UNIVERSITÀ DEGLI STUDI DI BARI ALDO MORO

Recent advances and future perspectives in LIBS for industry and environment

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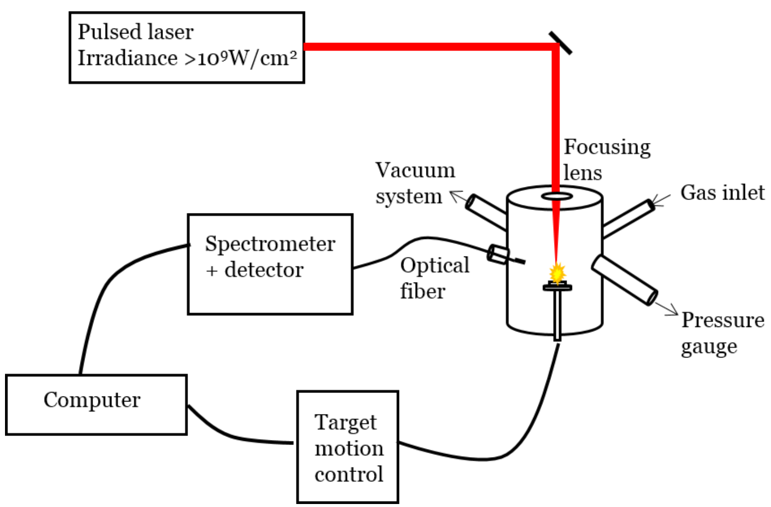
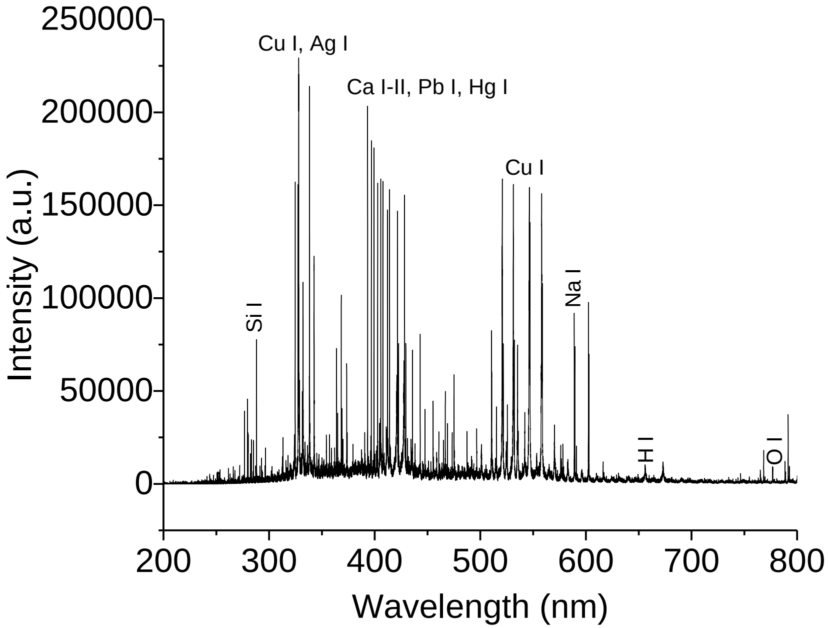
Laser-Induced Breakdown Spectroscopy (LIBS)





- Atomic plasma, few mm diameter
- Persistence time ~ 10 μs, supersonic expansion speed 10^3-10^6 cm/s
- Excited atoms and ions → emission of radiation ➡ LIBS signal
- Stoichiometric ablation

➢ Plasma characterization

➢ Production of novel materials

➢ Qualitative and quantitative elemental analysis

LIBS as an analytical technique

Versatility

- Suitable for any kind of samples
- Possibility of in situ and remote analyses
- Major and minor elements (~ppm)

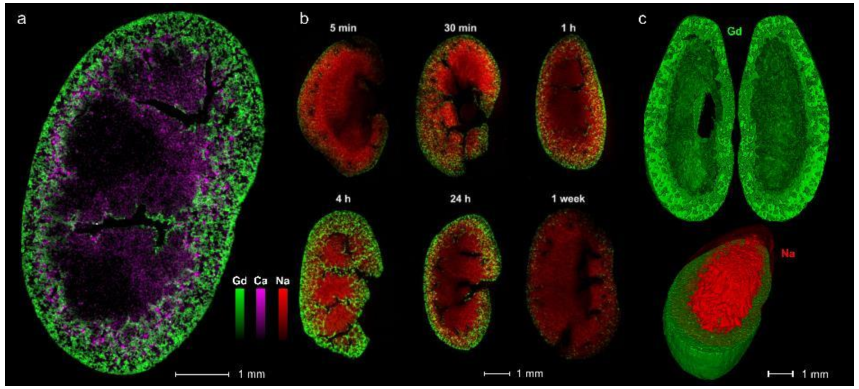
Speed

- Limited sample pre-treatment
- Real-time multielemental response

Spatial resolution

- Point analysis technique
- Depth-profile and spatially resolved analysis
- Micro-destructive analysis

Biomedical imaging

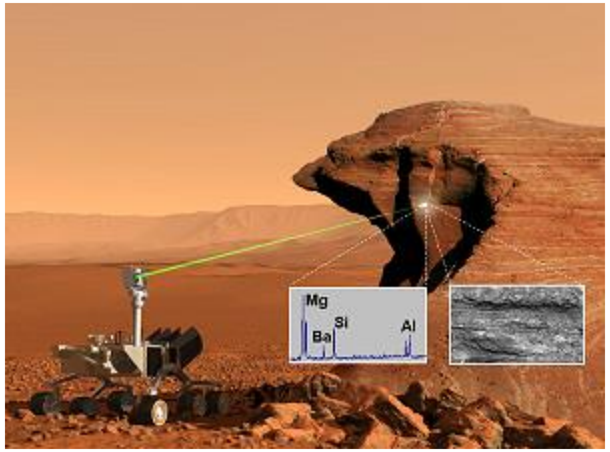


L. Sancey et al., ACS Nano 9 (2015) 2477.

Archaeology

R. Gaudiuso et al., Analyt. Chim. Acta 813 (2014) 15.

Mars exploration



https://mars.nasa.gov/msl/spacecraft/instruments

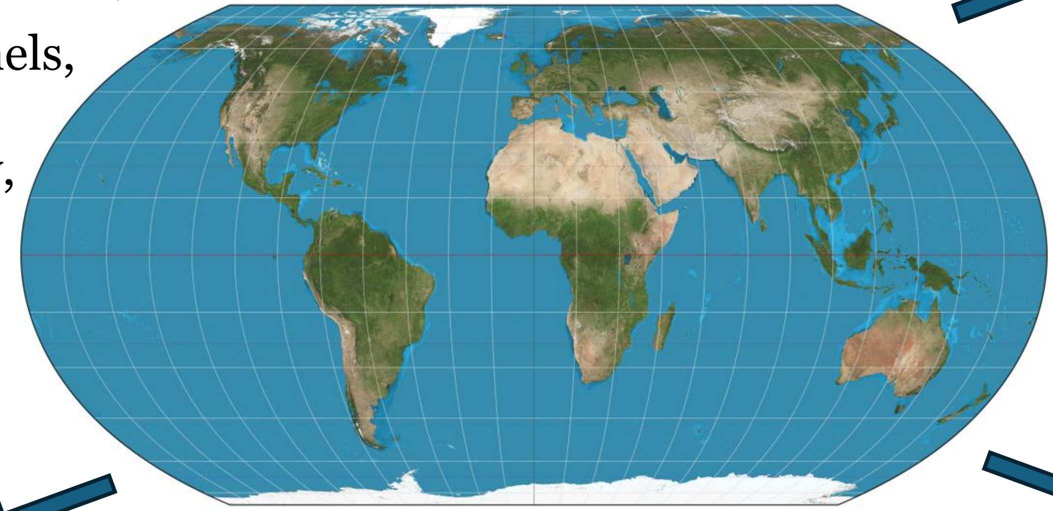
Key global priorities

Climate change

- ➢ Energy industry

- Renewable (solar panels, wind turbines)
- Nuclear (stratigraphy, isotopic analysis)
- Coal (ash content, calorific value)

Circular economy



Food security

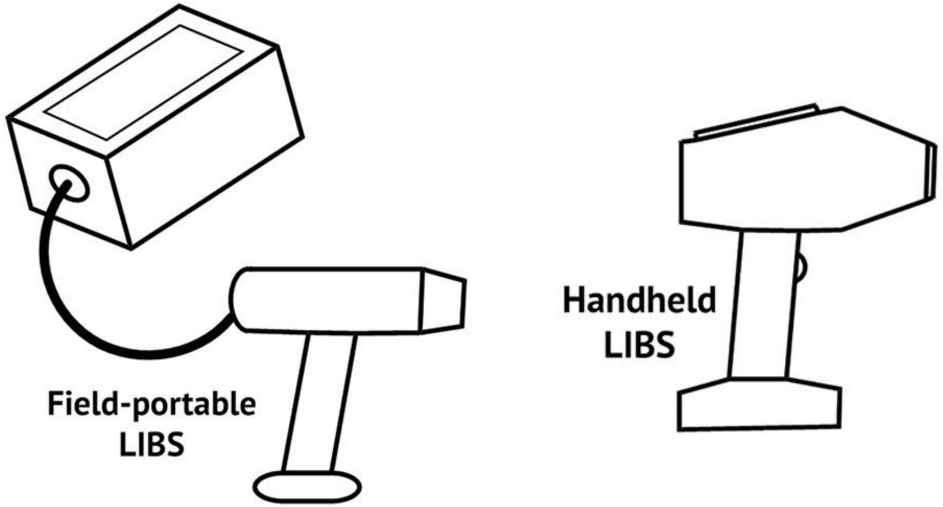
Aging population

Raw materials supply

- ➢ Mining industry
- ➢ Hydrothermal vents

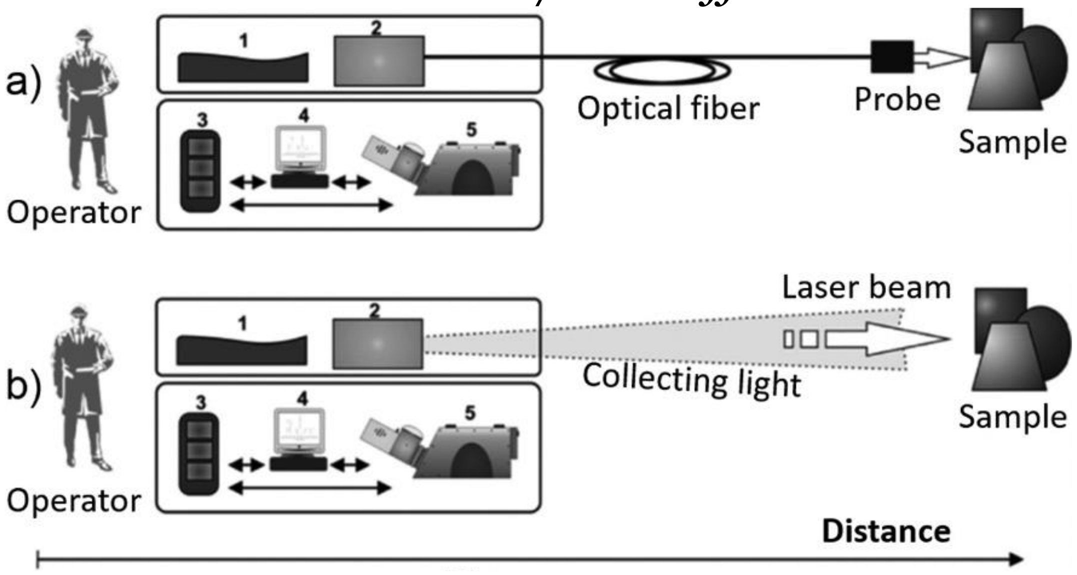
Fieldable LIBS

Portable



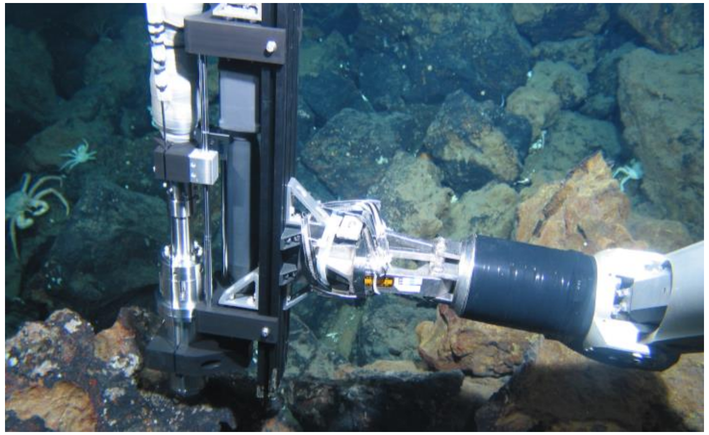
Senesi et al., Spectrochim. Acta B 175 (2021) 106013

Remote/standoff



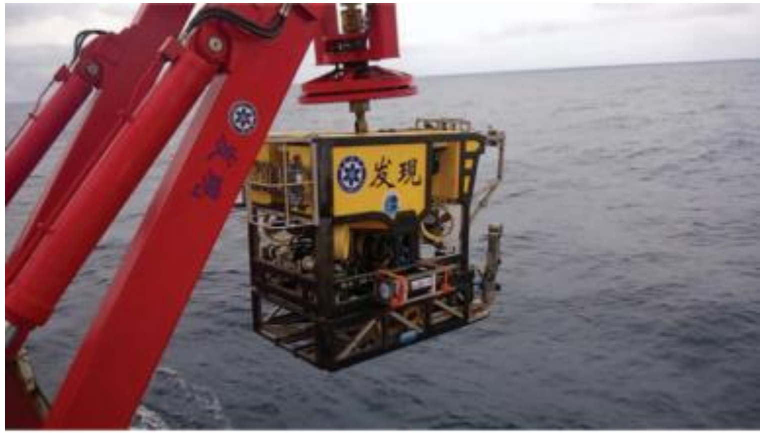
Fortes et al., Anal. Chem. 85 (2013) 640

Under water



http://ocean.iis.u-tokyo.ac.jp/research/laser_induced.html

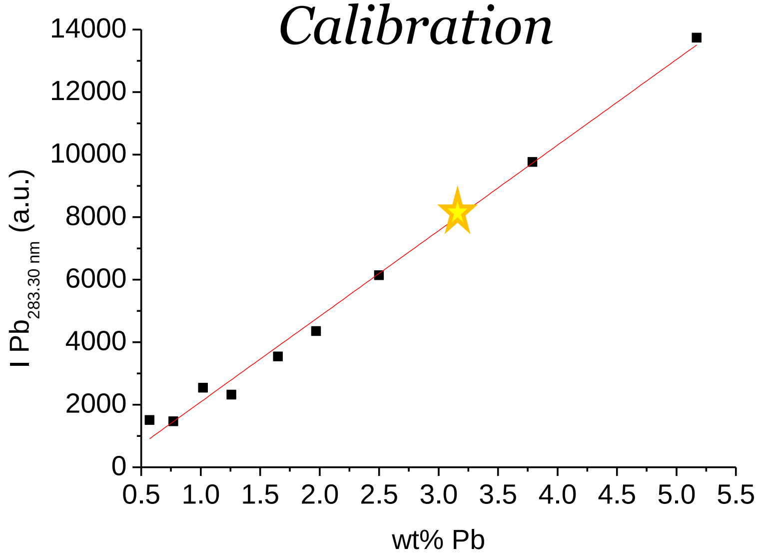
López-Claros et al., J. Cult. Herit. 29 (2018) 75



Guo et al., Appl. Opt. 29 (2017) 8196

Analytical methods

Calibration



Calibration-Free

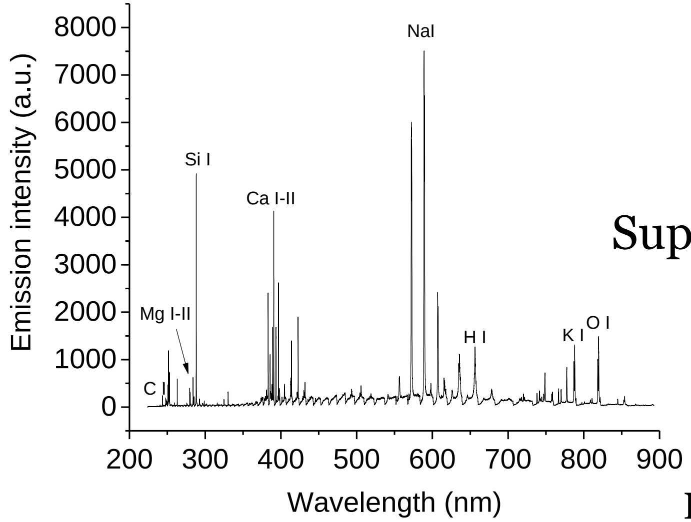
T, N_e, I_{ul} → LTE

$$N_{0,Tot,i} = N_{0,at,i} + N_{0,ion,i}$$

$$wt\%_i = \frac{N_{0,i,Tot} MM_i}{\sum_i N_{0,Tot i} MM_i} \times 100$$

Poggialini et al., J. Anal. At. Spectrom., 38 (2023) 1751

Machine learning



Supervised or unsupervised algorithms →

- Preprocessing
- Classification
- Clustering
- Regression

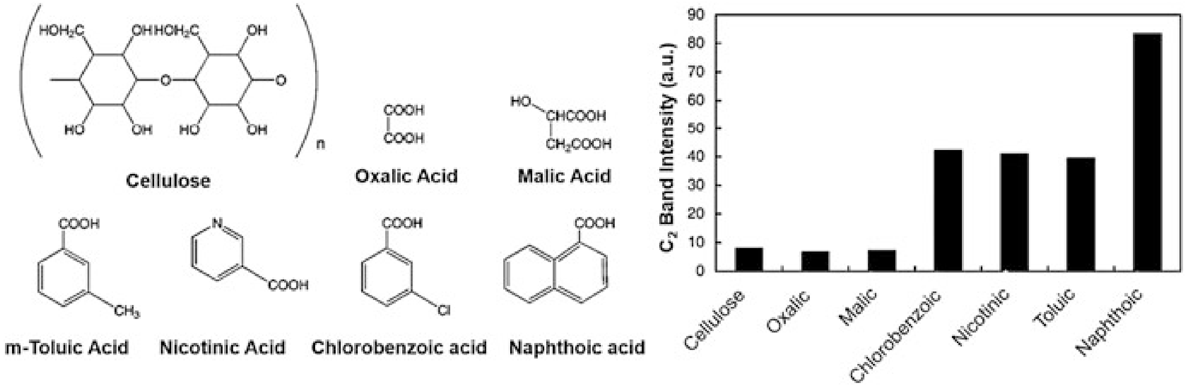
Hao et al., Front. Phys. 19 (2024) 62501

Circular economy: LIBS for waste sorting and inverse production

Metals →
- Steel, Al, Cu
- Scrap composition → quality
- Classification for recycling

R. Noll, 2023, Wiley.

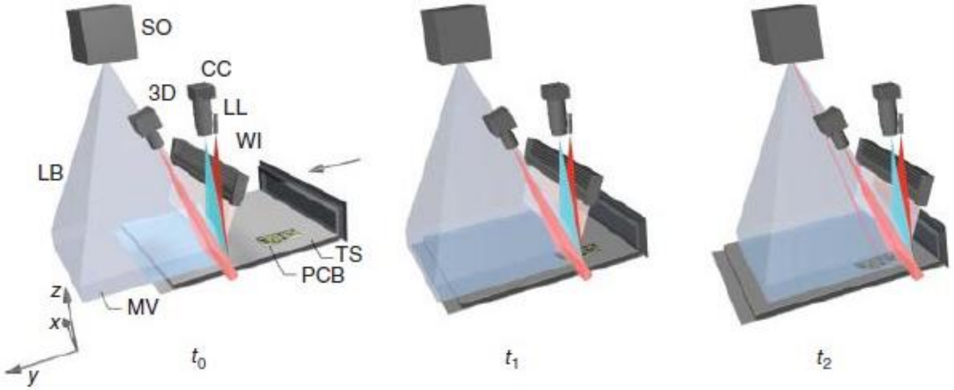
Polymers →
- Classification of different polymer types
- Sorting, recycling, safe disposal
- Monitoring of additives or contaminants



Z. Gajarska et al., 2022, Springer.

Electrical and electronic waste (E-Waste)

- Highly inhomogeneous (Polymers, Printed Circuit Boards, PCB → metals, ceramics)
- Device-dependent shape and kind
- Classification for recycling and inverse production



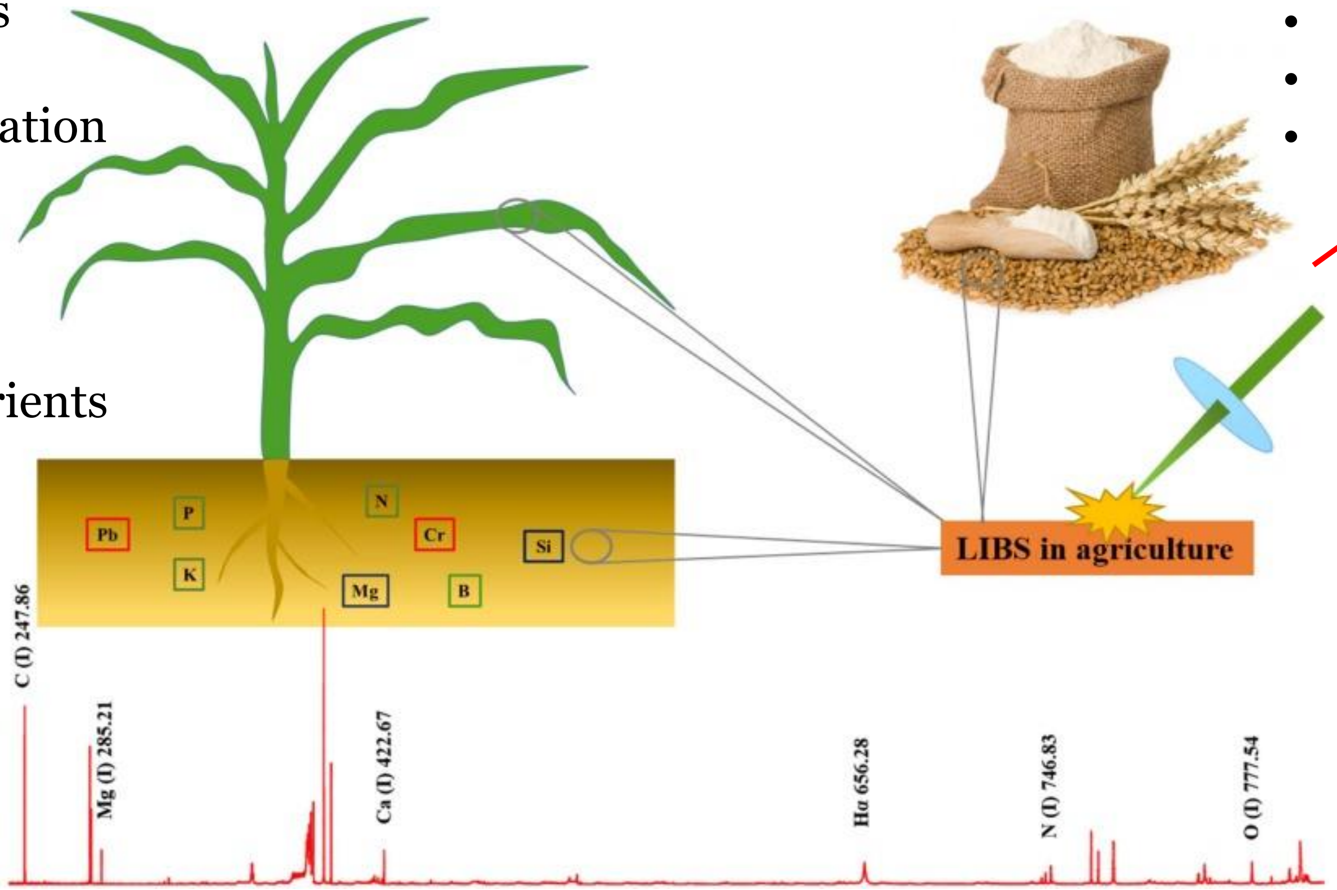
R. Noll, 2023, Wiley.

Food security: LIBS in agriculture and food science

Plant materials (dried or fresh)
- Nutritional deficiencies
- Pesticide residues
- Disease and pest infestation

Quality control and adulteration
- Contaminants
- Micro- and macro-nutrients
- Geographical origin

Soil
- Micro- and macro-nutrients
- Contaminants

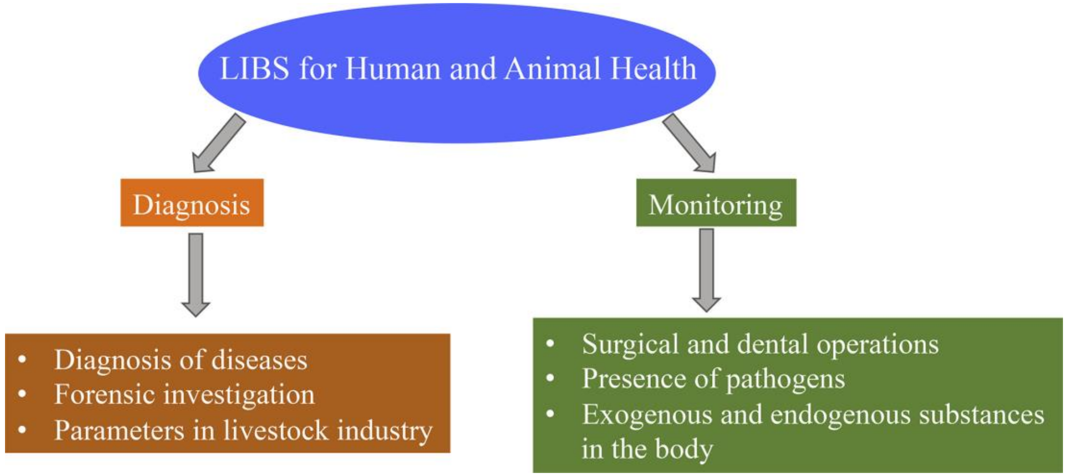


Herbs, spices and tea; honey; olive oil; wine; milk and dairy products; powdered milk; meat products; breakfast cereals; rice, wheat and soybeans; coffee beans; fruit and produce; ...

J. Peng et al., Trends in Analytical Chemistry 85, Part C (2016) 260

Aging population: Biomedical and pharmaceutical applications of LIBS

Biomedicine

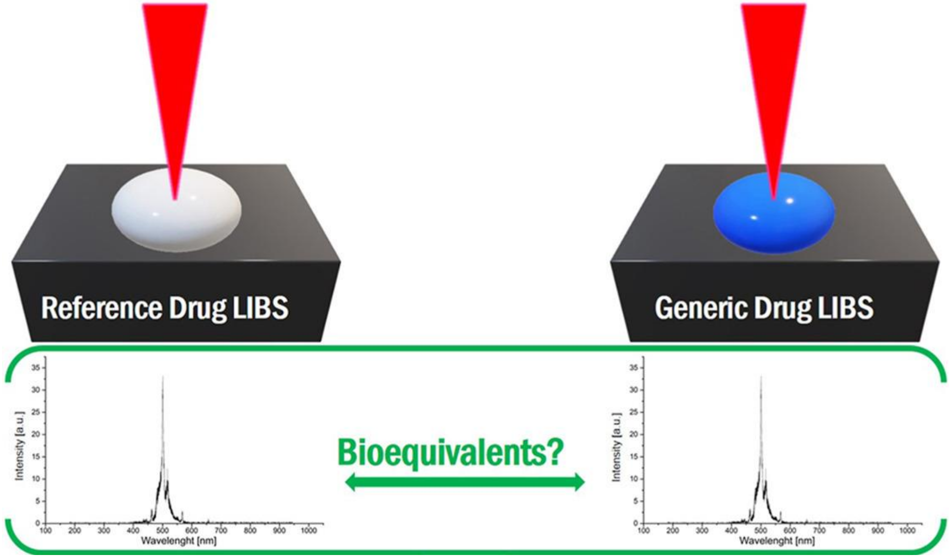


- Cancer
- Alzheimer's disease
- Diabetes

R. Gaudiuso et al., Spectrochim. Acta B 152 (2019) 123.

Pharmaceutical industry

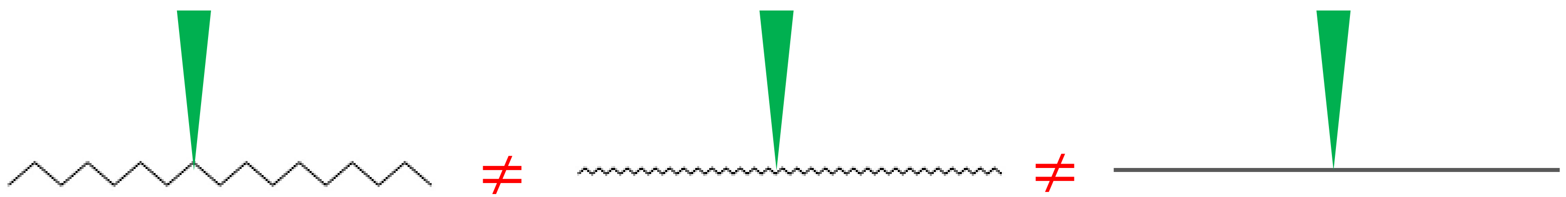
- Quality control (micro- and macronutrients; tablet coatings; blend uniformity studies)
- Counterfeit drugs, contamination
- Bioequivalence studies



J. Cardenas-Escudero et al., Analyt. Chimica Acta 1329 (2024) 343253

Targeting LIBS weaknesses: matrix effects

- Physical-chemical nature
- (Micro)heterogeneity
- Surface morphology
- Particle size



➢ Calibration with matrix-matched standards

➢ Calibration-free analysis

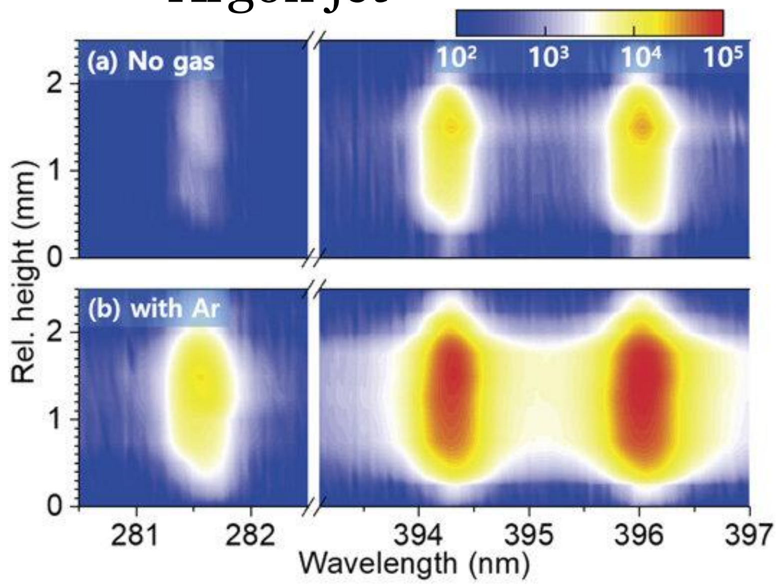
➢ Signal normalization →

- Total emission intensity
- Matrix element
- Background
- Reference signals (e.g., acoustic wave)

N.B. Zorov et al., Spectrochim. Acta B 65 (2010) 642

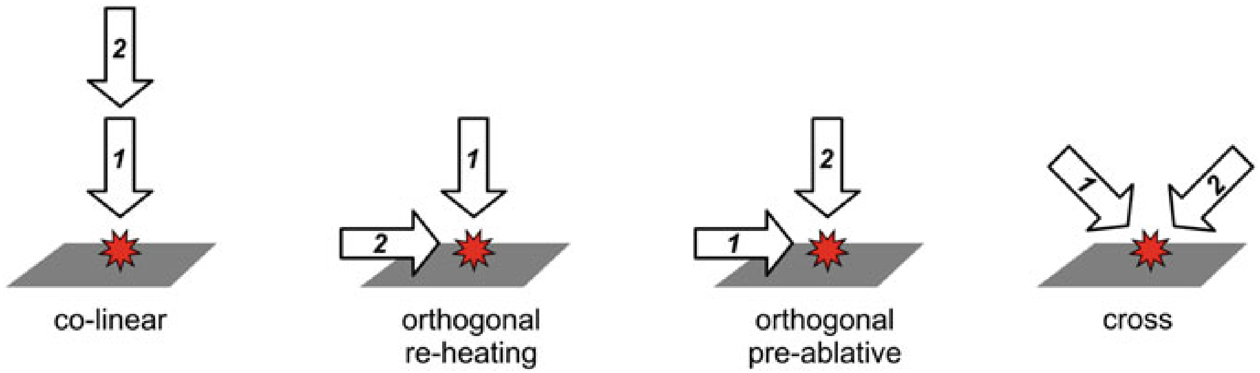
Targeting LIBS weaknesses: low sensitivity

Argon jet



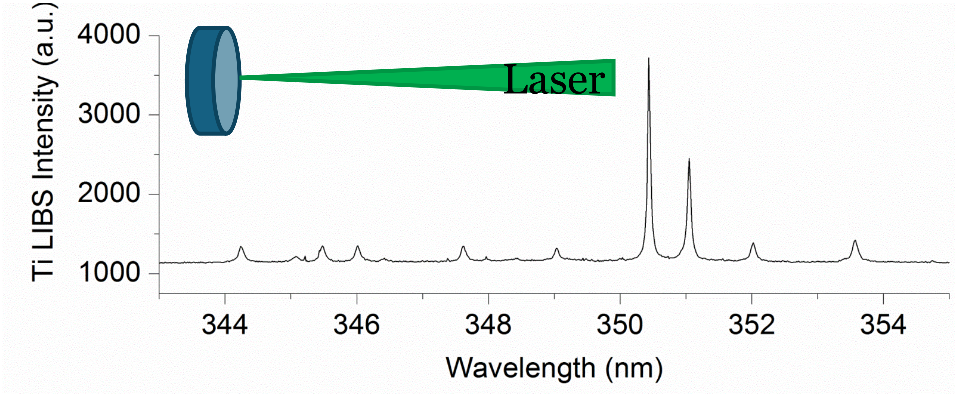
J.-G. Son et al., Appl. Phys. Express 11 (2018) 102401

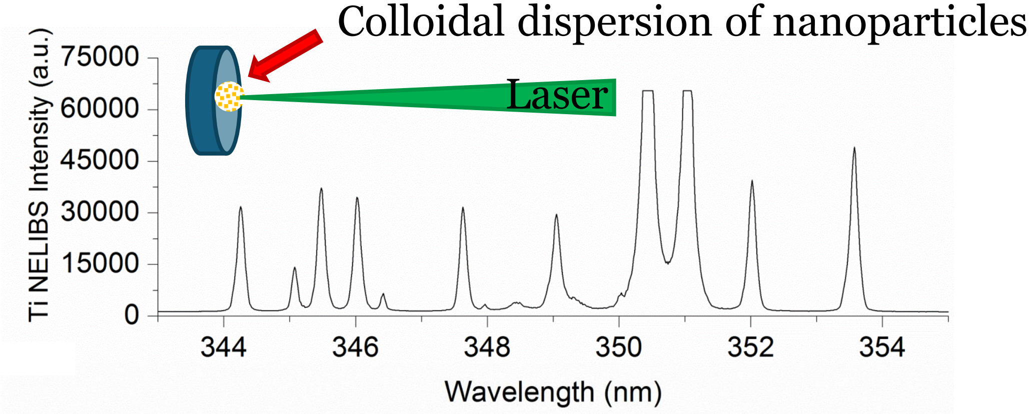
Double-pulse LIBS



G. Galbács et al., 2022, Springer.

Nanoparticle-Enhanced LIBS (NELIBS)





M.Dell'Aglio et al., Spectrochim. Acta B 148 (2018) 105

Further reading

S. Legnaioli et al., *Industrial applications of laser-induced breakdown spectroscopy: a review*, Analytical methods 12 (2020) 1014.

Laser-Induced Breakdown Spectroscopy (LIBS): Concepts, Instrumentation, Data Analysis and Applications, Volume 2, V. K. Singh, D.K. Tripathi, Y. Deguchi, Z. Wang (eds), 2023, John Wiley and Sons Ltd.

V. Costa et al., *Laser-induced breakdown spectroscopy (LIBS) applications in the chemical analysis of waste electrical and electronic equipment (WEEE)*, TrAC Trends in Analytical Chemistry 108 (2018) 65

G.S. Senesi et al., *Recent advances and future trends in LIBS applications to agricultural materials and their food derivatives: An overview of developments in the last decade (2010–2019). Part II. Crop plants and their food derivatives*, TrAC Trends in Analytical Chemistry 118 (2019) 453.

J. Naozuka and A.P. Oliveira, *Laser-Induced Breakdown Spectroscopy in Food Sciences*, in *Laser-Induced Breakdown Spectroscopy (LIBS): Concepts, Instrumentation, Data Analysis and Applications, Volume 2*, First ed. V. K. Singh, D.K. Tripathi, Y. Deguchi, Z. Wang, 2023, John Wiley and Sons Ltd.

P.K. Tiwari, P.K. Rai, A.K. Rai, *Applications of LIBS in drug analysis*, in Jagdish P. Singh, Surya N. Thakur, *Laser-Induced Breakdown Spectroscopy* (Second Edition), Elsevier, 2020, Pages 311-328.

Laser-Induced Breakdown Spectroscopy in Biological, Forensic and Materials Sciences, G. Galbács (ed), Springer, 2022.

Thank you for your attention

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