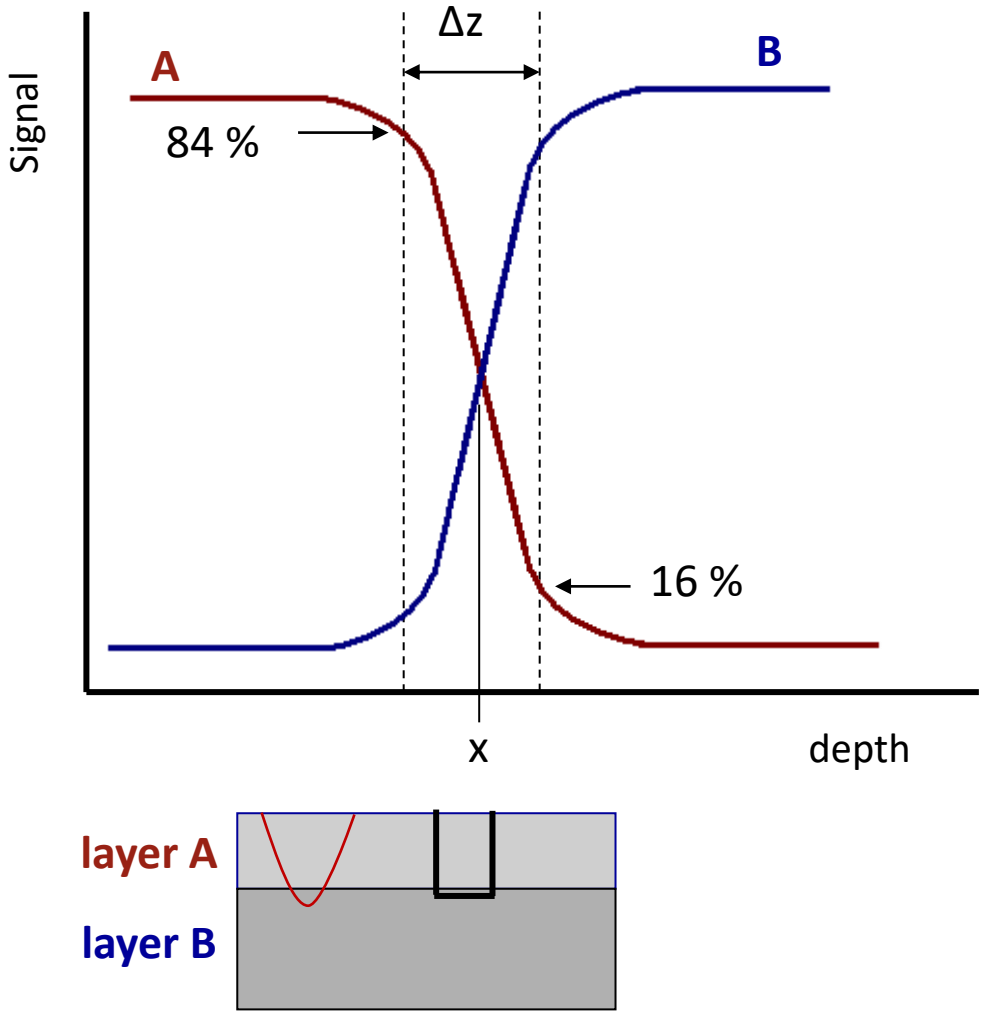


reheating mode

1. UV laser pulse - better **focusing** and **ablation parameters**
2. IR laser pulse - effective **re-heating** of the plasma



Depth profiling



Depth profiling by LIBS

- from nanometer to millimeter scale
- no or minimal sample preparation
- without restrictions on the shape, size or conductivity
- under atmospheric conditions
- on-line and in situ measurement

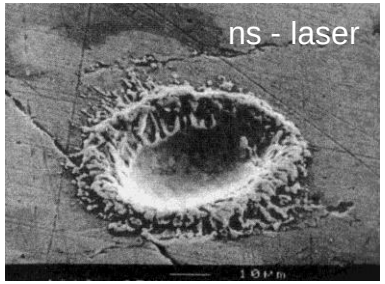
Δz – depth resolution

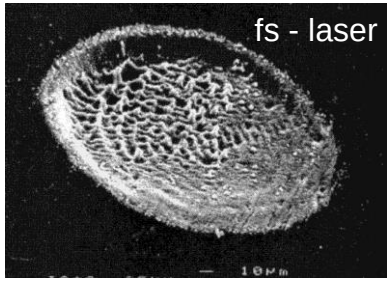
defined by convention: depth range over which the signal changes from 84 to 16% of its full value

Δz = Δp AAR

Δp – number of laser shots needed to reach 84 and 16% of signal

AAR – averaged ablation rate





K. Niemax, Laser ablation – reflection on a very complex technique for solid sampling, *Fresenius J. Anal. Chem*. (2001) 370:332-340)

Depth profiling

(zinc-coated iron sheets)

Different manufactures and different zinc-coating thicknesses:
previously analyzed by glow discharge optical emission spectrometry

Hoesch Stahl (20 μm)

electroplated Zn coating, Sollac (10 μm)

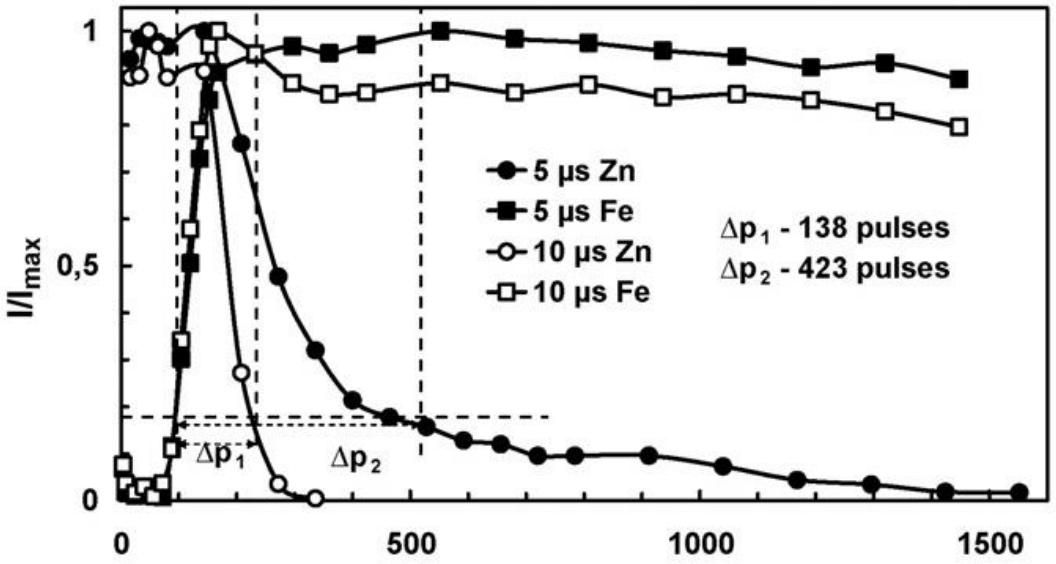
Aluzink, SSAB (24 μm)

Galfan, Voest Alpine (6 μm)

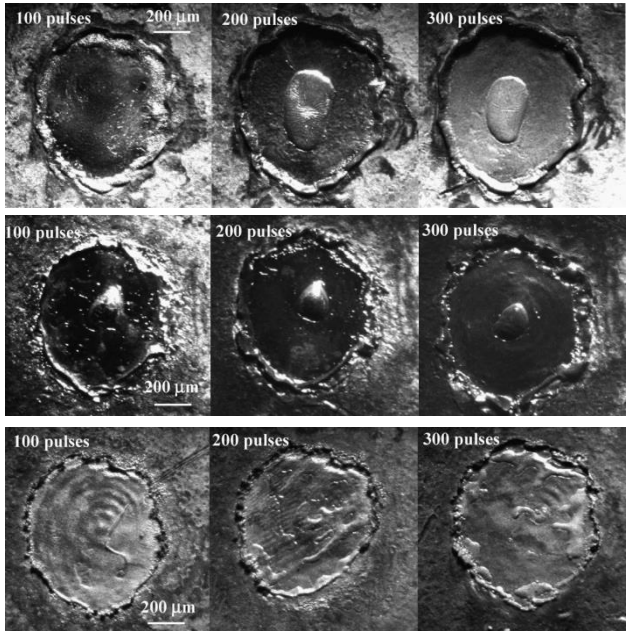
Galvanneal, British Steel (9 μm)

Optimized parameters

- laser pulse energy
- focusing condition
- different surrounding gases
- delay time



Depth profile of electroplated Zn in helium focusing at -20 mm. Comparison of LIBS signals of Zn(I) 280.08 nm and Fe(I) 344.06 nm at 5 and 10 ms delay times. Ablation was performed with an energy of 100 mJ/pulse.



air

Ar

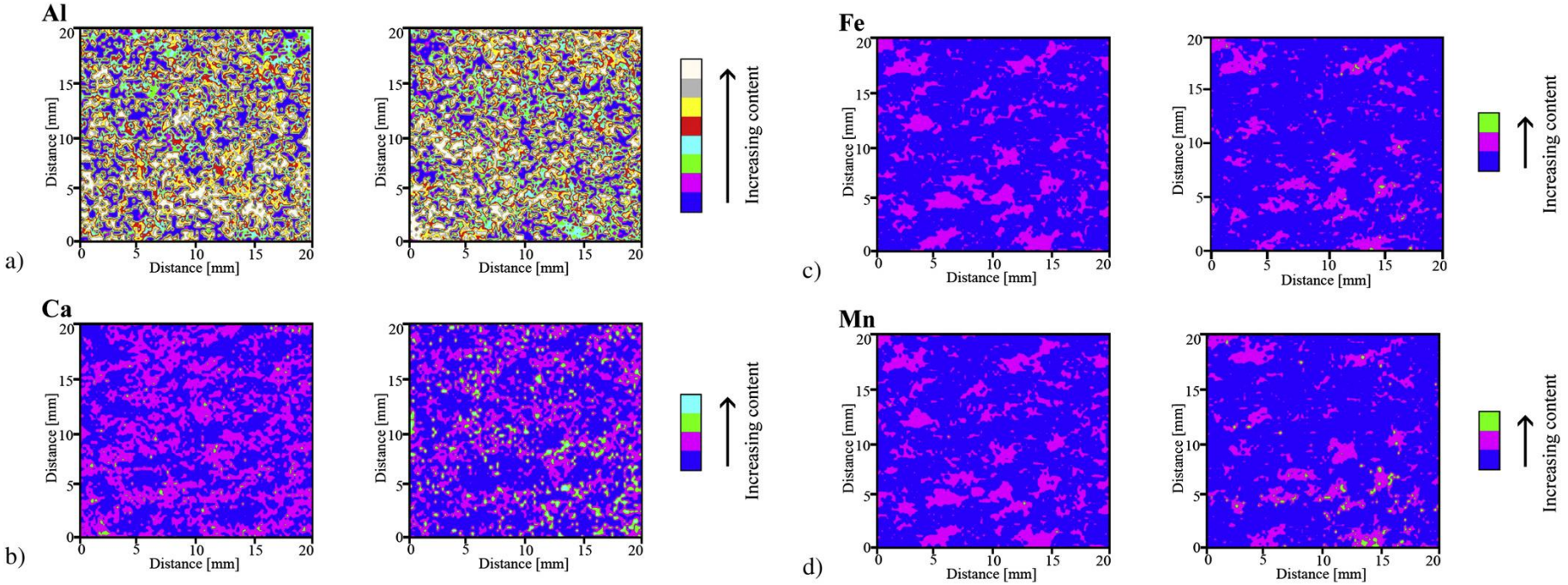
He

Novotny, K.; Vaculovic, T.; Galiova, M.; Otruba, V.; Kanicky, V.; Kaiser, J.; Liska, M.; Samek, O.; Malina, R.; Palenikova, K., The use of zinc and iron emission lines in the depth profile analysis of zinc-coated steel. *Applied Surface Science* 2007, 253, 3834-3842.

Elemental mapping (Imaging)

(geological sample)

100×100 individual sample points to map an area of 20×20 mm^2



Novotny, K.; Kaiser, J.; Galiova, M.; Konecna, V.; Novotny, J.; Malina, R.; Liska, M.; Kanicky, V.; Otruba, V., Mapping of different structures on large area of granite sample using laser-ablation based analytical techniques, an exploratory study. *Spectrochimica Acta Part B-Atomic Spectroscopy* 2008, 63, 1139-1144.

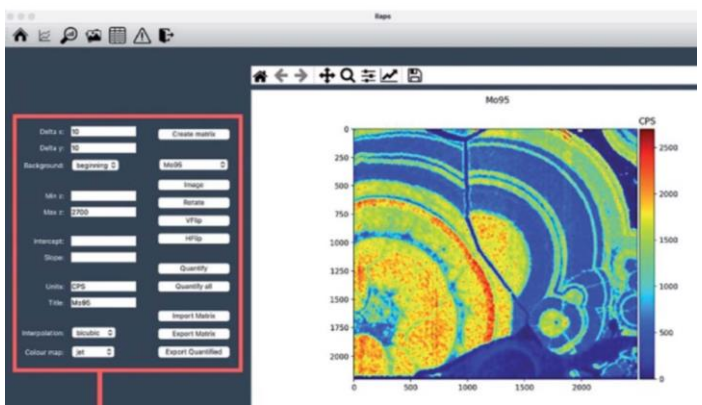
Combination of two elemental imaging techniques

LIBS

- simpler and cheaper instrumentation (in-situ, stand-off, underwater systems)
- **faster response** - on-line monitoring, **fast elemental imaging**
- other elements detection - F, Cl, C, O, H, N ...
- **detection of molecular bands** (CaF, CaCl, **UO** ....)
- monitoring of moisture
- matrix effects interpretations – additional information
- **advanced chemometric methods (PLS, PCA, ANN ...)**

LA-ICP-MS

- **lower detection limits**
- **higher spatial resolution**
- **isotope detection**, isotope dating



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Ilaps – python software for data reduction and imaging with LA-ICP-MS†

Veronika Faltusová, [a] Tomáš Vaculovič, [*ab] Markéta Holá [a] and Viktor Kanický [a]

Graphical user interfaces of Ilaps software:

Imaging screen with an elemental map of molybdenum in the sample of uraninite

Dual (LIBS and LA-ICP-MS) imaging

- simultaneous mapping

i. compromise conditions

ii. acquire a quick overview of a large sample area by the LIBS method to select important regions and detailed examination of their fine structures by the LA ICP MS at the same time is impossible

- **subsequent mapping**

i. LIBS: step size setting with respect to crater size, imaging speed requirements, size of image area

ii. LA-ICP-MS: line scanning - spot size, scan speed and line spacing setting according the number of detected isotopes, detection limit, spatial resolution and imaging sped requirements

Spectrochimica Acta Part B: Atomic Spectroscopy 186 (2021) 106312

Contents lists available at ScienceDirect

Spectrochimica Acta Part B: Atomic Spectroscopy

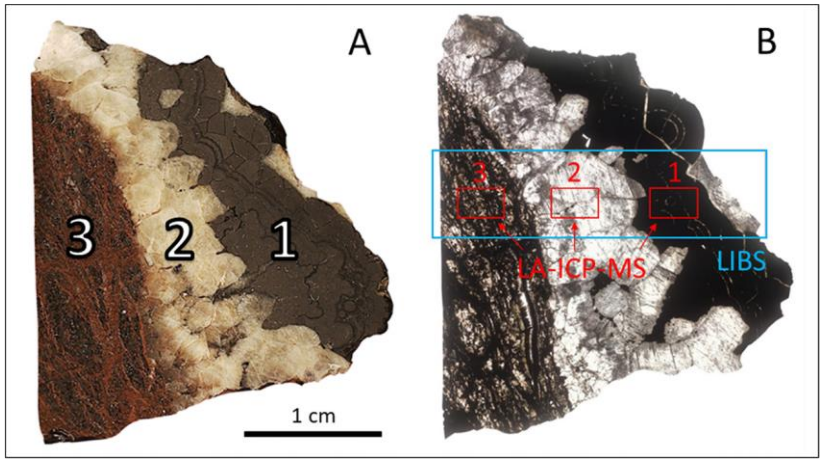
journal homepage: www.elsevier.com/locate/sab

Dual imaging of uranium ore by Laser Ablation Inductively Coupled Plasma Mass Spectrometry and Laser Induced Breakdown Spectroscopy

Markéta Holá [a], Karel Novotný [a,*], Jan Dobeš [a], Ivo Krempl [a], Vojtěch Wertich [b], Juraj Mozola [b], Martin Kubeš [b], Veronika Faltusová [a], Jaromír Leichmann [b], Viktor Kanický [a]

[a] Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic
[b] Department of Geological Sciences, Faculty of Science, Masaryk University, Kotlářská 2, 61137 Brno, Czech Republic

- sample of U-mineralisation from Rožná



(1) massive uraninite vein (2) carbonate vein and (3) metasomatite

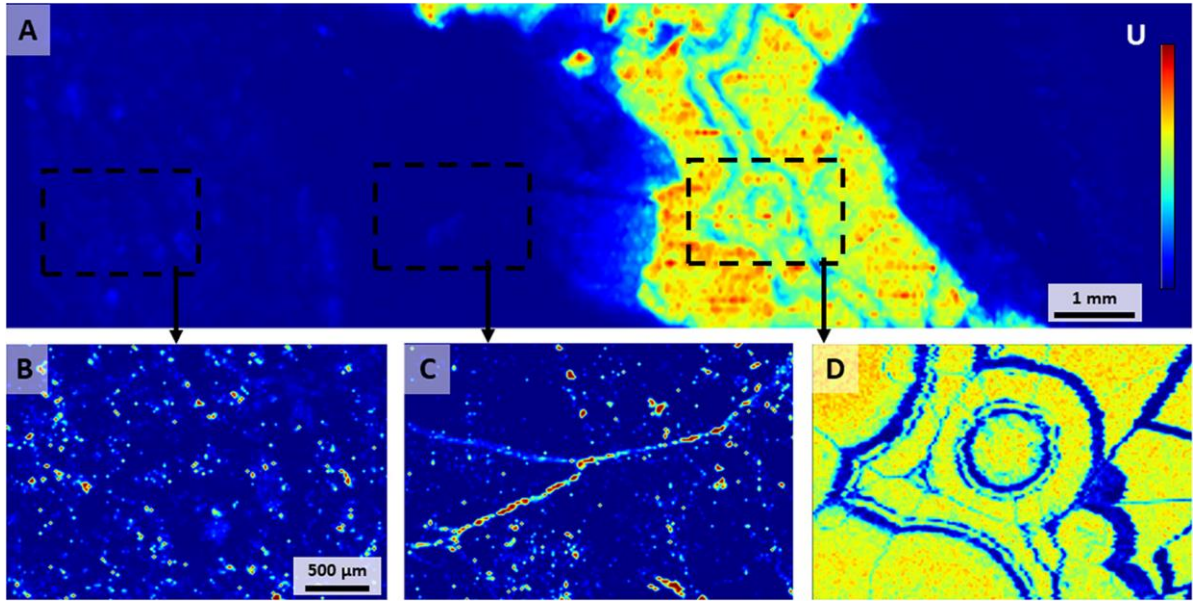
Dual (LIBS and LA-ICP-MS) imaging

LIBS

- high speed imaging of large area
- fast identification of minerals based on spectra fingerprint
- additional evaluation of the whole spectrum for LIBS

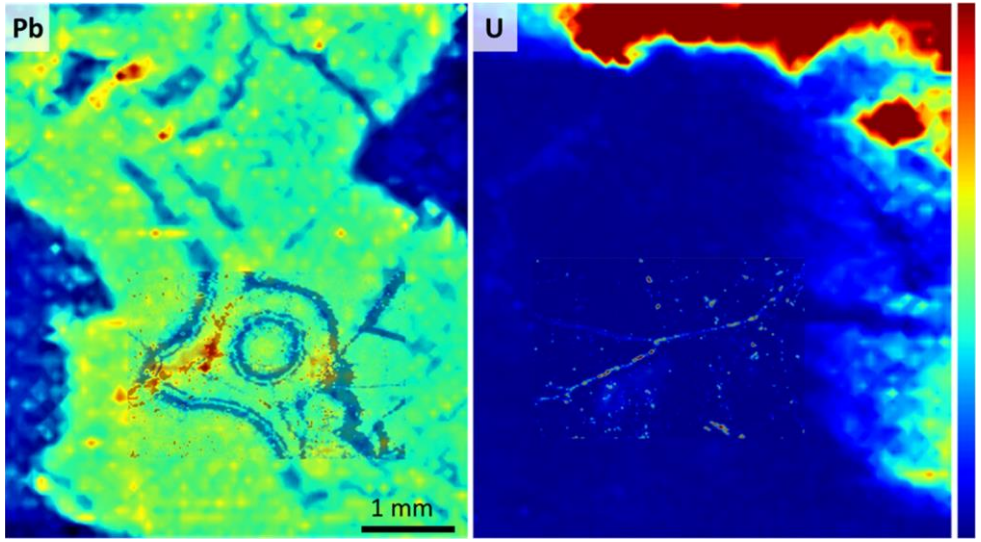
LA ICP MS

- high resolution imaging with low detection limits
- isotopic imaging



merging LIBS and LA-ICP-MS imaging data (ILAPS software)

detailed structures on the background of the overall sample image



The image helps to understand the evolution of geological processes and to identify the structures responsible for uranium migration

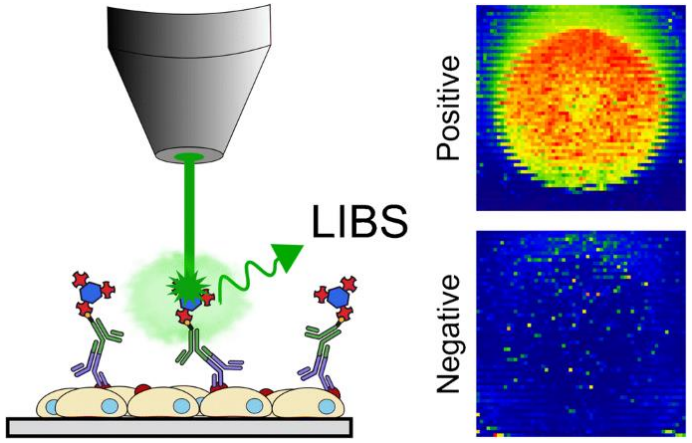
Current topics of specific projects:

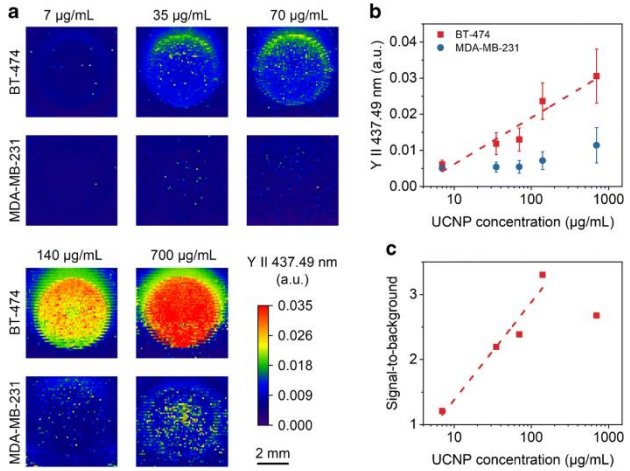
GA22-27580S

Laser spectroscopy in immunoassay and imaging with nanometallic tags (IMMUNOLIBS) (project in cooperation with the Institute of Biochemistry)

- labels such as antibody conjugates with various nanoparticles (often fluorescent)
- number of imaging methods (e.g. multidetector readers, microscopes)
- limited number of combinations of fluorescent labels

The LIBS technique offers a high potential in a huge number of combinations when using nanoparticles containing various elements (multiplexing)





P. Pořízka, K. Vytisková, R. Obořilová, M. Pastucha, I. Gábriš, J. C. Brandmeier, P. Modlitbová, H. H. Gorris, K. Novotný, P. Skládal, J. Kaiser, Z. Farka, Laser-induced breakdown spectroscopy as a readout method for immunocytochemistry with upconversion nanoparticles, Microchimica Acta volume 188, Article number: 147 (2021)

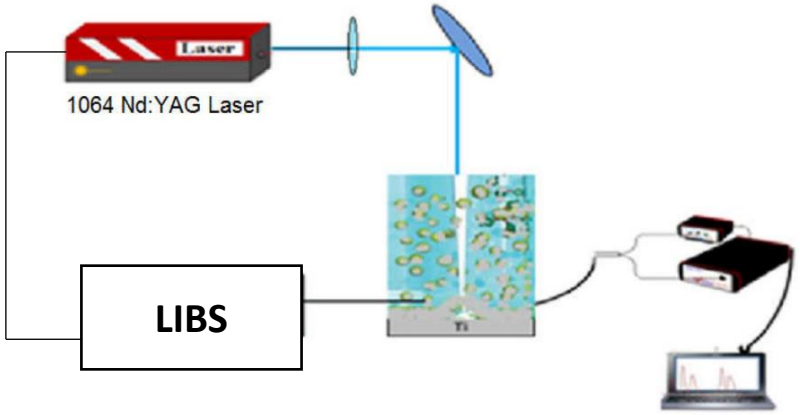
Current topics of specific projects:

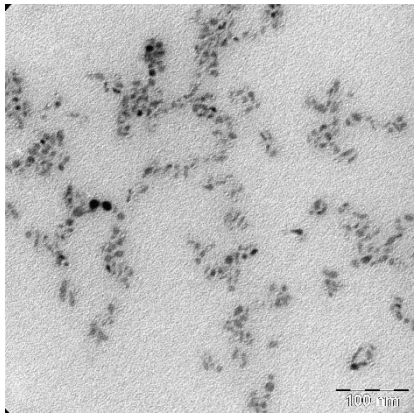
GA22-07635S

Advanced methods for the preparation of tellurides of semi-metals and non-transition metals
(in cooperation with the University of Pardubice)

- optimization of **deposition/synthesis** conditions to prepare high-quality **telluride thin films and (nano)structured or nanoparticles**

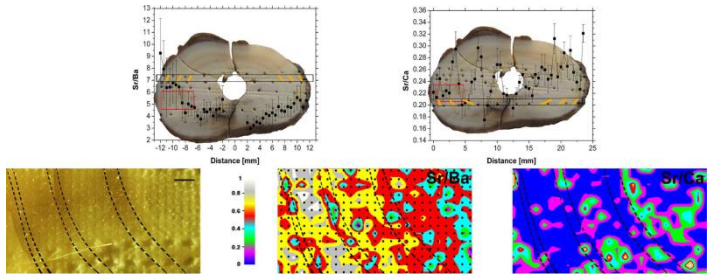
- use of LIBS technique for monitoring the process of **Laser ablation synthesis** of nanoparticles.

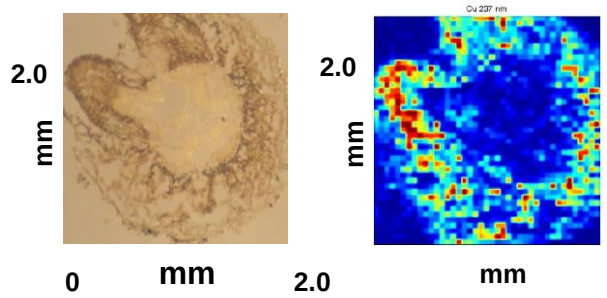




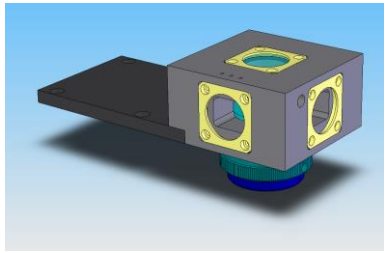
Some examples of results achieved in the past:

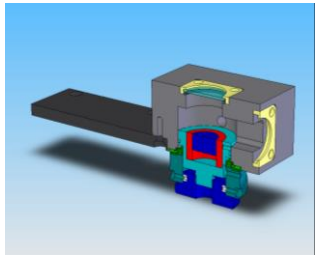
- development and application of two-dimensional mapping methods (geological samples, archaeological samples, building materials, objects of cultural heritage, biological samples)



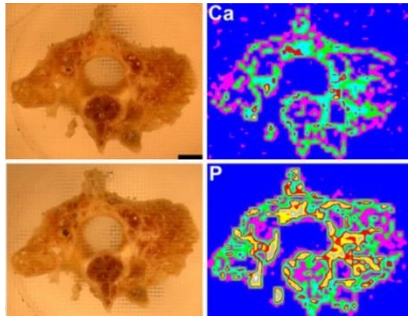


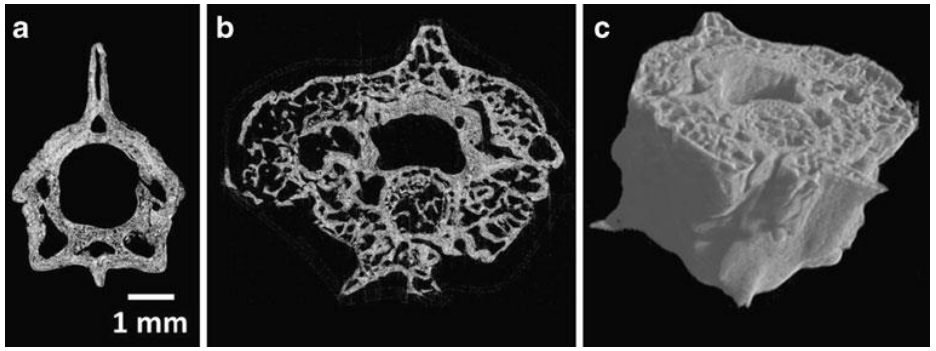
- development of methods for combination of laser techniques (LIBS, LA-ICP-OES, LA-ICP-MS) development and improvement of instrumentation





- combination with other techniques (computed microtomography, Raman spectroscopy...)



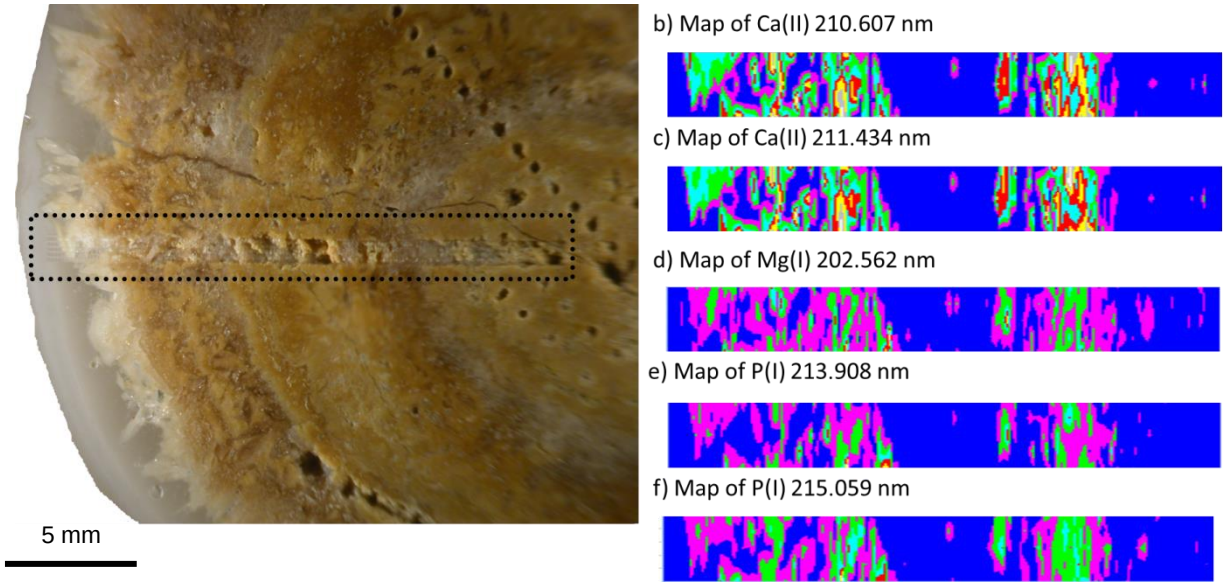


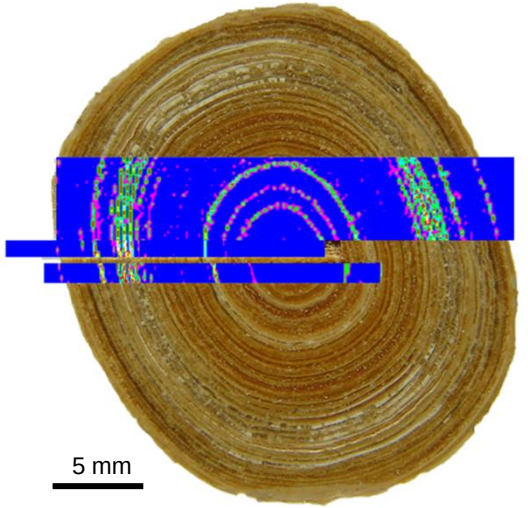
Elemental mapping
(urinary stones)

Mineralized tissues and bio-mineral structures are “archives” related to living habits, nutrition and exposure to changing environmental conditions.

Line scans of the urinary concrement cross-sections may provide information about the accumulation history of the elements of interest.

Four categories of urinary stones: a) oxalates, b) phosphates c) uric acid and d) cystine.





Ca distribution

Correlation between calcium and phosphorus indicates the presence of apatite.

Distribution of iron is connected with accumulation of blood clot during the growth of urinary stones in the urinary bladder.

Sample no. 10806: oval, ellipsoidal, pale yellow-brown zone.
The main components:
uric acid (90%) weddellite (10%)

weddellite ($CaC_2O_4 \cdot 2\ H2O$)

Study of penetration of silver nanoparticles into plant roots

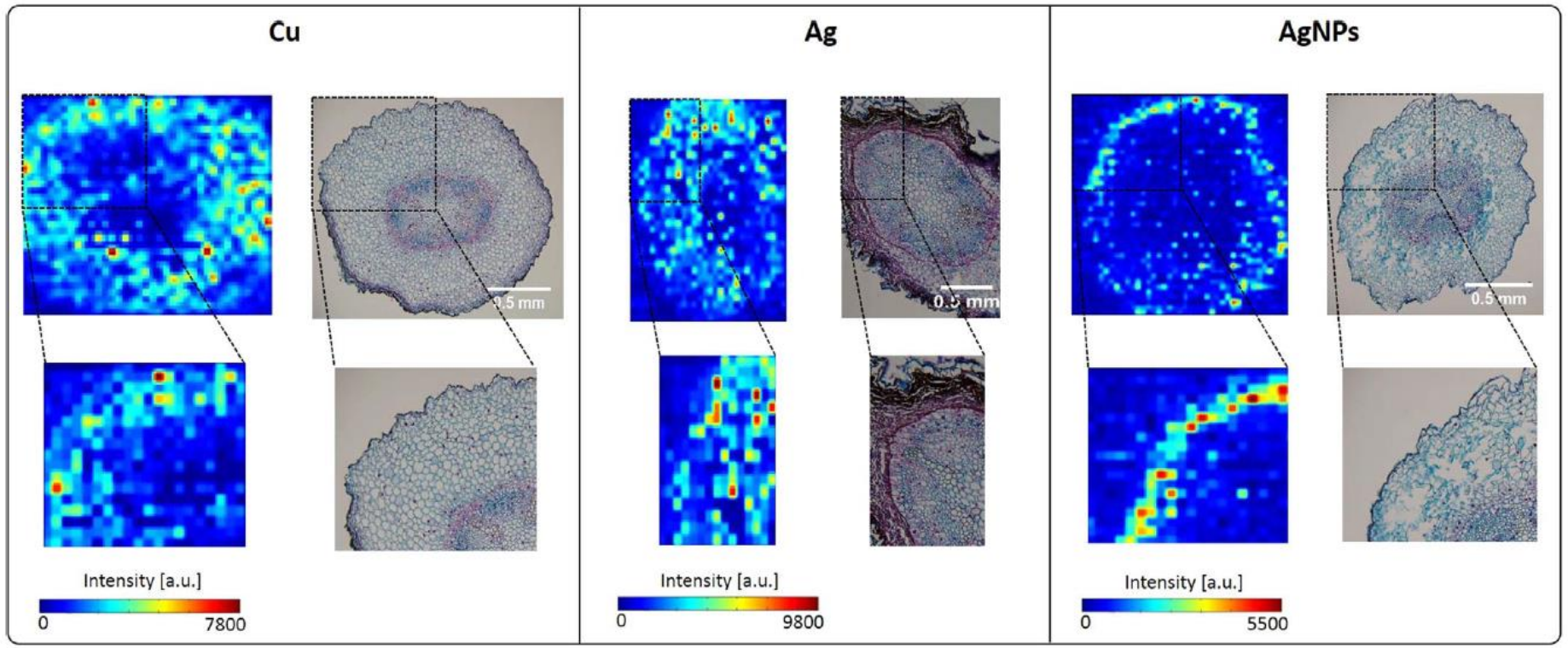
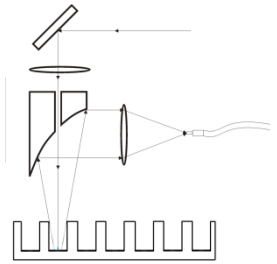
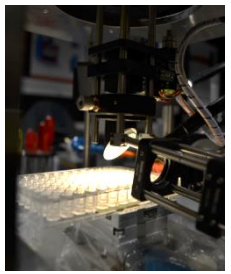


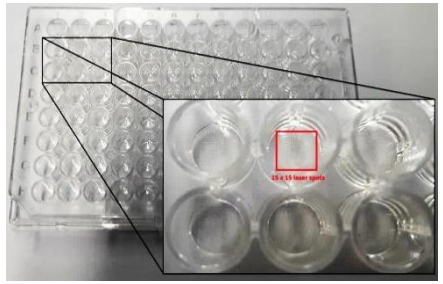
Fig. 5. Microscopy images and the corresponding distribution maps of Ag and Cu in root cross sections of *Vicia faba* plants cultivated in Cu^{2+}, Ag^{+}, and AgNP solutions over 7 days.

Some examples of results achieved in the past:

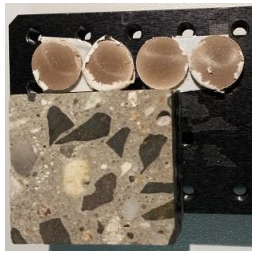
- detection of nanoparticle-labeled biomolecules in microtitre plates

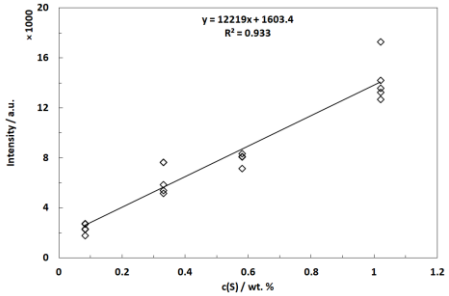






- development of methods for sulfur detection (concrete, asphalt ...)





- **close cooperation with the Faculty of Mechanical Engineering BUT - precision mechanics and optics, CEITEC BUT, Lightigo**

- rich foreign cooperation

Individual projects
Bachelor theses
Diploma theses
Doctoral theses

University of Malaga (Španělsko) - prof. Javier Laserna

LAS

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- Doc. Mgr. Karel Novotný, Ph.D.
- Mgr. Markéta Holá, Ph.D.
- Mgr. Aleš Hrdlička, Ph.D.
- Doc. Mgr. Tomáš Vaculovič, Ph.D.
- Mgr. Michaela Kuchyňka, Ph.D.