Femosecond LIBS experiments from polymer targets

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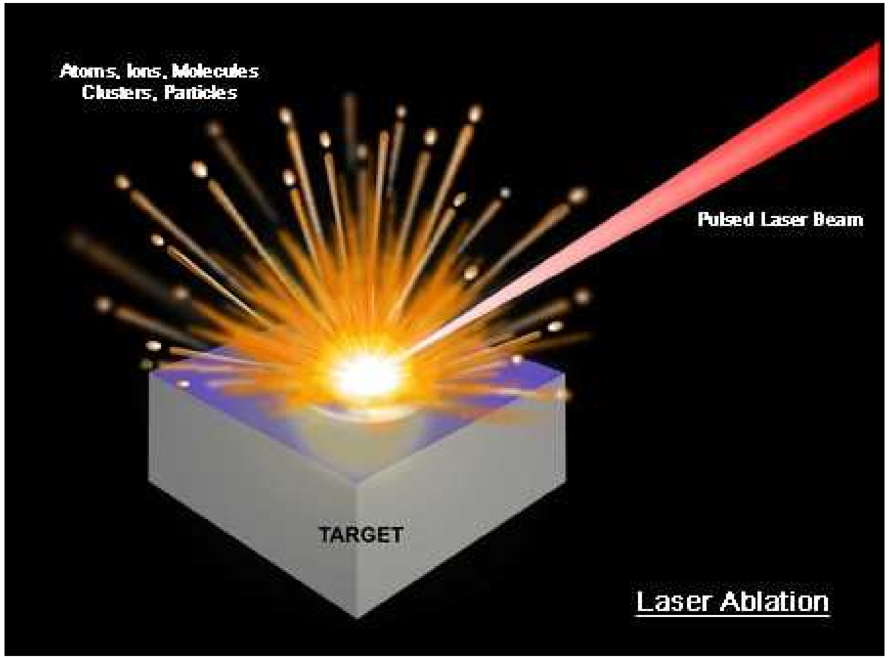
Laser Induced Breakdown Spectroscopy (LIBS)

LIBS: is a chemical analysis technology that uses a short (fs- ns) laser pulse to create a micro-plasma on the sample and based on atomic emission spectroscopy to measure elemental composition.



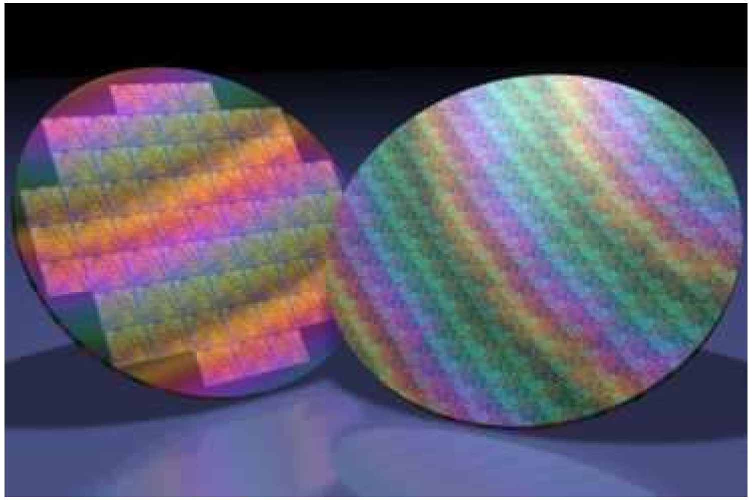
https://appliedspectra.com/technology/libs.html

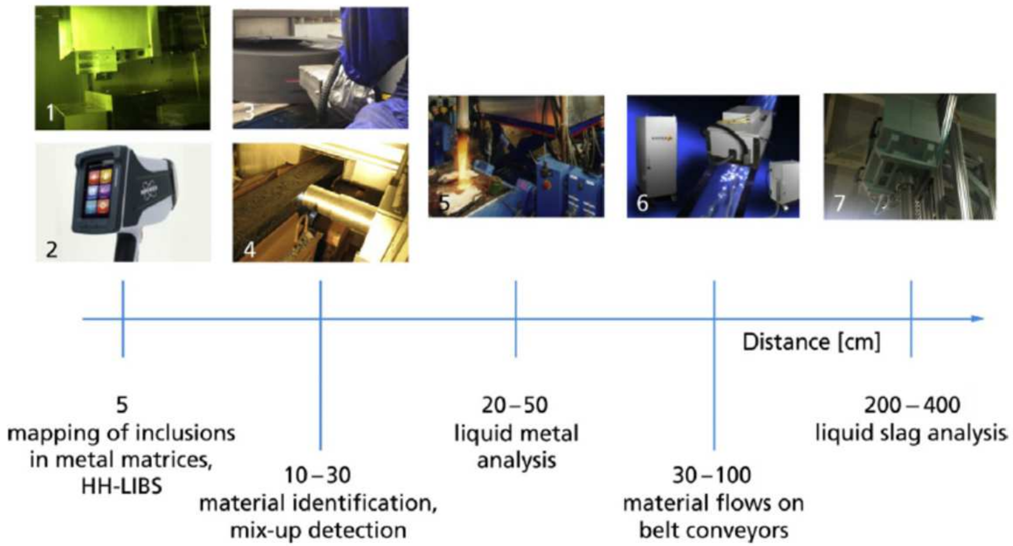
- Sample preparation-free measurements
- It can be used on any material, whether solid, liquid, or gas, foil
- Broad elemental coverage, including lighter elements, such as H, He Li, C, N, O, Na, and Mg, and heavy metallic elements too

Applications of LIBS

Field of applications:

- Food science application: Measurement essential (Mg, Ca, and K) and toxic elements (Pb, Hg, St, Mn)
- Study of geological samples: identification of minerals
- Investigation of biological samples
- Pollution Monitoring
- Industrial application: in chemical industry material identification during manufacturing processes, in semicunductor industry used in semiconductor wafer and coating characterization and for quality control.
- The most appropriate applications of LIBS are in the nuclear and chemical industry, where quantitative or qualitative remote analysis, without any physical contact with the sample, is preferred.
- Further perspective in space exploration (for example on Mars rover)





Applied laser systems for LIBS

ns pulsed laser:

-Nd:YAG Laser System:

- wavelength: 1064 nm, 532 nm
- pulse duration: 5–10 ns
- typical pulse energy: 10-300 mJ

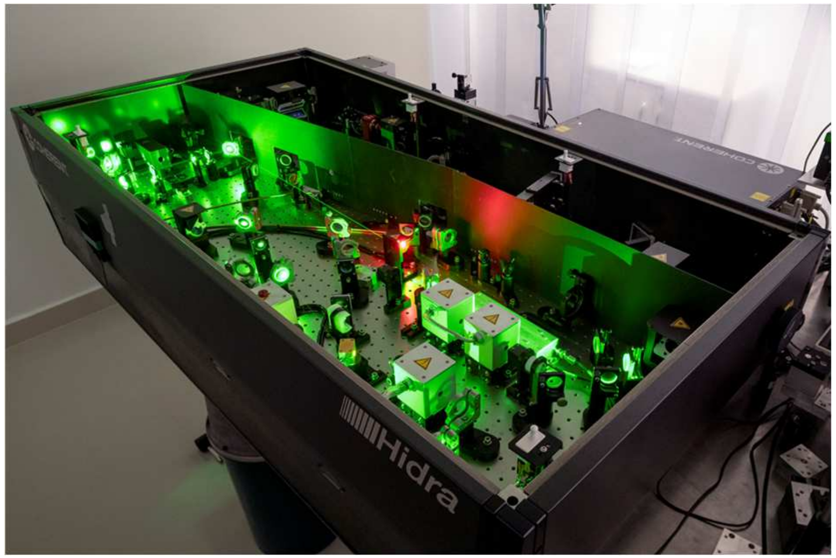
-The ruby laser:

- wavelength: 693 nm
- pulse duration: 20 ns;

fs pulsed laser:

- Ti:Sapphire chirped-pulse amplifier (CPA):

- wavelength: 800 nm
- pulse duration: 30–100 fs
- typical pulse energy: 10-50 mJ

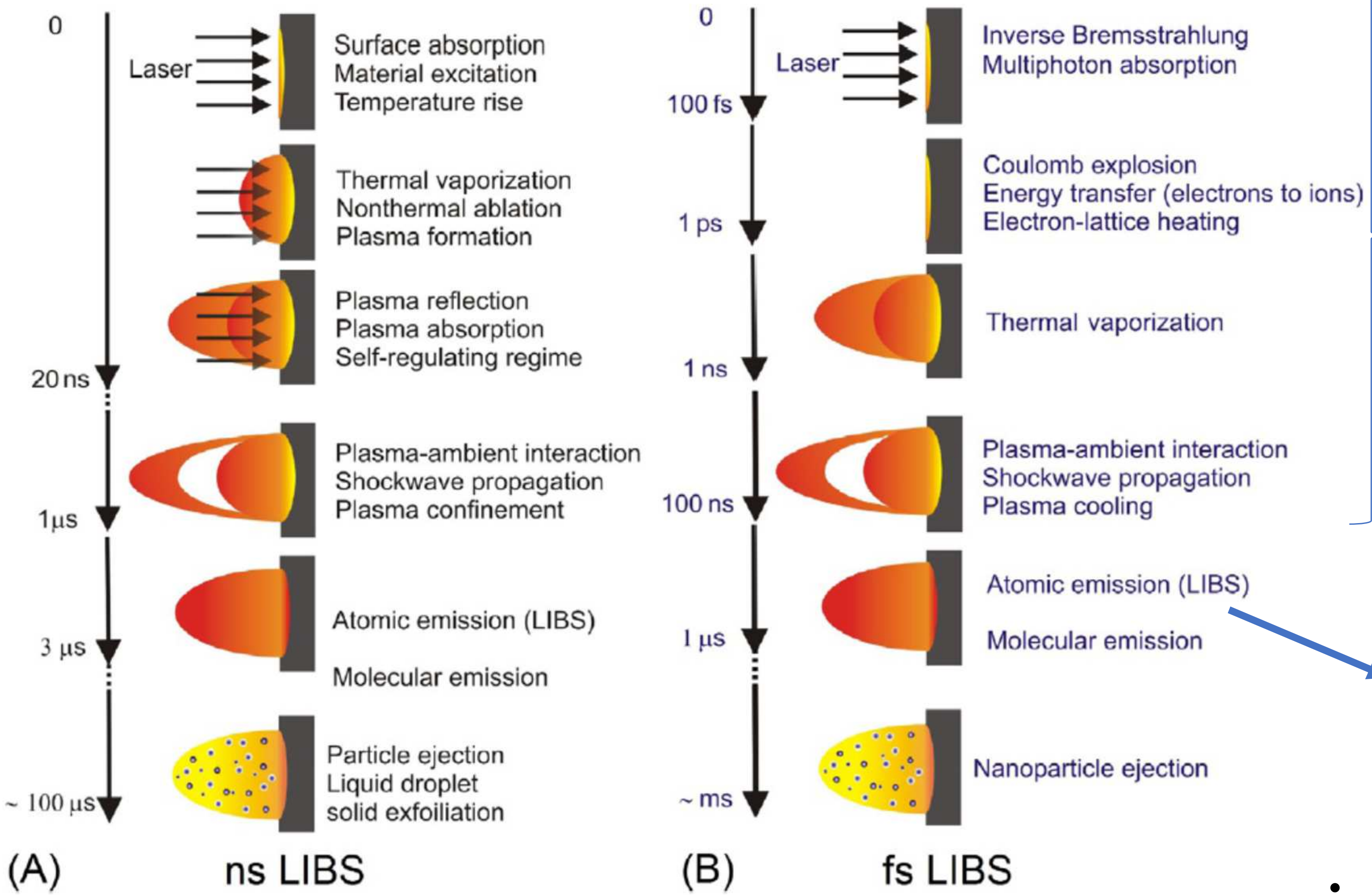


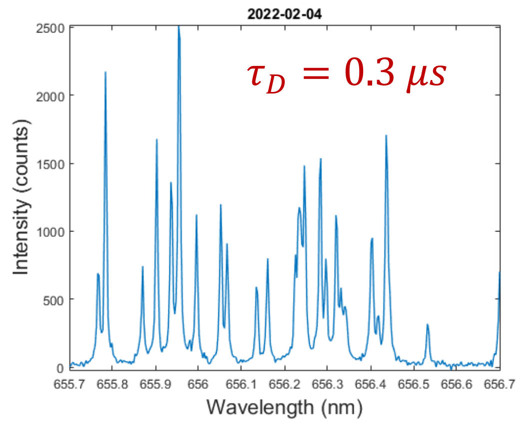
Advantages of fs-LIBS:

- low ablation threshold,
- improved spatial resolution for 3D mapping applications,
- small ablated mass, and reduced sample damage

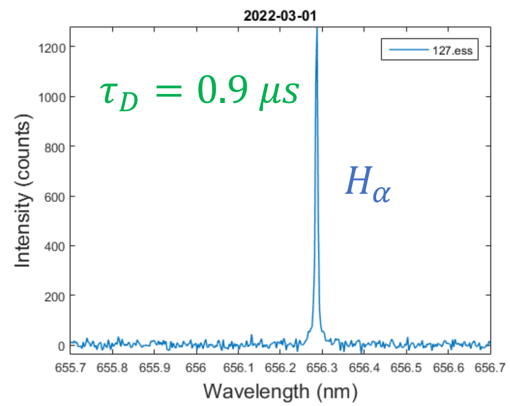
Laser Ablation Process

- Approximate time scales of nanosecond and femtosecond energy absorption and laser ablation along with various processes happening during and after the laser pulse is given





- Continuum light emmission
- < 0.1 ~ 0.3 μsec

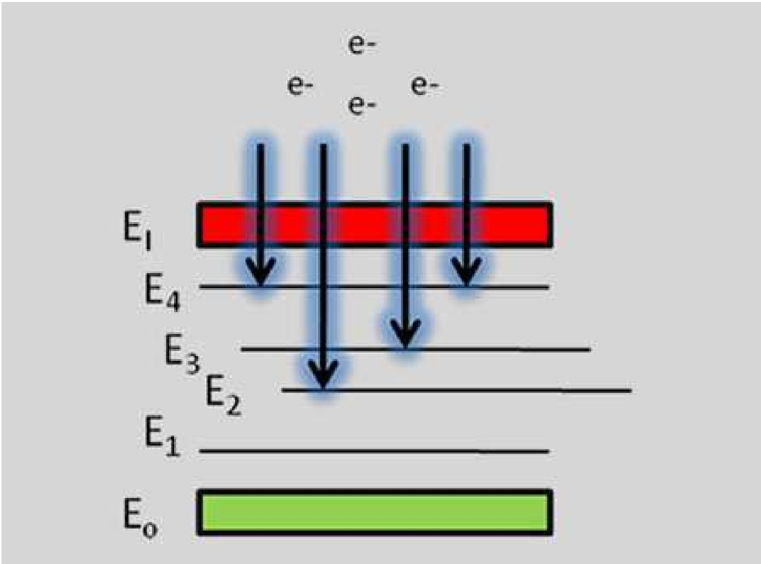


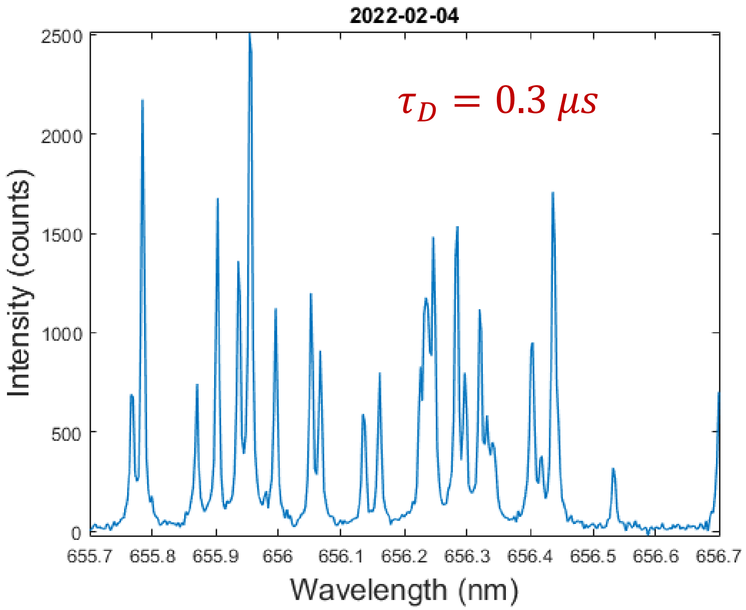
- Emission of discrete atomic lines at later times (~ 1 μsec).

Sergio Musazzi, Umberto Perini: Laser-Induced Breakdown Spectroscopy, Springer Berlin 2014

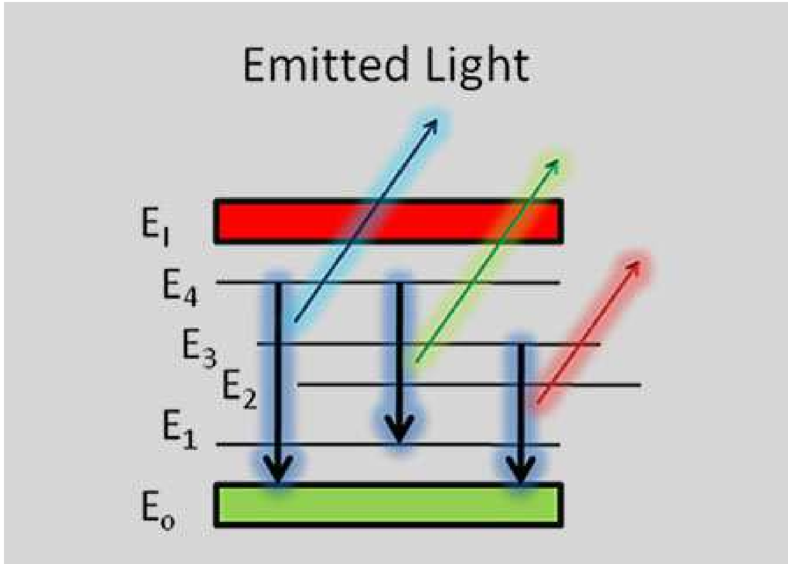
Timescales

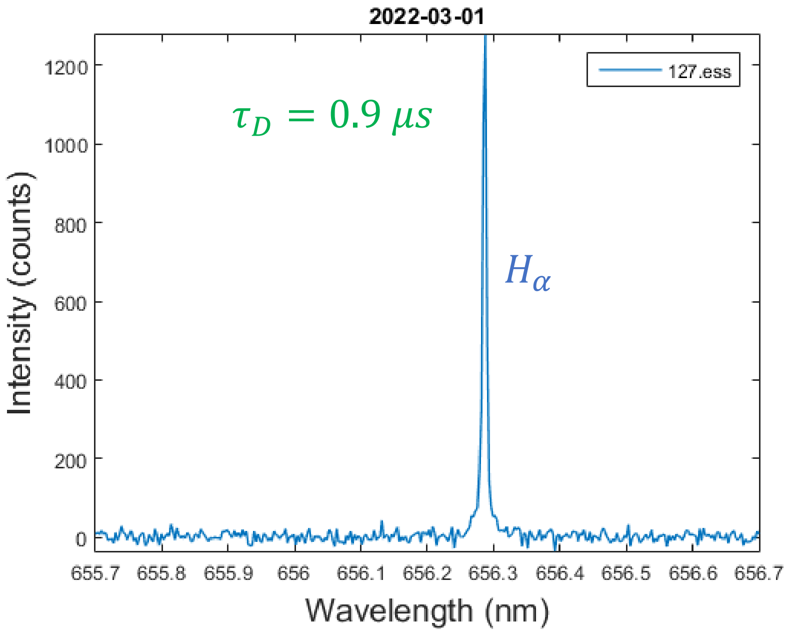
- τ< 0.1 ~ 0.3 μsec
- Plasma temperature 10000-20000 K
- Continuum light emmission (Recombinations, ion lines)



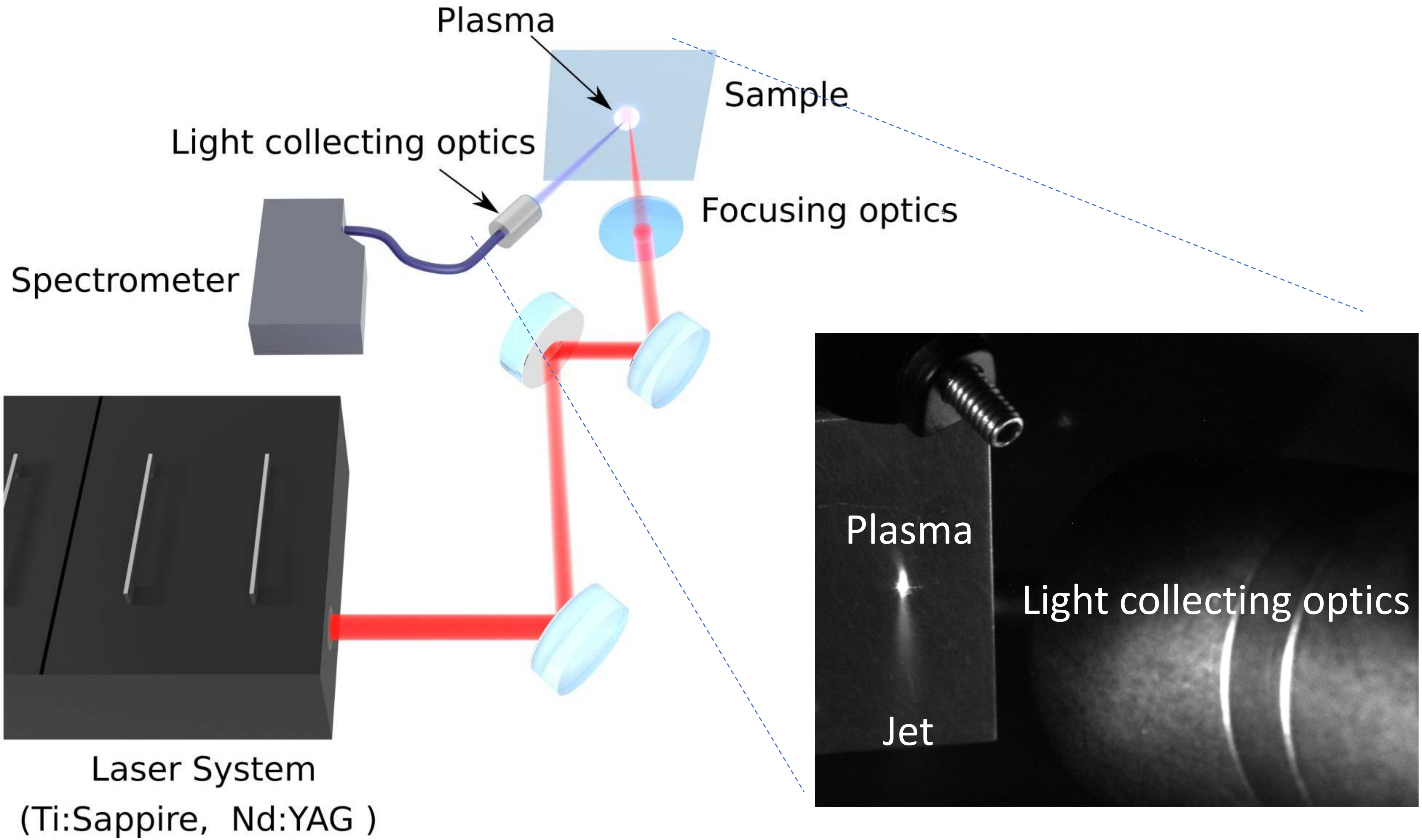


- τ ~ 1 μsec
- Plasma temperature 1000-2000 K
- Emission of discrete atomic lines





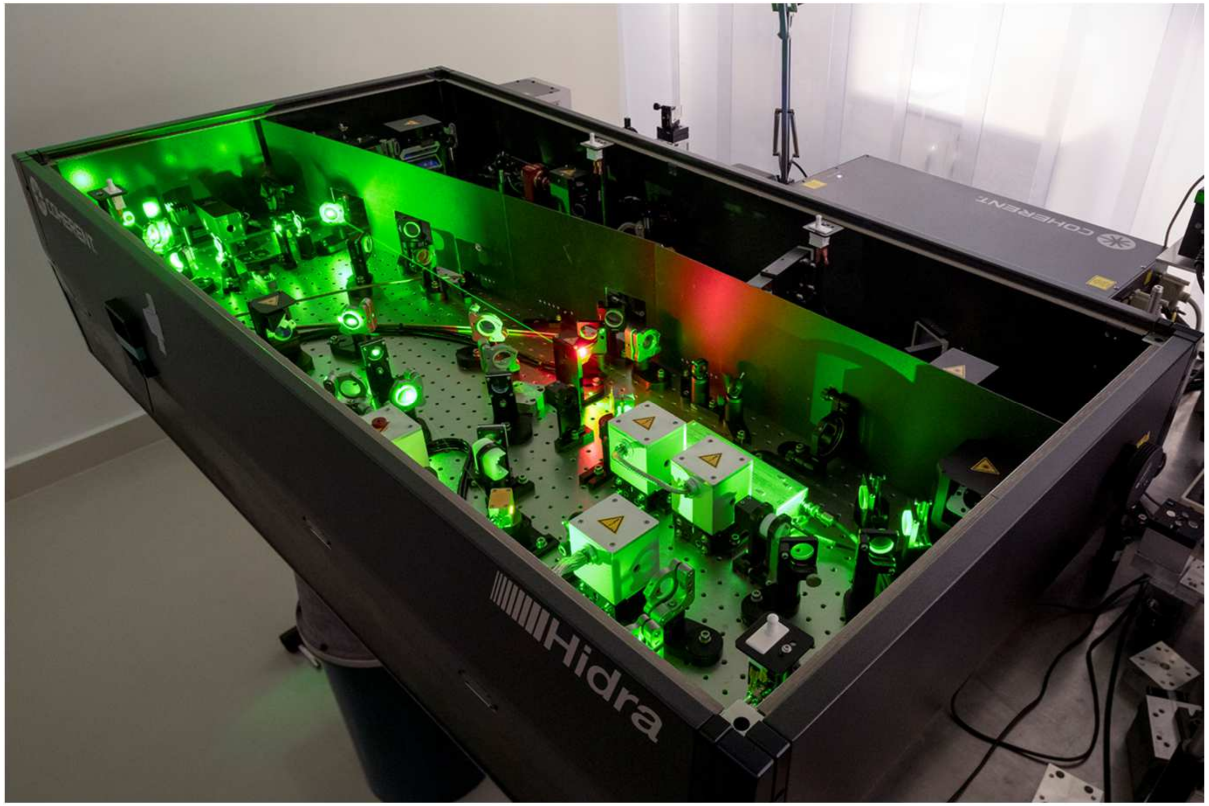
Instrumentation for LIBS



Applied laser system

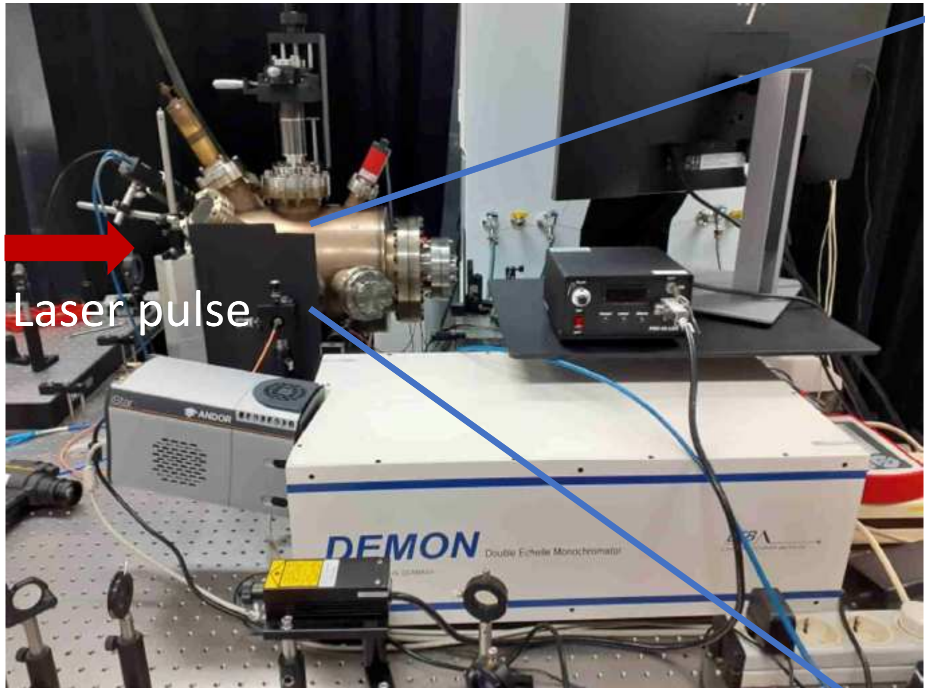
Femtosecond Ti:Sapphire chirped-pulse amplifier

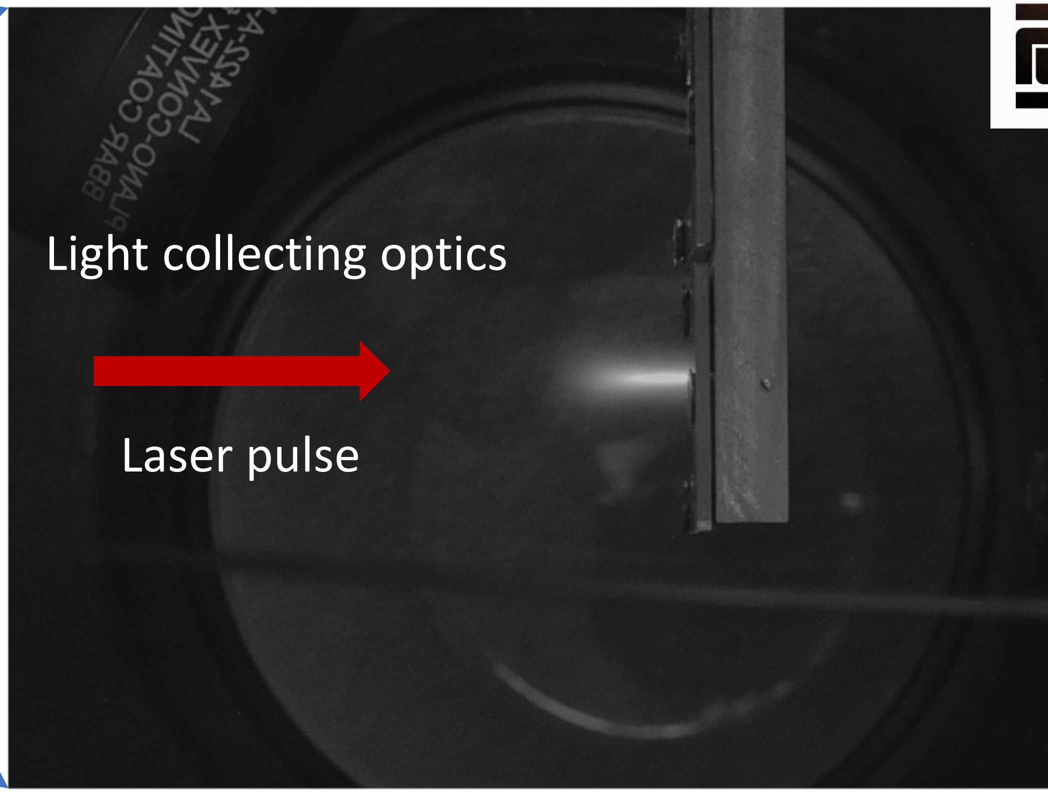
Coherent Hidra-25:



- Pulse energy: max. 25-30 mJ
- Pulse length min. 40 fs
- Central wavelength 795 nm
- Repetition rate: 10 Hz
- Max Peak Power ca. 1 TW
- Focused max. peak intensity approx. 10^{18} W/cm^2

Experimental Setup

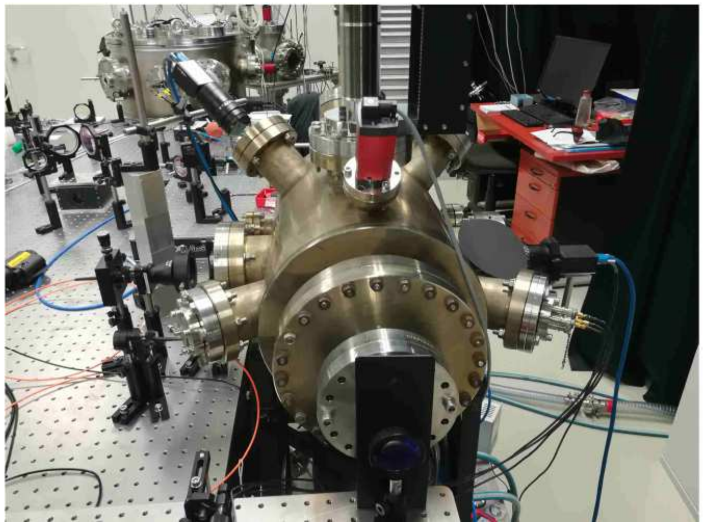




Spectrometer:

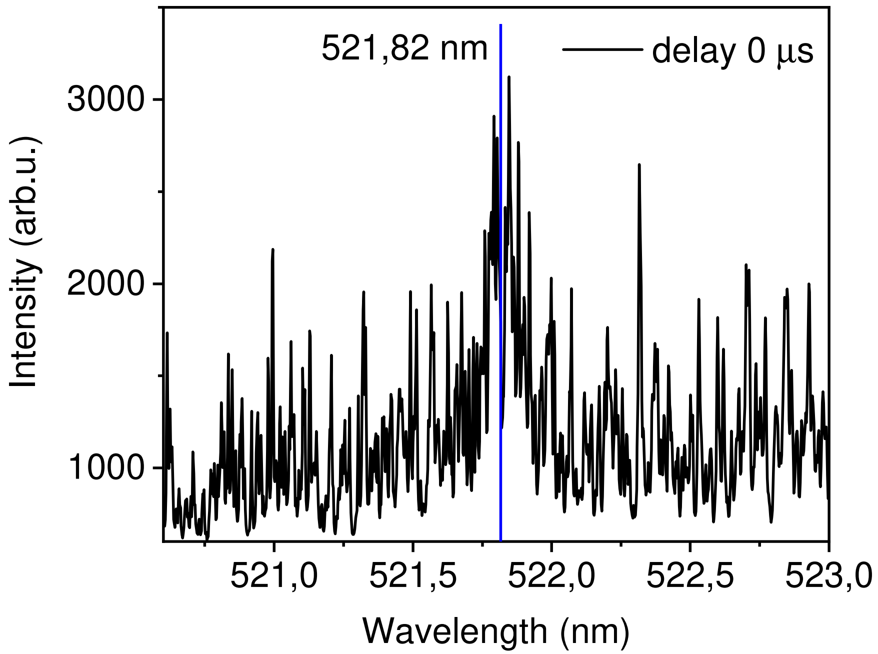
- LTB Demon spectrometer (Double Echelle Monochromator)
- Detector : ICCD
- Wavelength range: 190-900 nm
- Spectral resolution: 2.5-12 pm
- Simultaneous inspection range: 3 nm

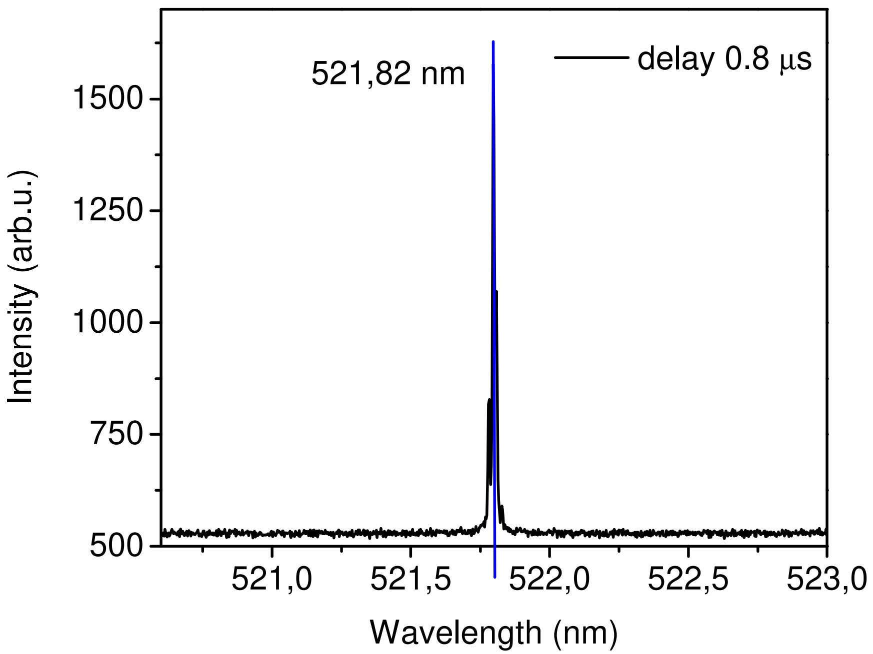
Environme conditions:
In vacuum (10^{-5} mbar)
Ar gas ~2-5 mbar for higher level signal

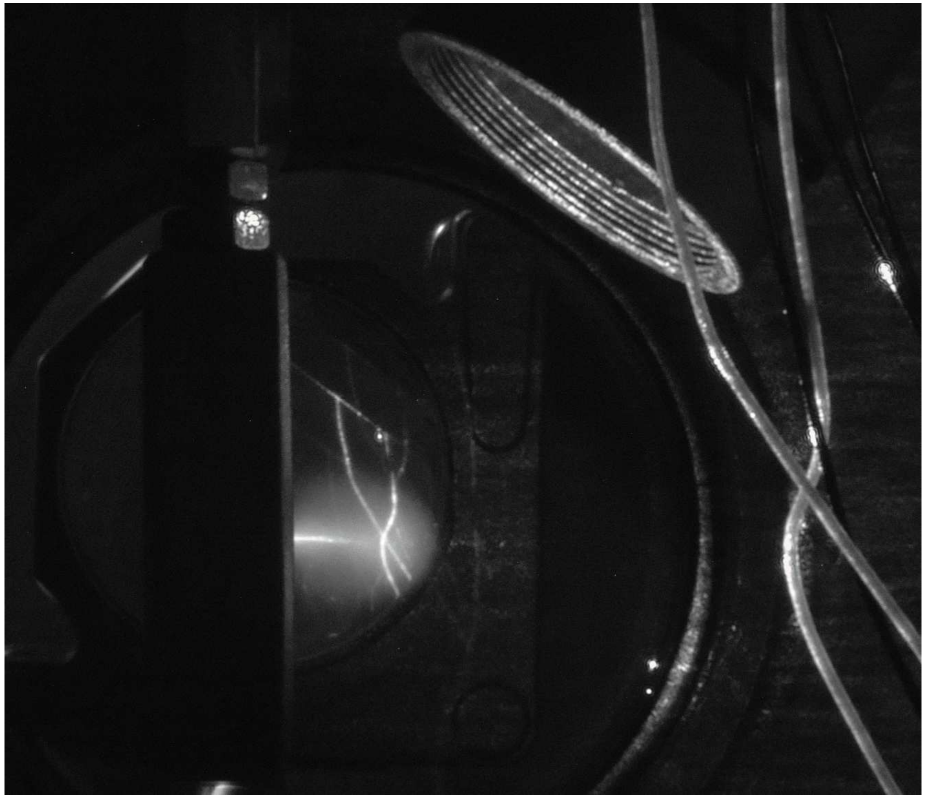


Signal optimisation experiment

LIBS measurements from copper target







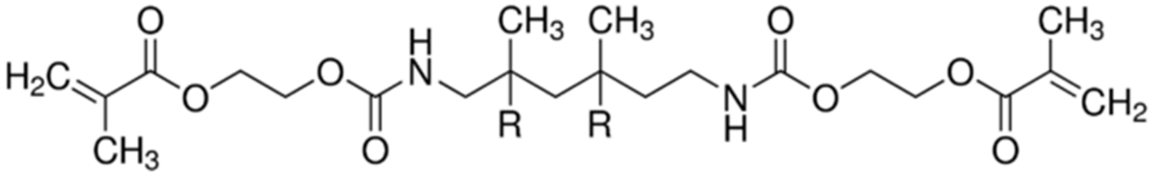
Polymer targets

1. type

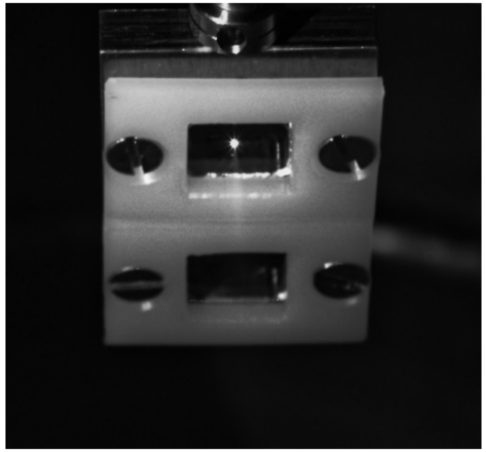
UDMA:TEGDMA mixture (3:1)

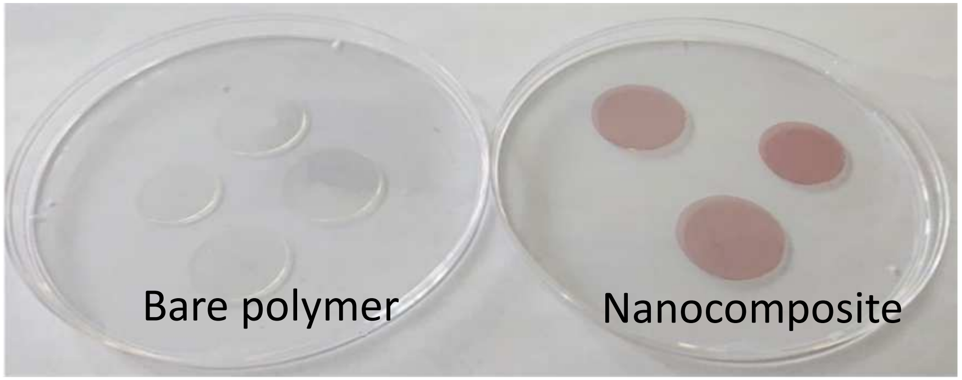
UDMA (urethane dimethacrylate), $C_{23}H_{38}N_2O_8$

Used in in dental medicine

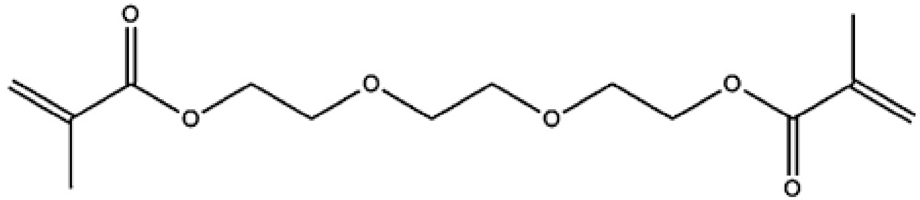


R = H or CH_3 (~1:1)





TEGDMA (triethylene glycol dimethacrylate), $C_{14}H_{22}O_6$



2. type

Nanocomposite: UDMA:TEGDMA mixture (3:1) + AU nanorods

Size of AU nanorods: 85 nm x 25 nm, Plasmonic resonance to 795 nm

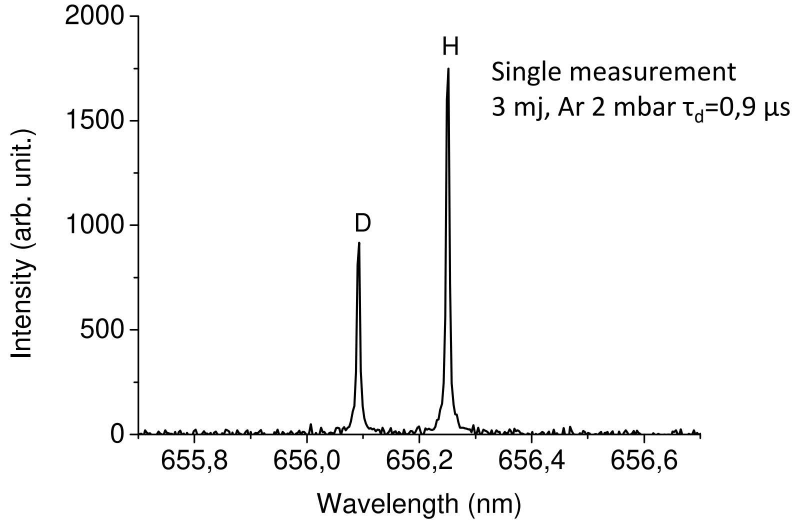
3. type: Deuterated samples

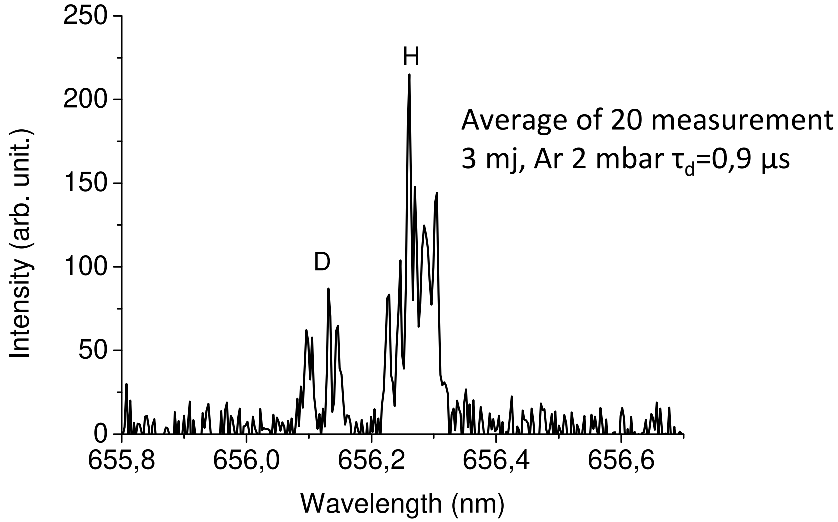
UDMA:MMA-D mixture (3:1) **MMA-D (**Methyl methacrylate**):** $C_5D_8O_2$ $\frac{\text{No.of D atoms}}{\text{No.of H atoms}}$=0,32

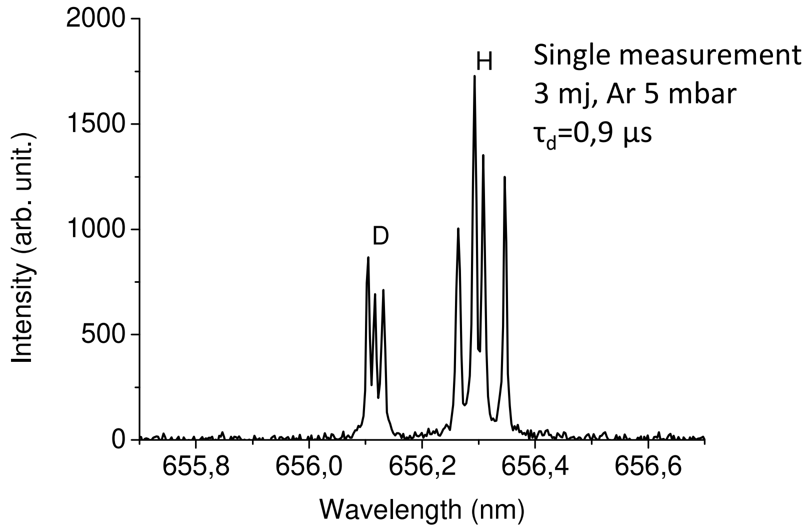
See details in Attila Bonyár presentation

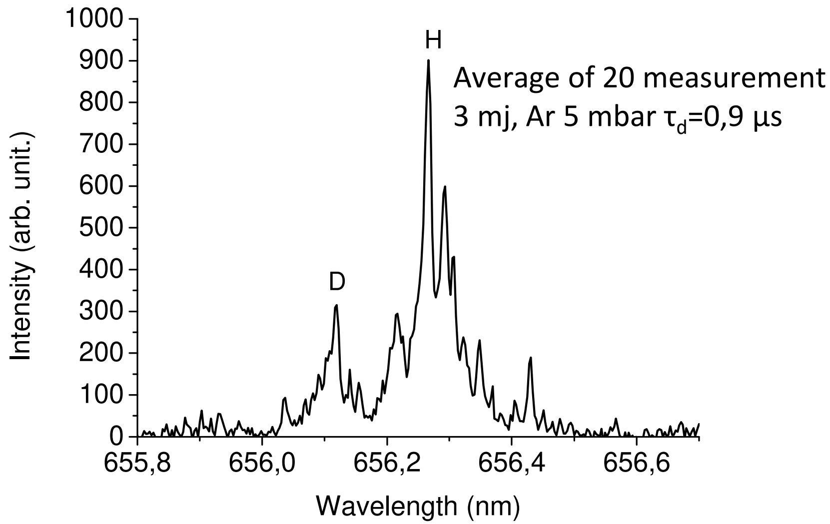
Measurements from deuterated sample

- Balmer α lines: hydrogen 656.28 nm and deuterium 656.11 nm.
- UDMA:MMA-D mixture (3:1)





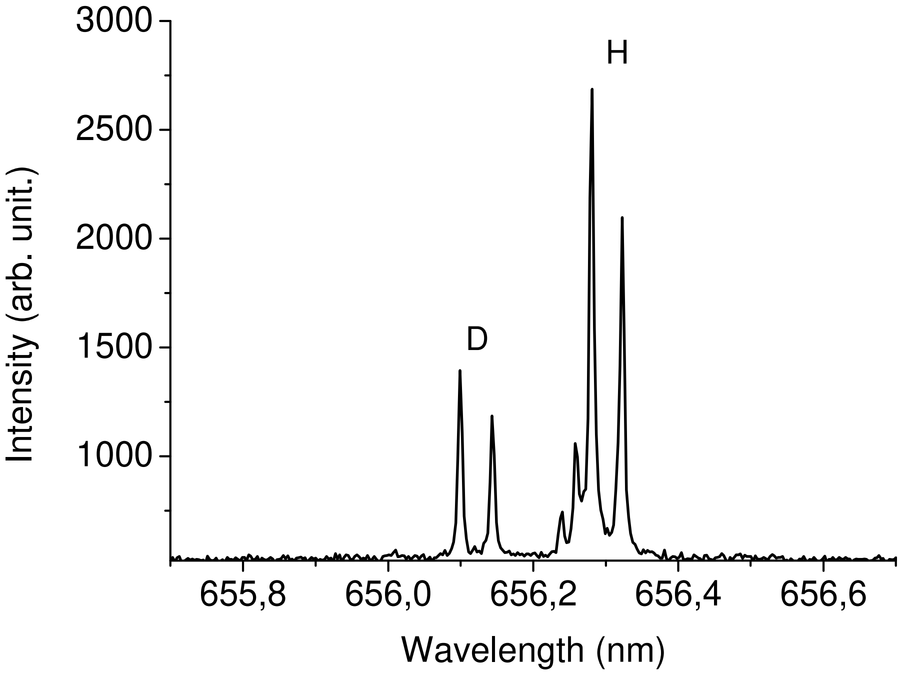




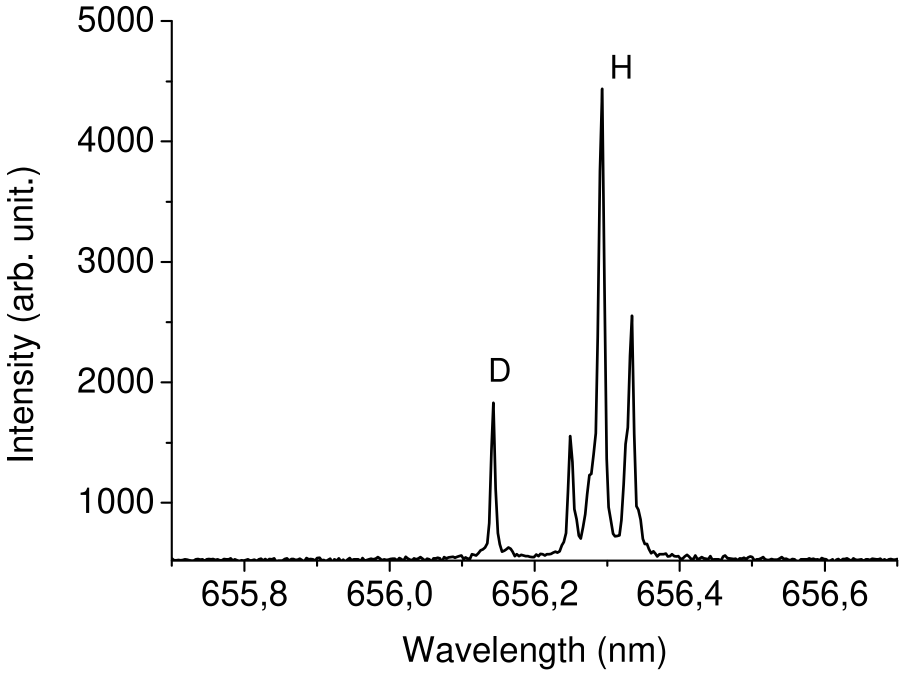
Measurements from bare polymers and nanocoposite samples

- Preliminary results
- Nanocomposite: UDMA:TEGDMA mixture (3:1) + AU nanorods

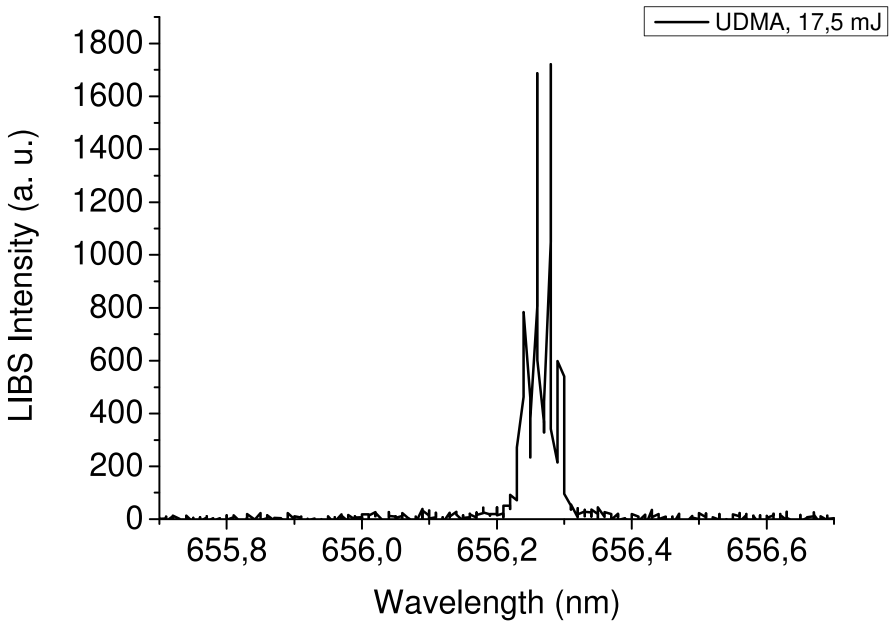
Single measurement
25 mj, Ar 2 mbar τ_d=0,9 µs

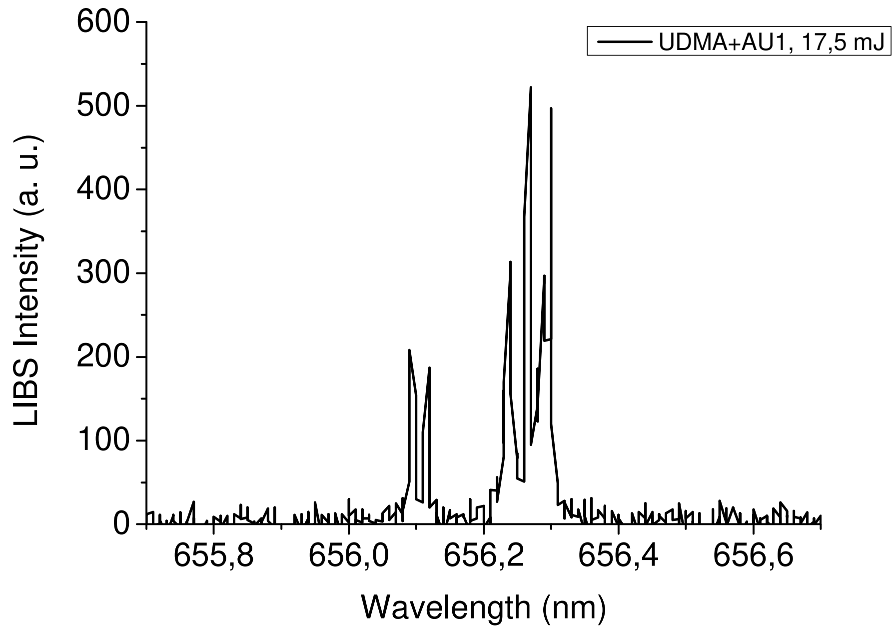


Single measurement
25 mj, Ar 2 mbar τ_d=0,8 µs



- Preliminary results
- Bare Polymer: UDMA:TEGDMA mixture (3:1)
- Nanocomposite: UDMA:TEGDMA mixture (3:1) + AU nanorods





Summary

- LIBS experiment from deuterated polymer samples
- We can detect deuterium with LIBS method

- Measurements from nanocoposite targets (UDMA:TEGDMA mixture (3:1) + AU nanorods
- Deuterium signal also present in this type of targets
- Possible explanation: deuterium production
- Next step: incrising the signal

Thank you for your attention!

Norbert Kroó, Tamás Biró, László Csernai, Miklós Veres, Márk Aladi, Miklós Kedves, Archana Kumári, Judit Kámán, István Rigó

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Concetration

$1.9x10^{12}$ pice/ml	0.1236 m/m%