Introduction to
Laser Induced Breakdown Spectroscopy

J.J. Laserna
Department of Analytical Chemistry
University of Málaga, Málaga, Spain

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laserna@uma.es

http://laser.uma.es

Winter School on Underwater Sensing Science
Aberdeen Scotland UK 22 March 2017

Malaga: 600,000 inhabitants

University of Málaga created in 1973
ca. 37,000 students

The Laser Laboratory Group

Department of Analytical Chemistry
University of Malaga

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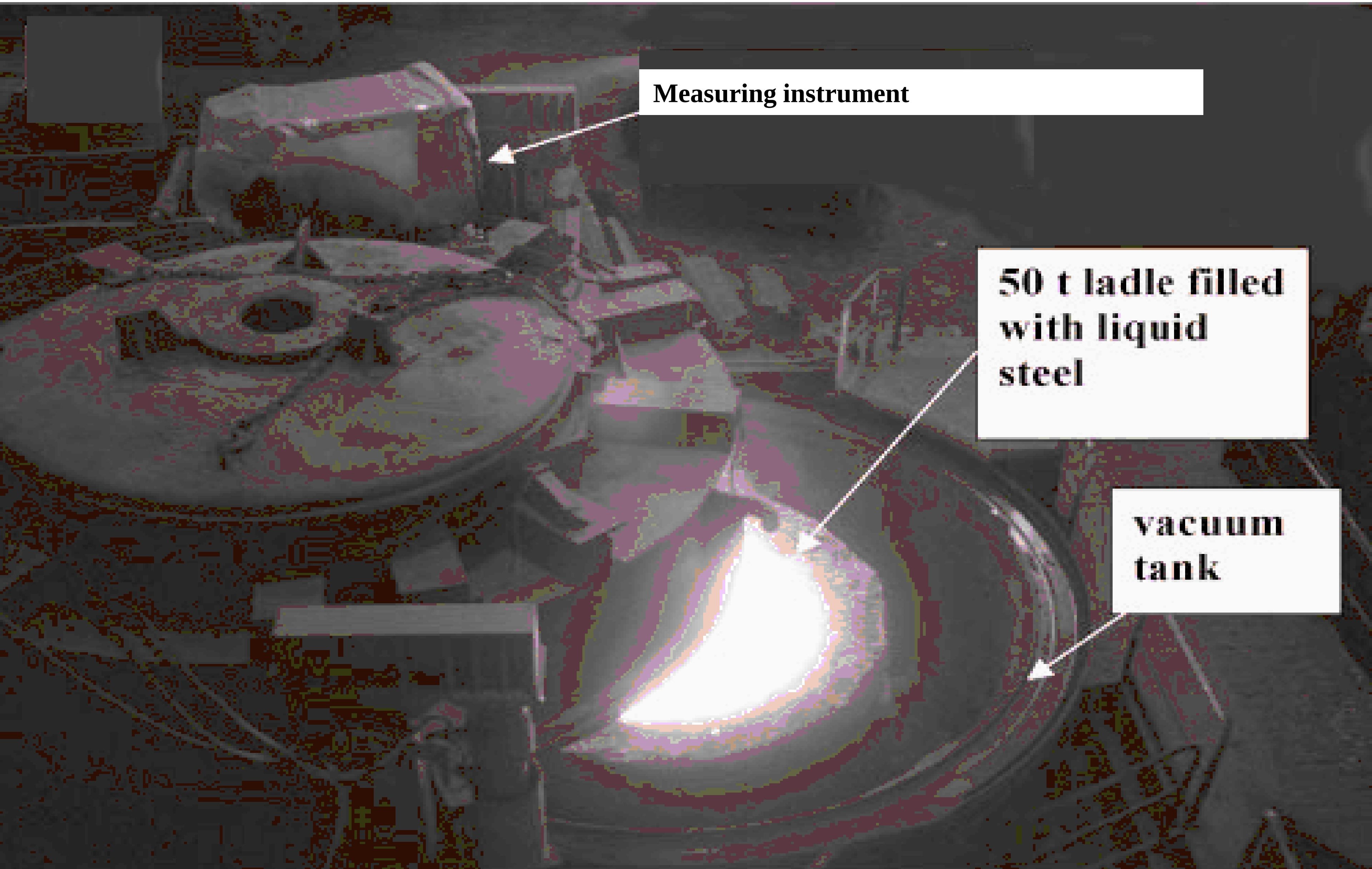
In situ analysis of liquid steel



Standoff detection of explosives

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Submarine analysis of solids

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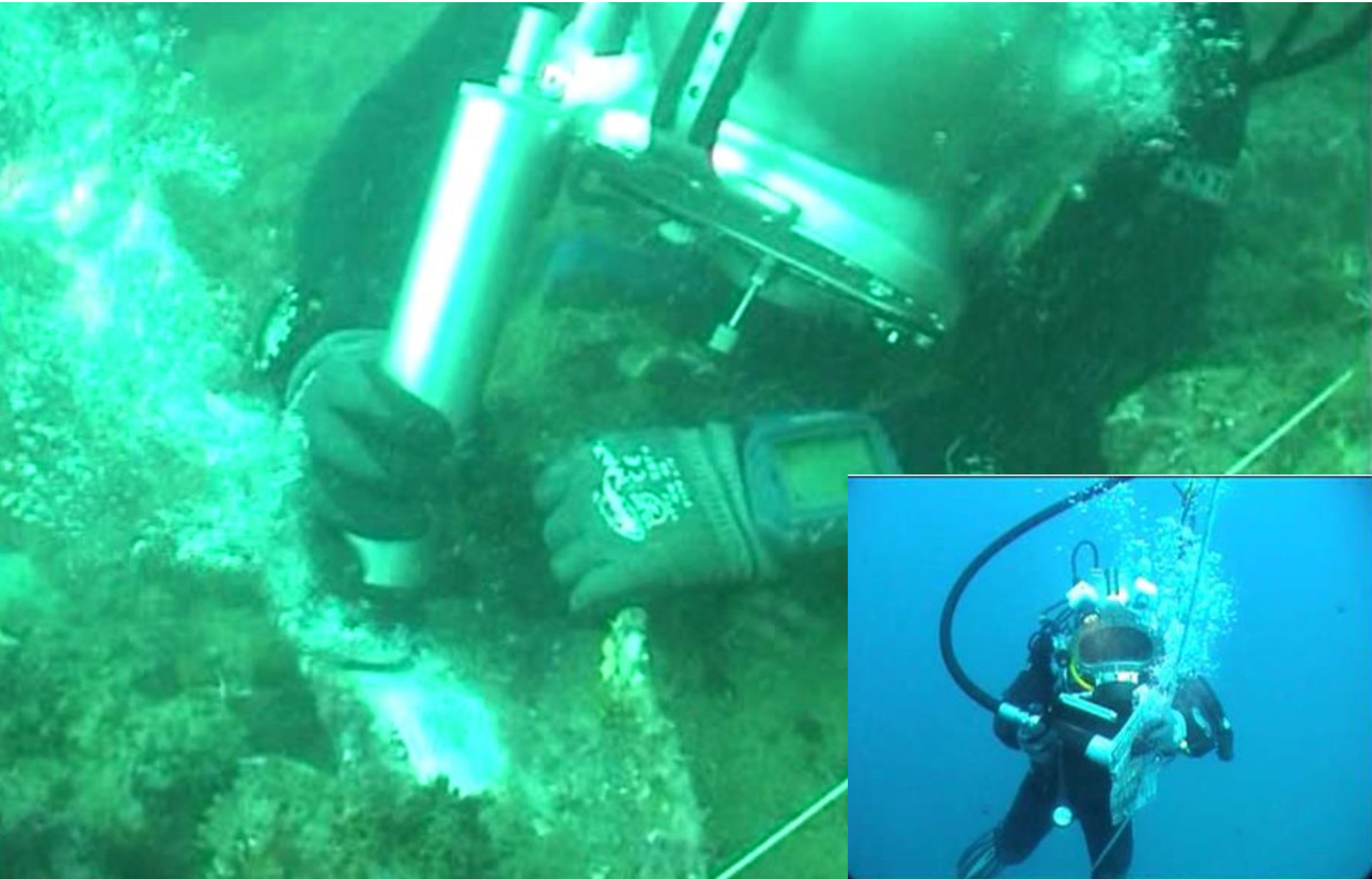
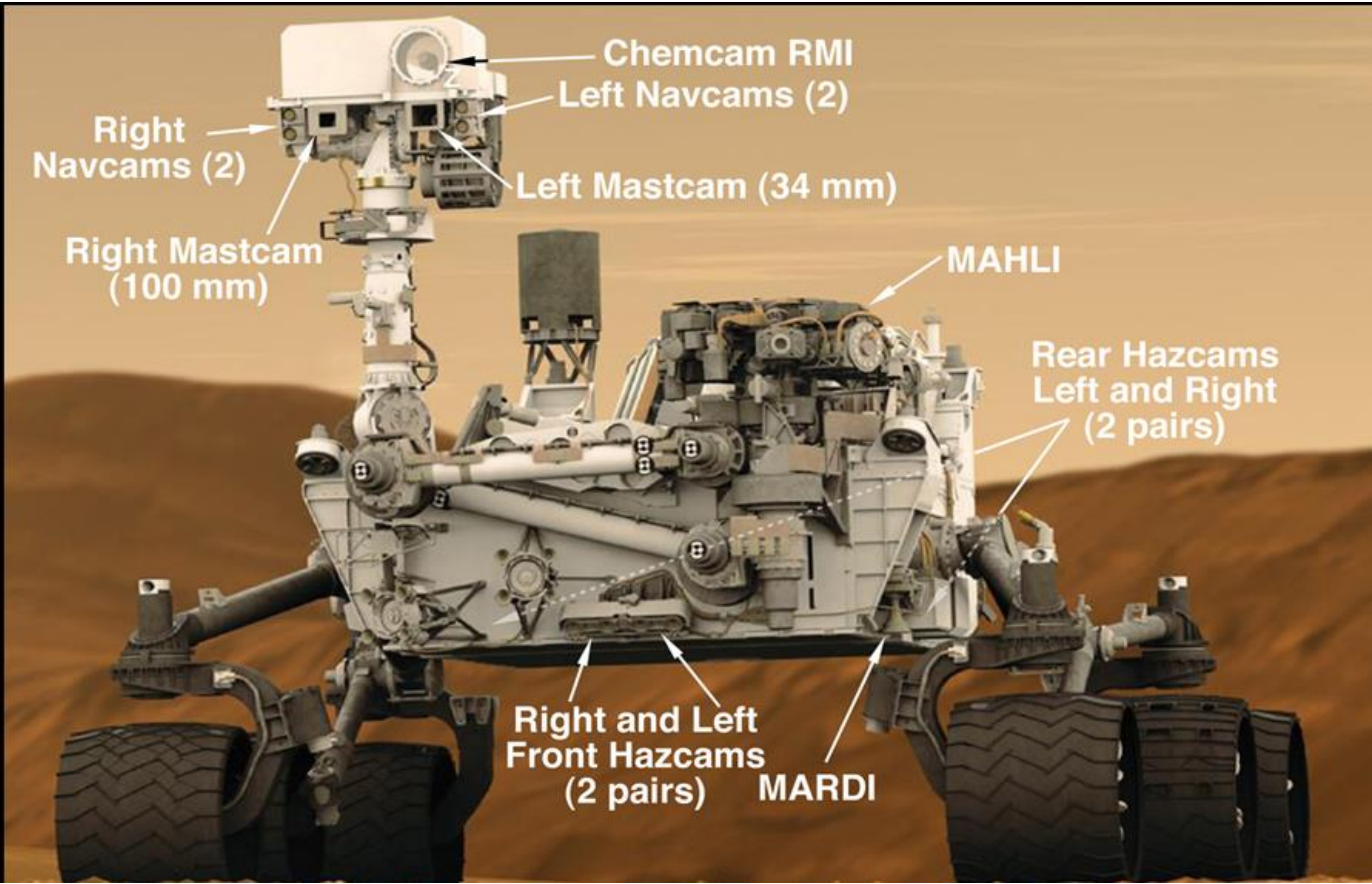
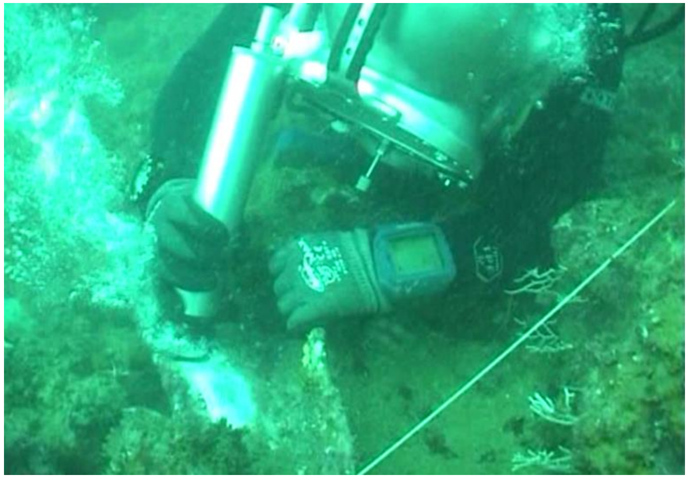
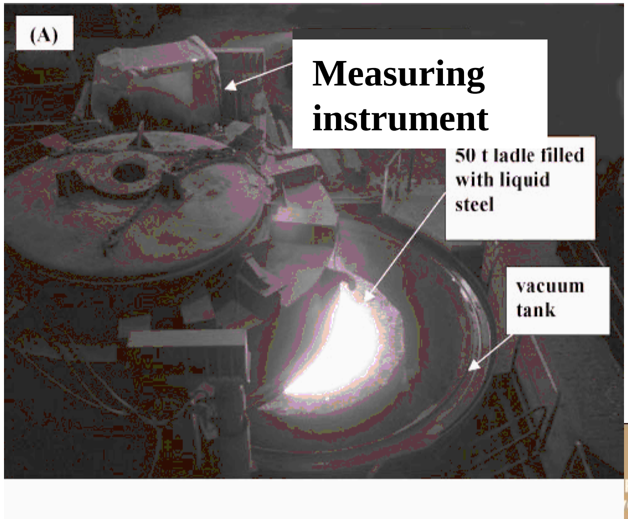


Standoff inspection of architectural heritage

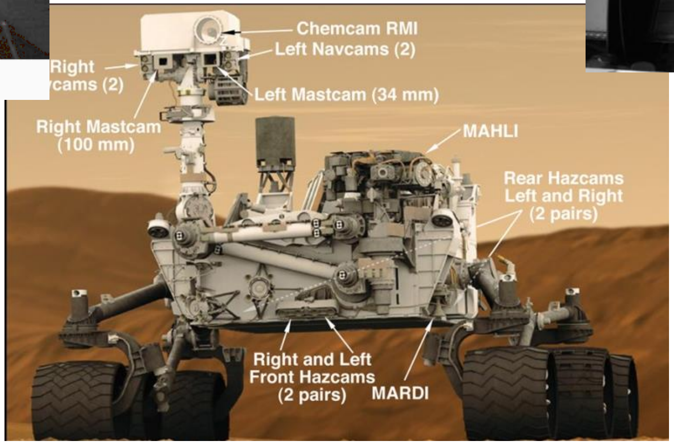
Space exploration – Mars Curiosity rover







What in common???



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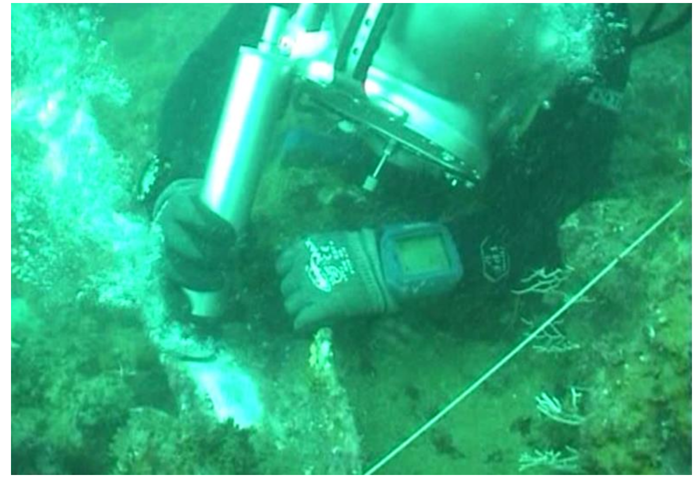
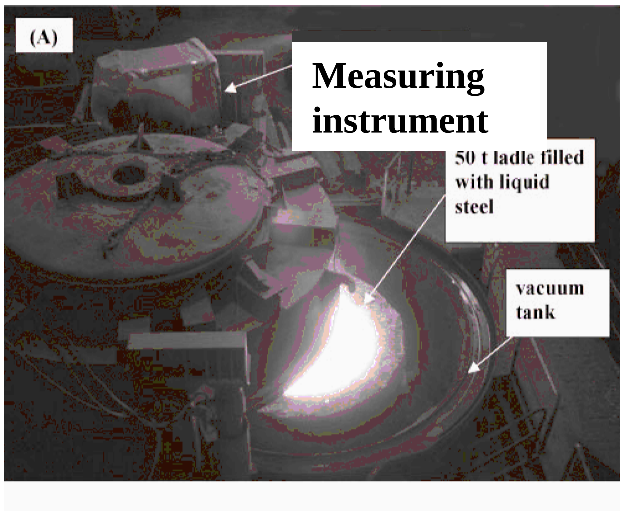
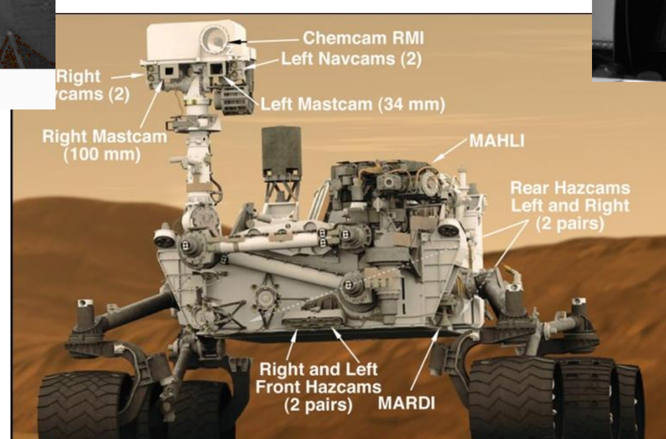


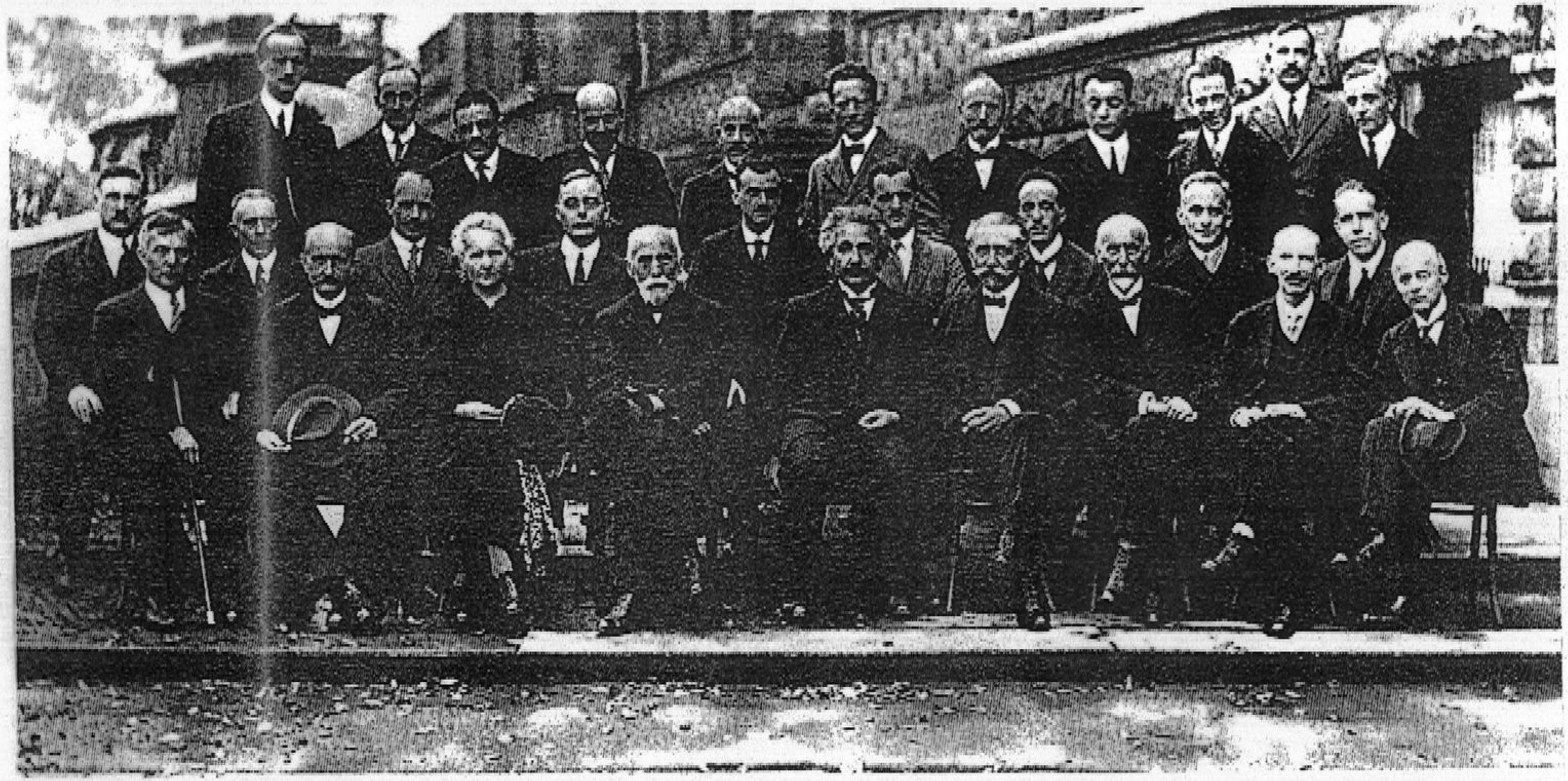


LIBS



V Solvay Conference

Brussels, 1927

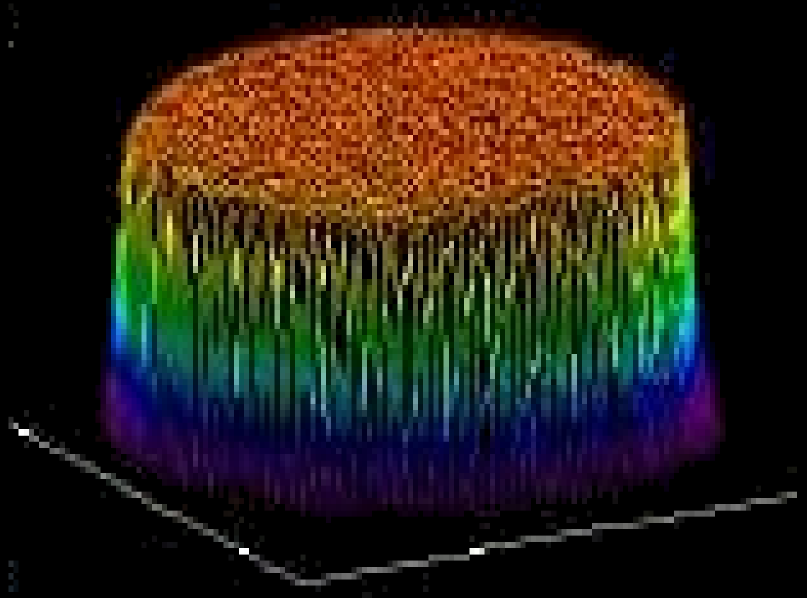


A. PICCARD E. HENRIOT P. EHRENFEST Ed. HERZEN Th. DE DONDER E. SCHRODINGER E. VERSCHAFFELT W. PAULI W. HEISENBERG R.H. FOWLER L. BRILLOUIN

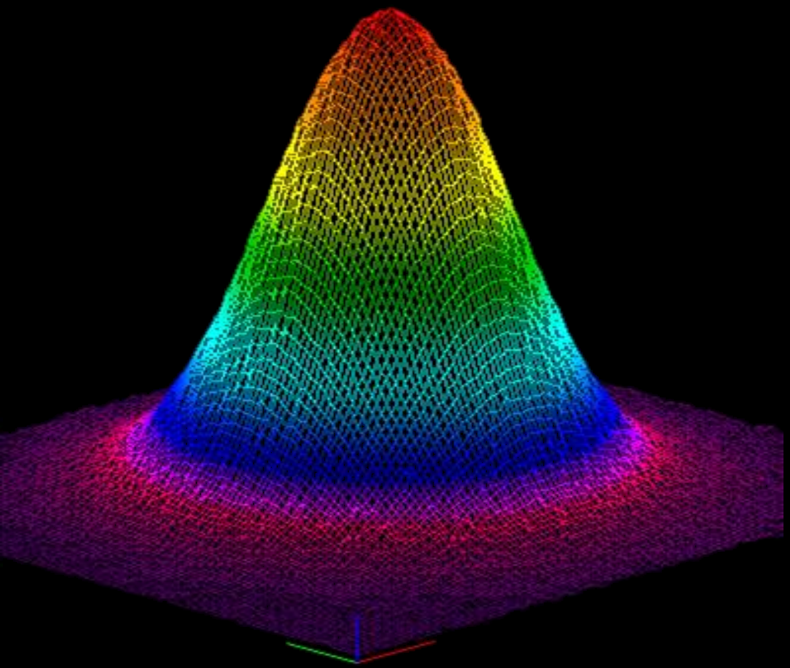
P. DEBYE M. KNUDSEN W.L. BRAGG H.A. KRAMERS P.A.M. DIRAC A.H. COMPTON L. de BROGLIE M. BORN N. BOHR

I. LANGMUIR M. PLANCK Mme CURIE H.A. LORENTZ A. EINSTEIN P. LANGEVIN Ch.E. GUYE C.T.R. WILSON O.W. RICHARDSON

Absents : Sir W.H. BRAGG, H. DESLANDRES et E. VAN AUBEL



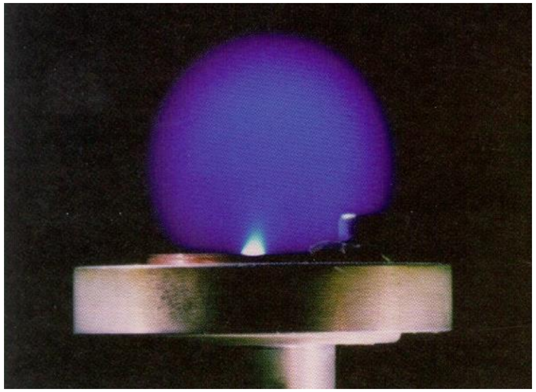
‘The laser, a solution in search of a problem’



Anne Thorne, commenting on the opinion of scientists in 1960

Laser Induced Breakdown Spectroscopy
Acronyms

- **LIBS: Laser Induced Breakdown Spectroscopy**
- **LIPS: Laser Induced Plasma Spectroscopy**
- **LIESA: Laser Induced Emission Spectral Analysis**
- **LA-OES: Laser Ablation Optical Emission Spectroscopy**
- **LM-OES: Laser Microanalysis-OES**
- **LM-OES: Laser Microprobe-OES**
- **LMSA: Laser Micro-Spectral Analysis**
- **LSS: Laser Spark Spectroscopy**
- **LISWPS: Laser-Induced Shock Wave Plasma Spectroscopy**
- **LPS: Laser Plasma Spectroscopy**



LIBS Advantages

- ***Real-time measurements*: online monitoring and quality control of industrial processes**

- ***Noninvasive, nondestructive* technique: valuable samples can be reused, sensitive materials can be analyzed, suitable for in-situ biological analysis**

- ***Remote measurements* can be done from up to 50+ meters distance: can be used in hazardous environments and for space exploration missions on other planets**

- ***Underwater analysis* of chemical composition**

- ***Compact and inexpensive equipment*: can be widely used in industrial environments, perfect for field measurements**

- ***High-spatial resolution*: can obtain 2D chemical profiles of virtually any solid material with 1 μm precision or better**

Continues…

LIBS Advantages (Ctnd.)

- **Non or very *little sample preparation* is required:**
reduced measurement time, greater convenience, less opportunity for sample contamination

- **Samples can be in virtually *any form*: gas, liquid, solids, aerosols**

- **Analysis can be performed with a *very small amount of sample* (nanograms):**
very useful in chemistry for characterization of new chemicals and
in material science for characterization of new composite materials or nanostructures

- **Virtually *any chemical element* can be analyzed,**
such as heavier elements unavailable for X-ray fluorescence

- **Analysis can be done on *extremely hard materials* like ceramics and superconductors;**
these materials are difficult to dissolve or sample to perform other types of analysis

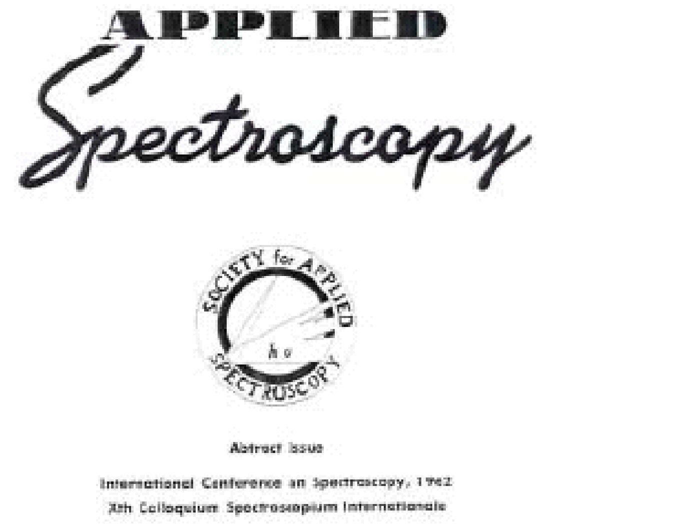
- **In aerosols both *particle size and chemical composition* can be analyzed simultaneously**

Distribution of LIBS papers in the literature

ca. 2250 papers published in the last 5 years

Name of the periodical journal	Number of papers	Percentage
Spectrochimica Acta B	220	9.6%
Applied Spectroscopy	218	9.5%
Journal of Analytical Atomic Spectrometry	126	5.5%
SPIE Proceedings	124	5.4%
Applied Surface Science	106	4.6%
Analytical Chemistry	50	2.2%
Analytical and Bioanalytical Chemistry	48	2.1%
Applied Physics A	42	1.8%
Total	**934**	**40.8%**

Development of LIBS



Optical Microemission Stimulated by a Ruby Maser, F. Brech and L. Cross, 1962

- 1962 to 1980: First experiments
  - Inadequate instrumentation (lasers, detectors)
  - Quantitative measurement difficult
- 1980 to 1990: Evolution in laboratory
  - Lasers and detectors become more reliable
  - Better analytical performances
  - Quantitative analysis demonstrated
- 1990 to 2000: Applications emerge
  - Industrial lasers, intensified detectors and echelle spectrometers enter commercial market
  - Growth in research activity
- 2000 to present: New approaches, commercial instruments and deployment in real scenarios
  - Standoff LIBS
  - Underwater LIBS
  - Instruments in steel production plants

First monograph - 1966

Einführung in die Laser-Mikro-Emissionsspektralanalyse

Horst Moenke, Lieselotte Moenke-Blankenburg

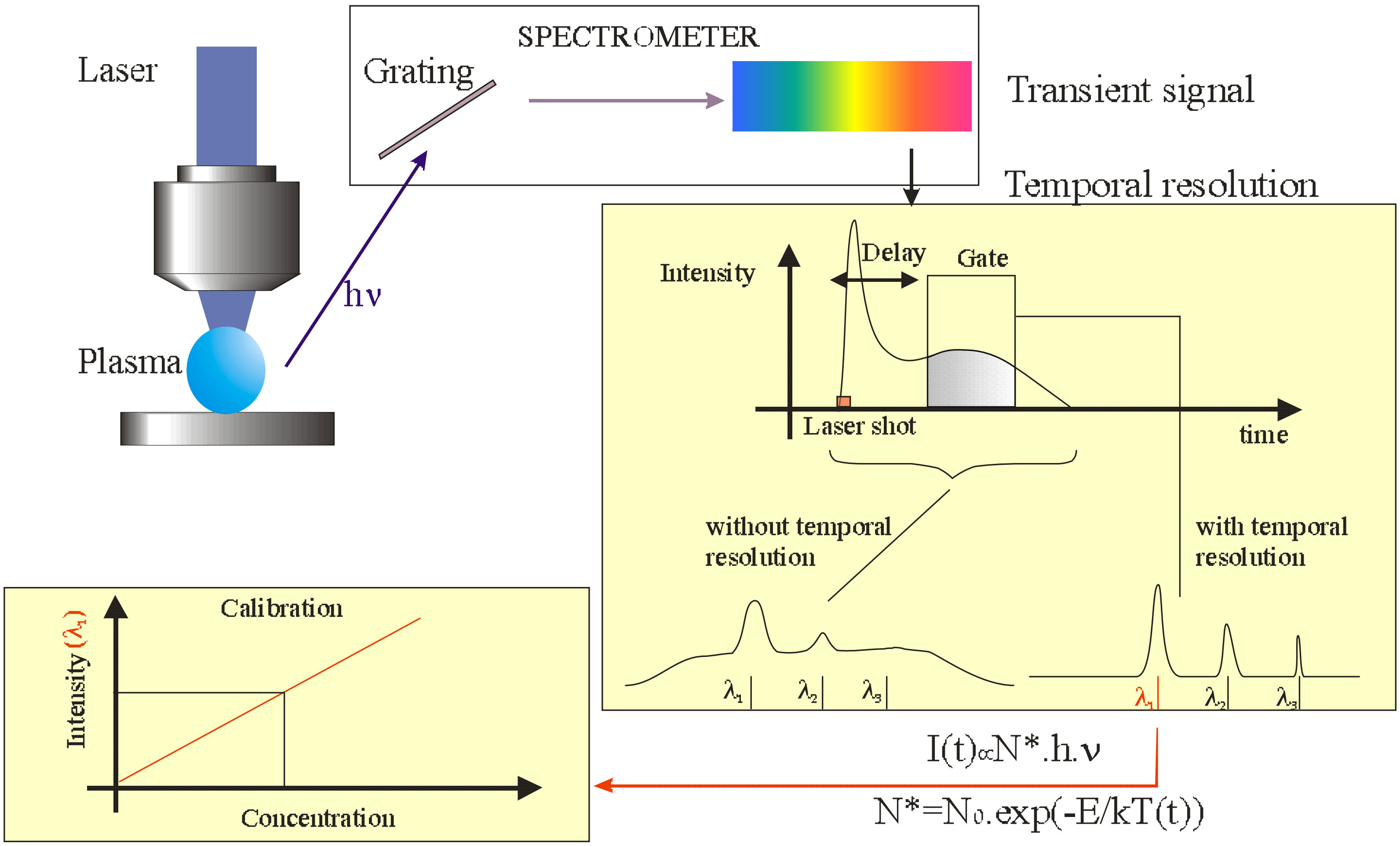
Akademische Verlagsgesellschaft, Geest und Portig, Leipzig 1966 -

182 pages

Second edition Leipzig, 1968.

Fourth edition Laser micro-spectrochemical analysis
London: Hilger, 1973

LIBS Fundamentals at a glance

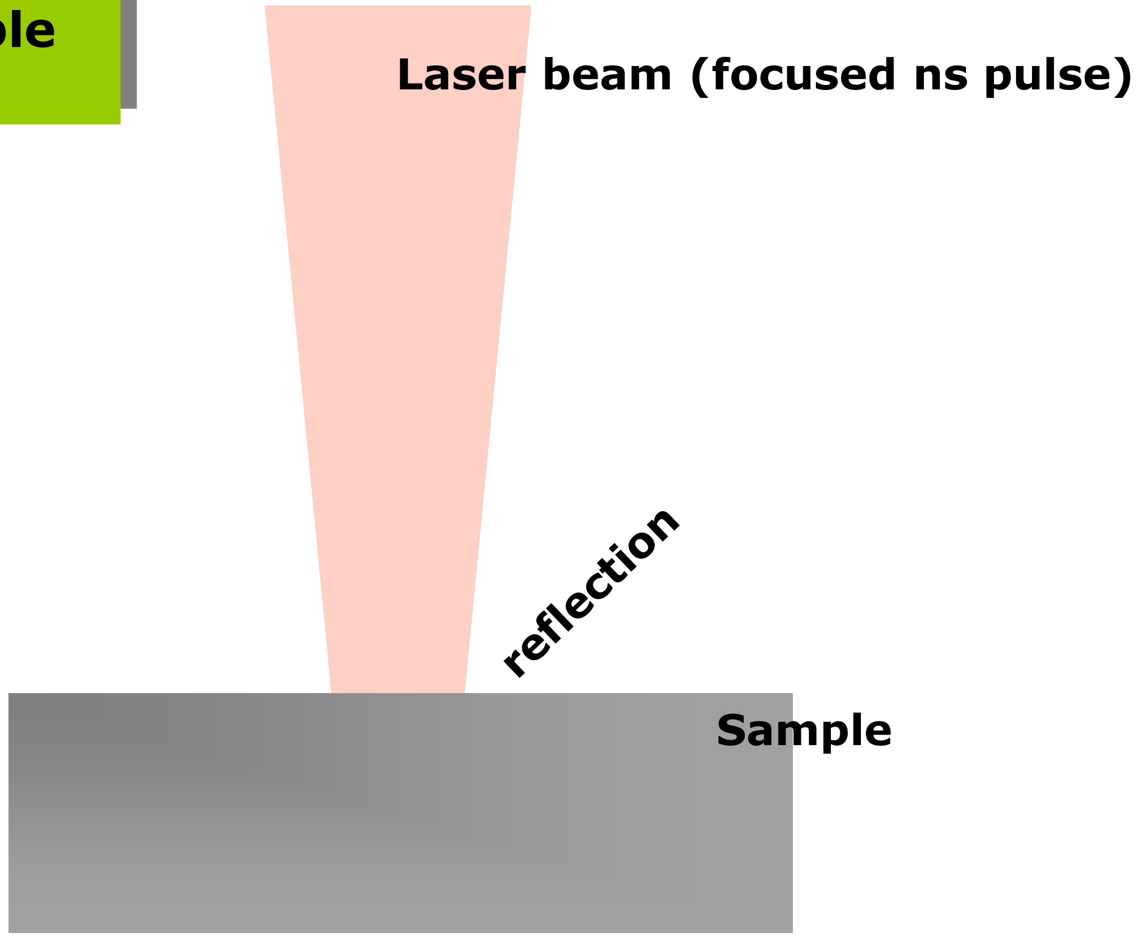


Laser-Induced Breakdown Spectroscopy (LIBS)

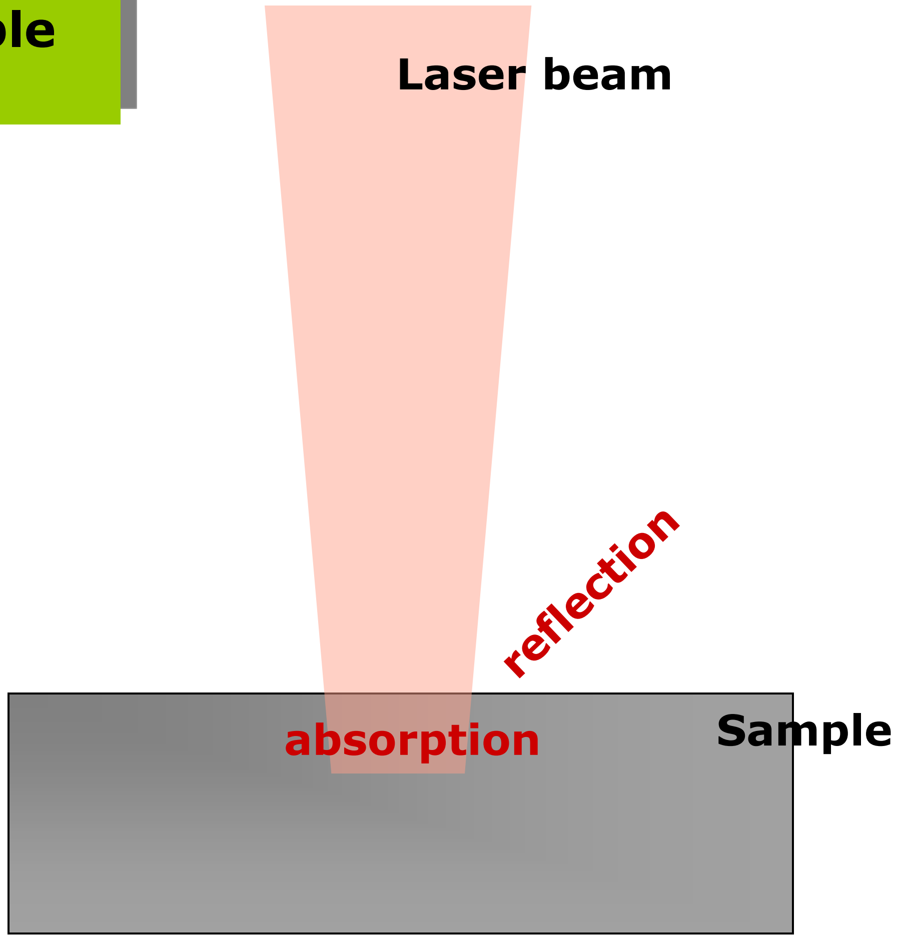
Elements of LIBS

1. Laser-sample interaction
2. Separation of material ⇒ Ablation
3. Plasma formation ⇒ Vapor ionization (breakdown)
4. Plasma spectral analysis ⇒ Atomic Emission spectrometry

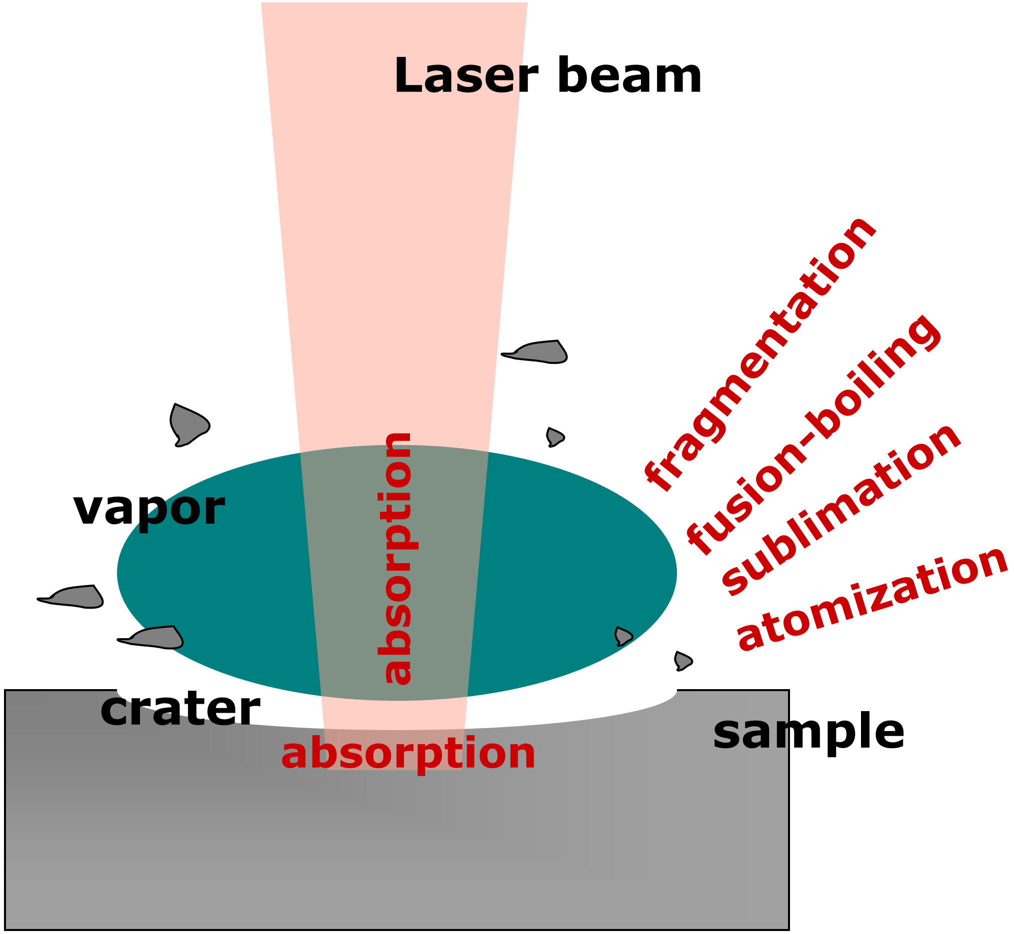
1. Laser-sample interaction



1. Laser-sample interaction

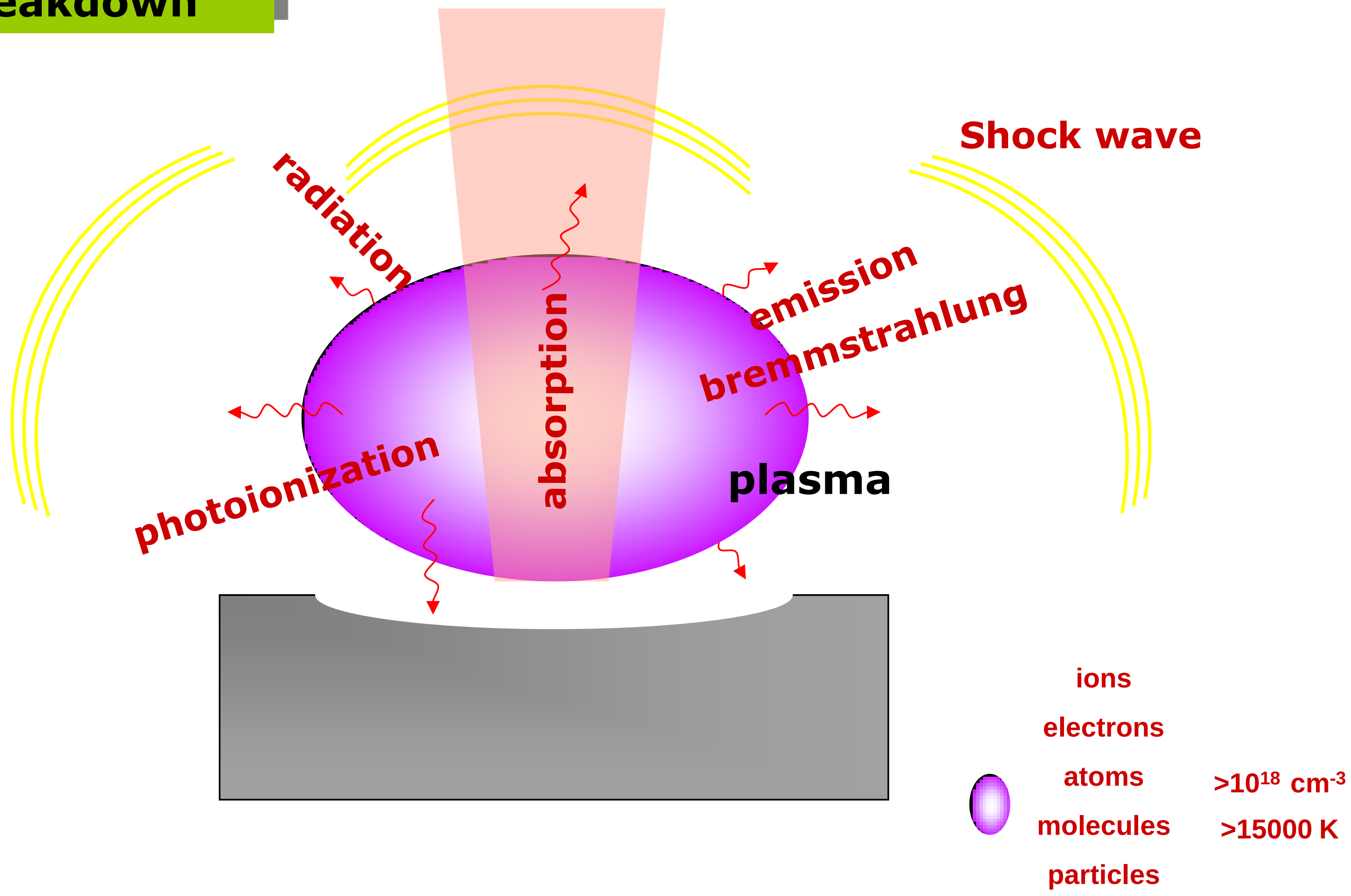


2. Ablation

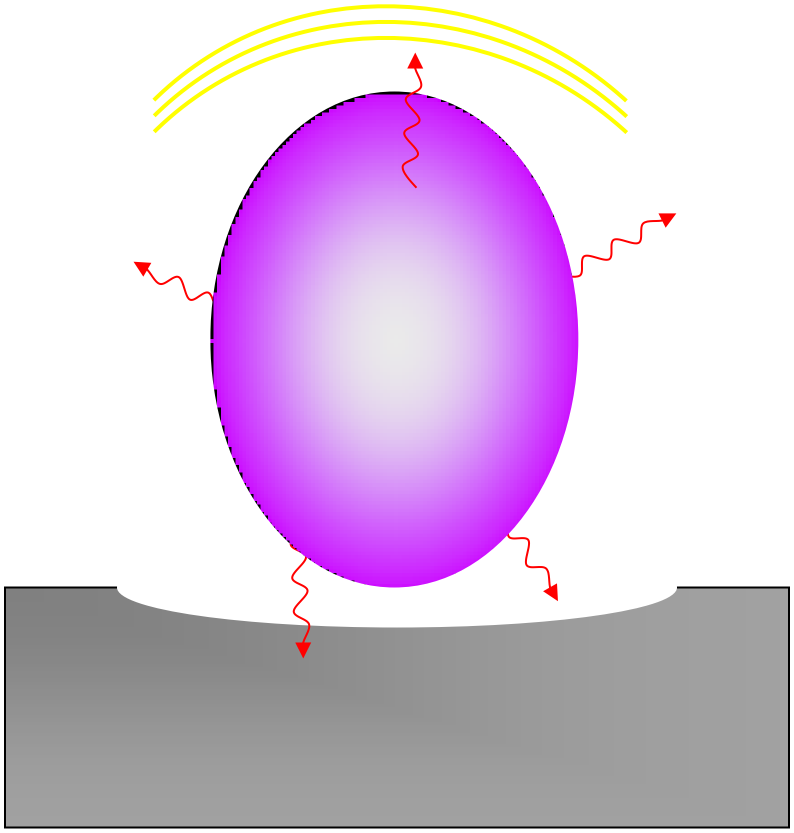


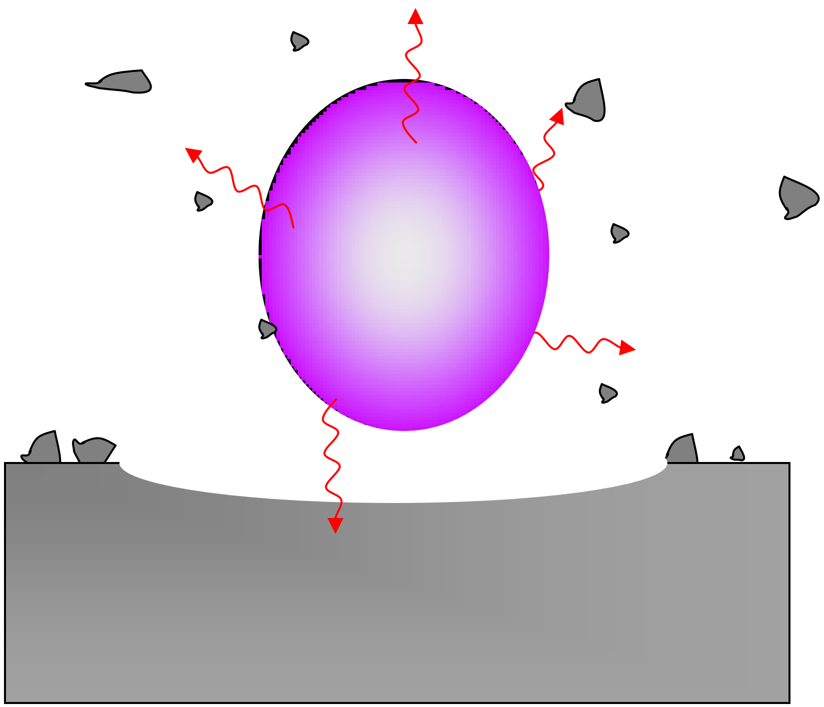
Laser beam
fragmentation
fusion-boiling
sublimation
atomization
vapor
absorption
crater
sample
absorption

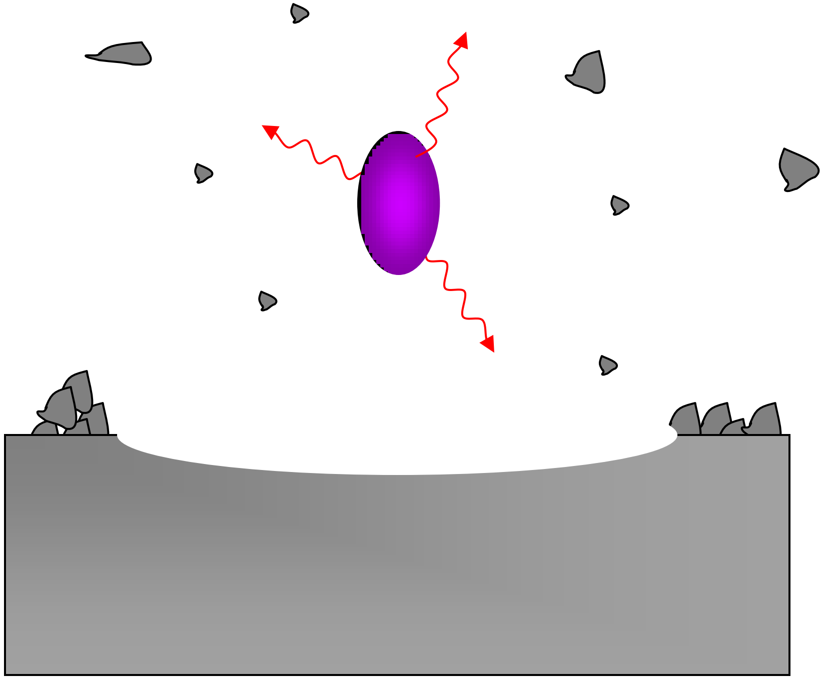
3. Breakdown

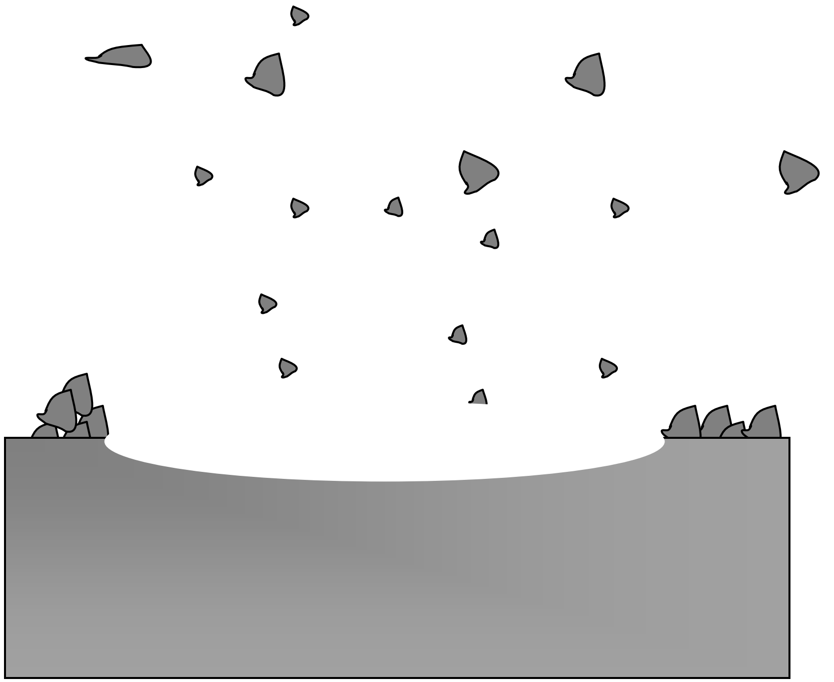


Shock wave
radiation
absorption
emission
bremmstrahlung
photoionization
plasma
ions
electrons
atoms
molecules
particles
>10[18] cm[-3]
>15000 K

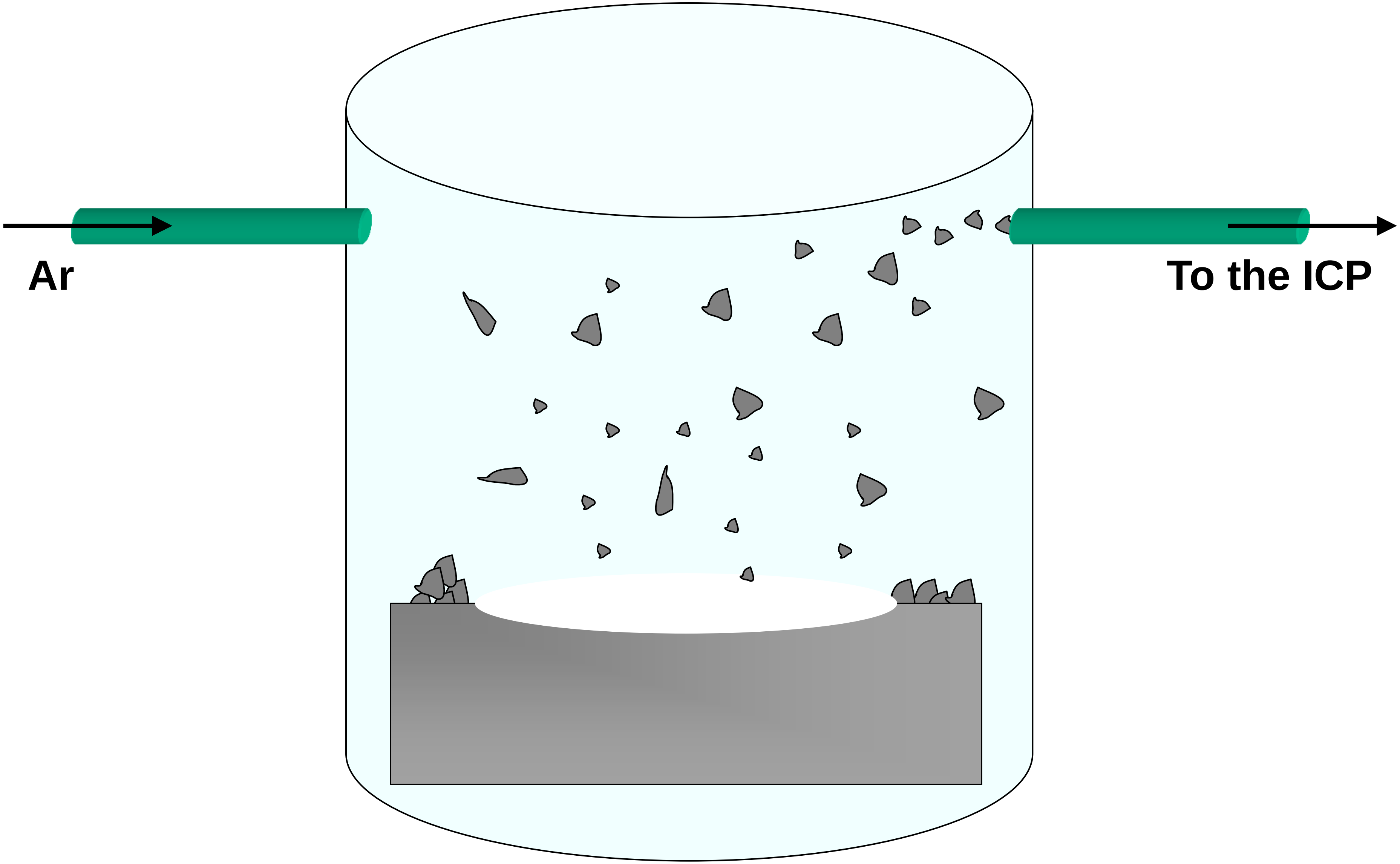




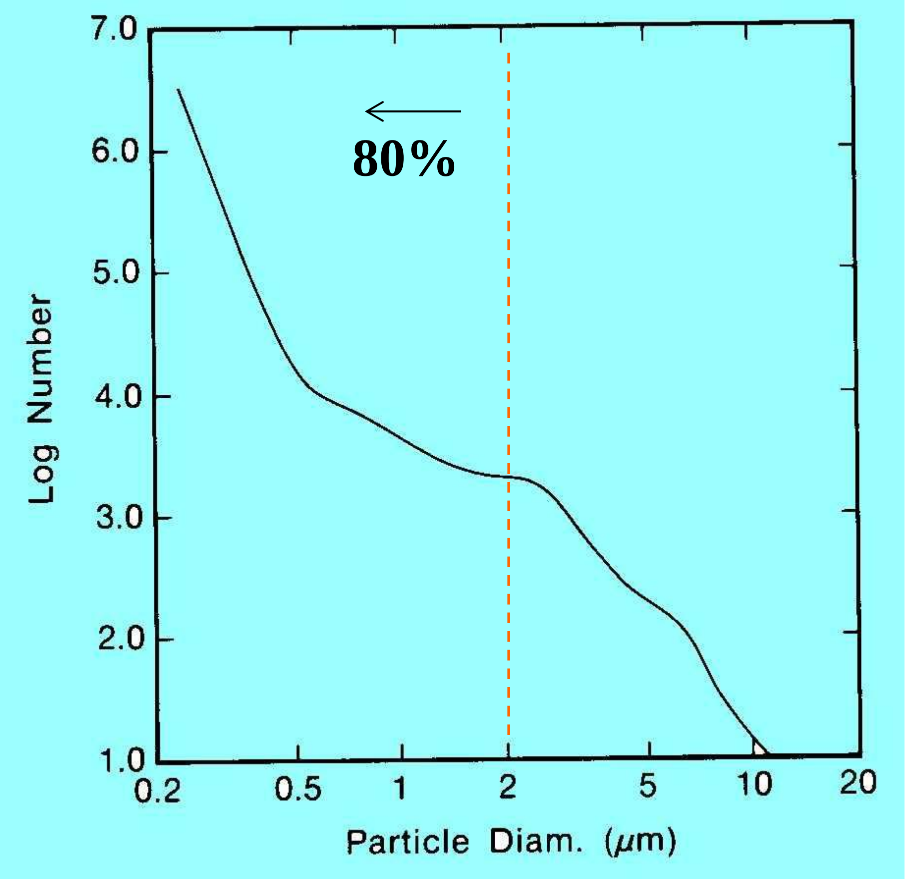




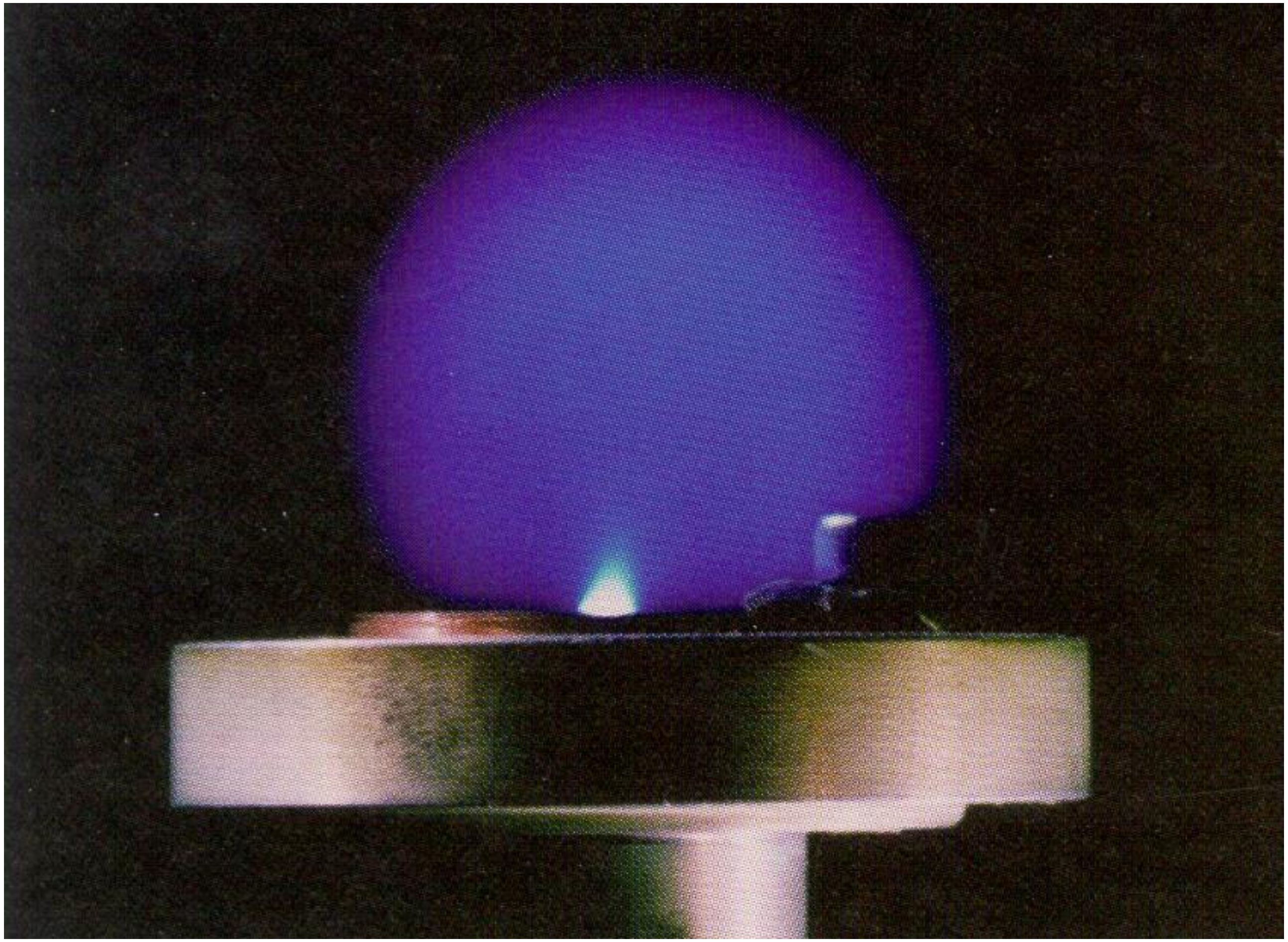
Transport of ablated material to an ICP



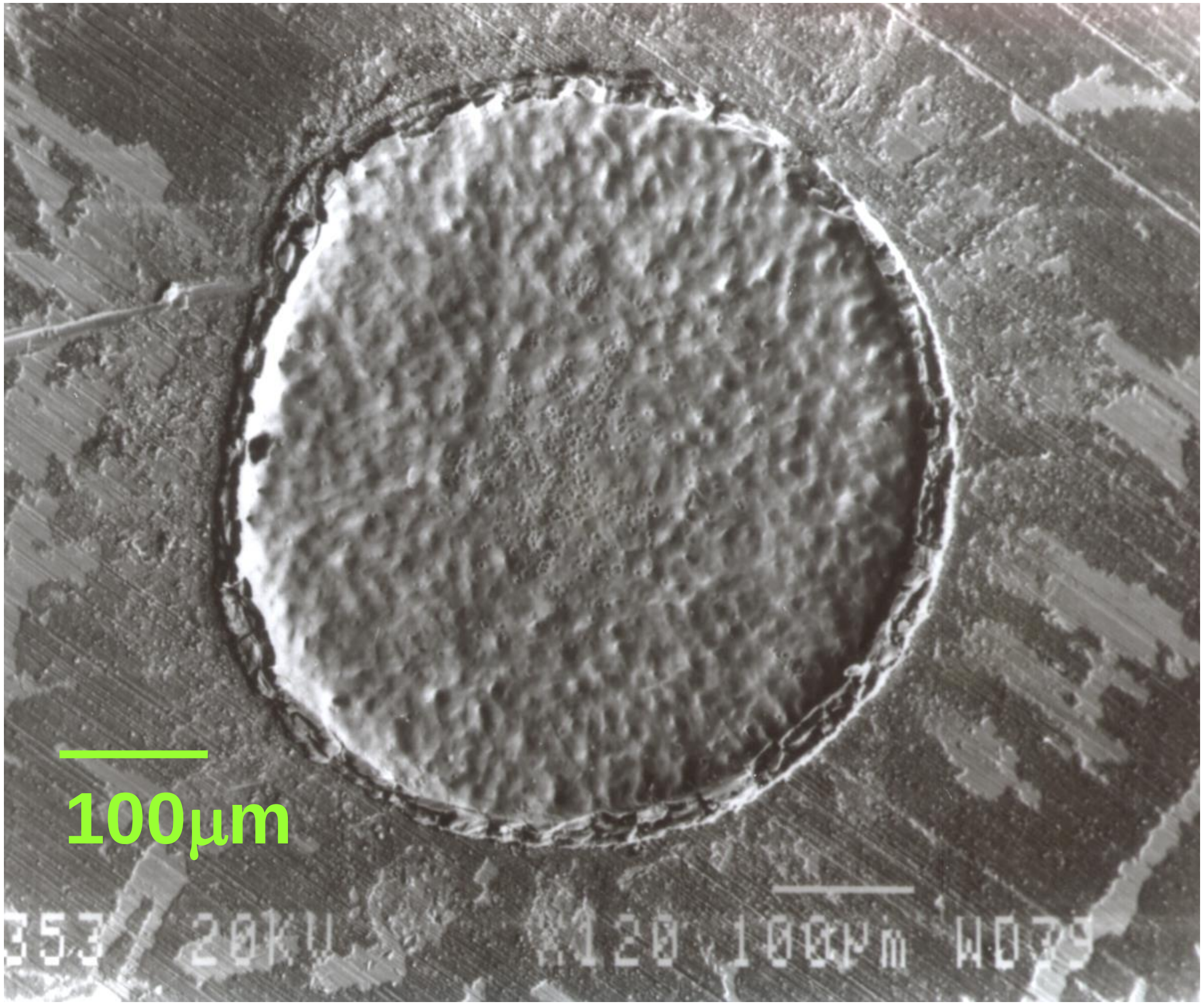
Particle size distribution
Mo
Nd:YAG (1064 nm)



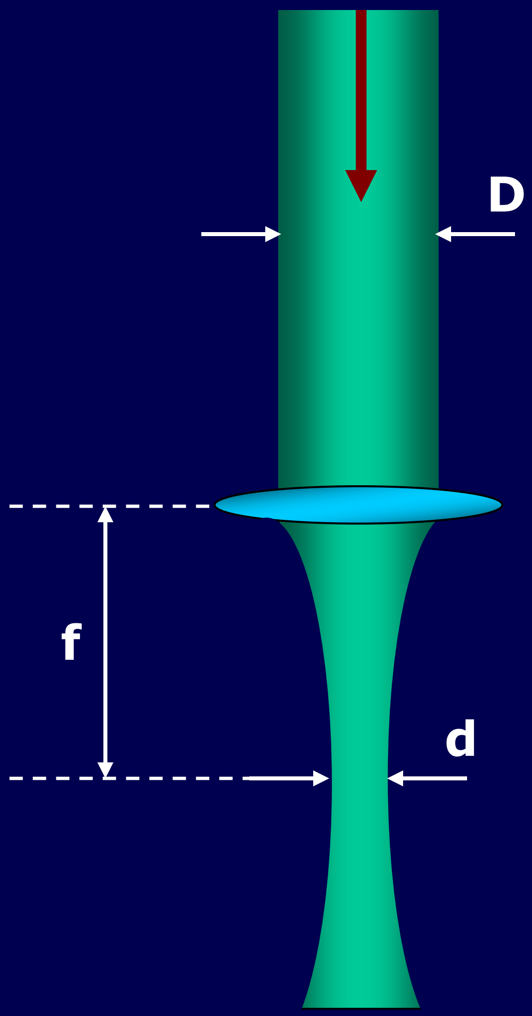
Copper plasma
λ: 248 nm
Irradiance: 3 x 10^9 W cm^{-2}



Crater left on stainless steel
Irradiance 5.7 GW cm^{-2}
150 laser shots



Focusing Gaussian beams



Difraction Limit

$$(d)_{min} = \frac{2{,}44\,\lambda\, f}{D}$$

$$(d)_{crat} = \frac{2{,}44\,\lambda\, f}{D} + \delta$$

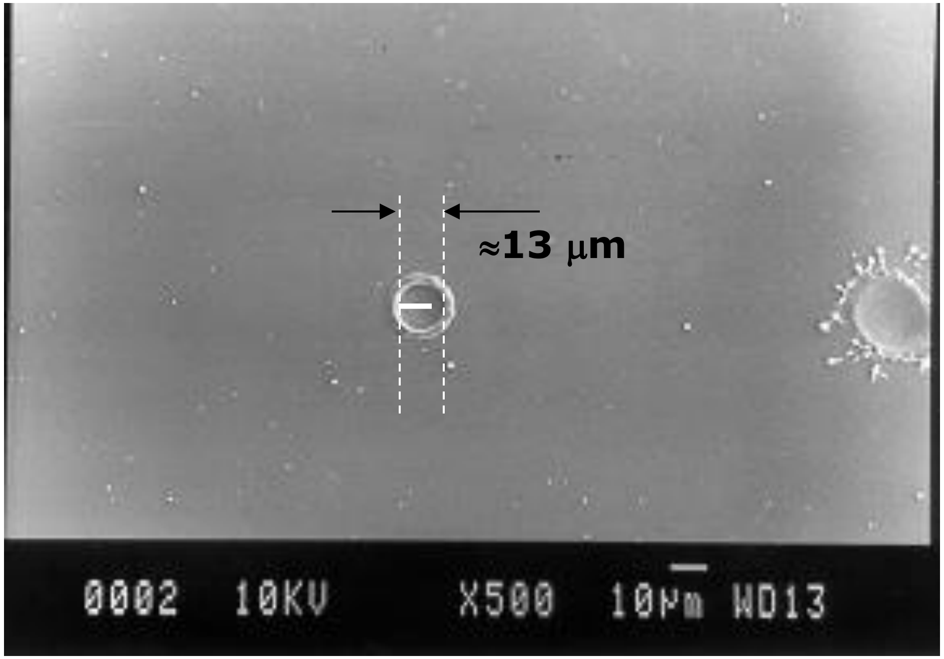
$$\delta = h\,(k, E)$$

k Thermal conductivity

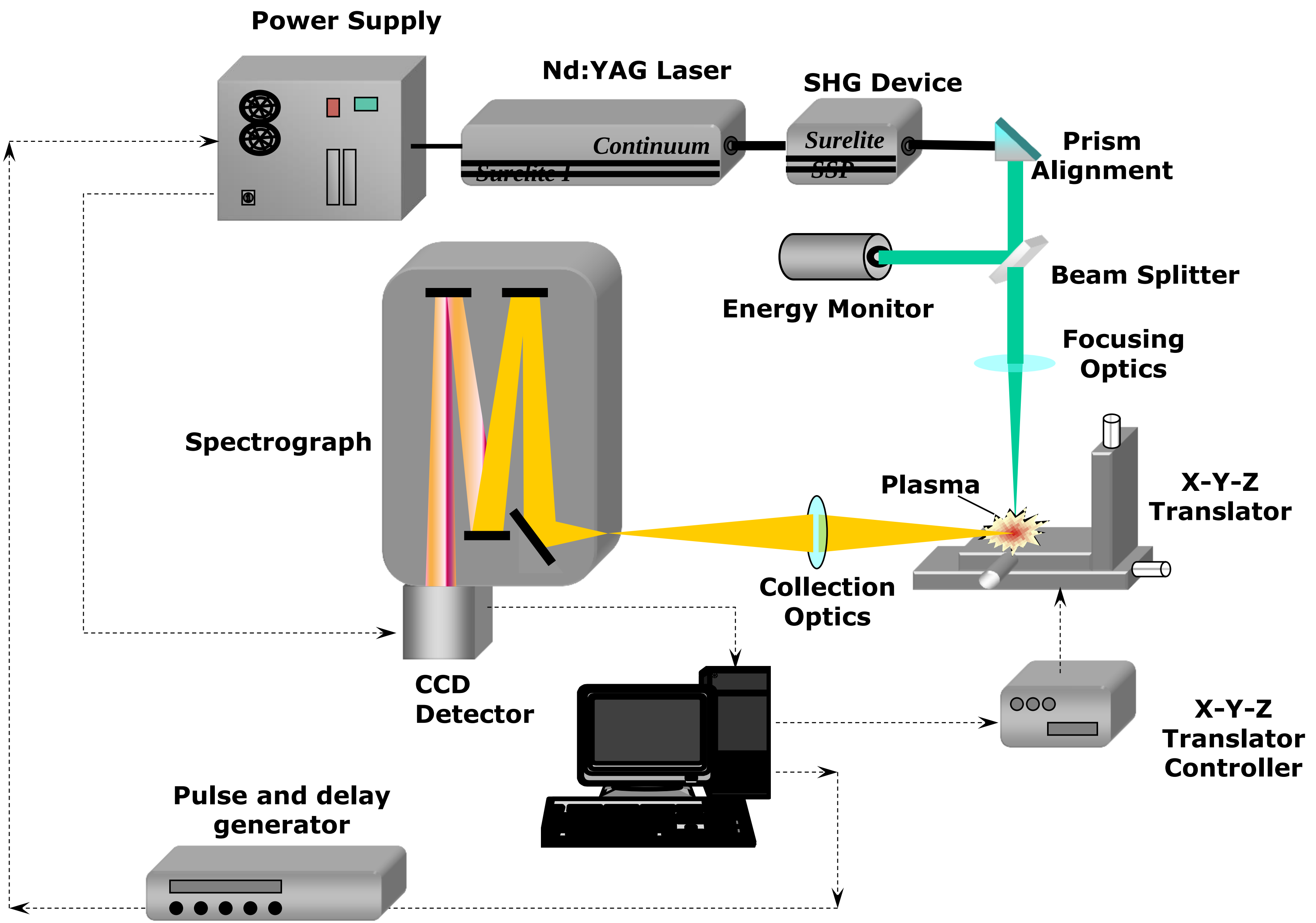
E Pulse energy

Sample: stainless steel (AISI 304)

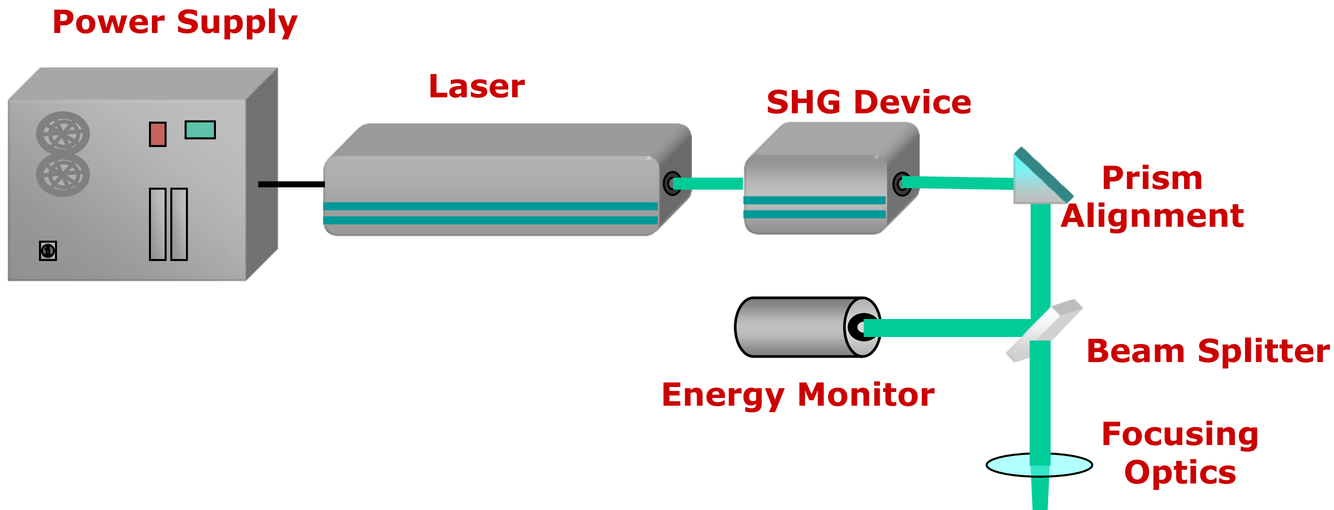
Laser: Nd:YAG, 532 nm; 0,06 mJ pulse^{-1}; 1 pulse



4. Plasma spectral analysis



Laser (nanosecond)



- **Solid state lasers**

Rubí	694 nm
Nd:YAG	1064 nm
	532 nm
	355 nm
	266 nm
	213 nm

- **Gas lasers**

CO_2	10.6 μm
N_2	337.1 nm

- **Excimer lasers**

XeF	351 nm
XeCl	308 nm
KrF	248 nm
KrCl	222 nm
ArF	193 nm
F_2	157 nm

Laser manufacturers
- Spectra-Physics
- Coherent
- Quantel
- LambdaPhysik

Energy/pulse: 10 μJ-500mJ
Nd:YAG and its harmonics 2w, 3w, 4w are used the most in LIBS applications.

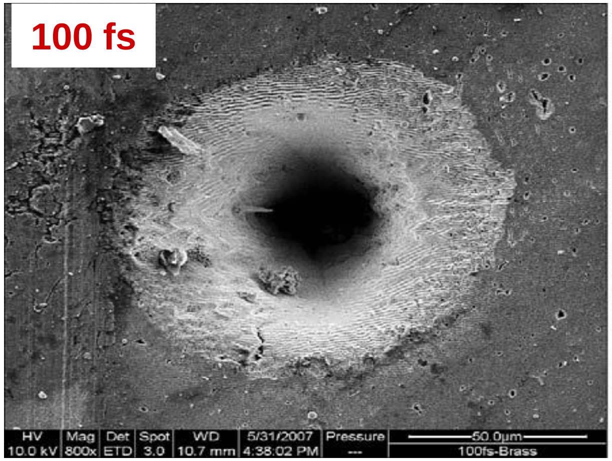
Cost: €30-50K

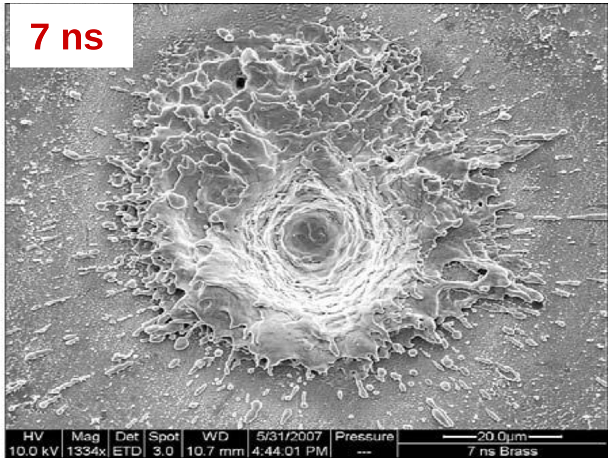
LIBS using fs lasers

- Better understanding of laser-matter interaction
- Improved ablation efficiency
- Background free spectra
- Free of plasma shielding effects
- Less fractionation effects
- Better lateral resolution (less heat affected zone)
- Limited depth resolution

  as with ns pulses (conical craters)
- Longer distances in standoff analysis

Craters in brass
in air at atmospheric pressure*





Spectrometers and Detectors

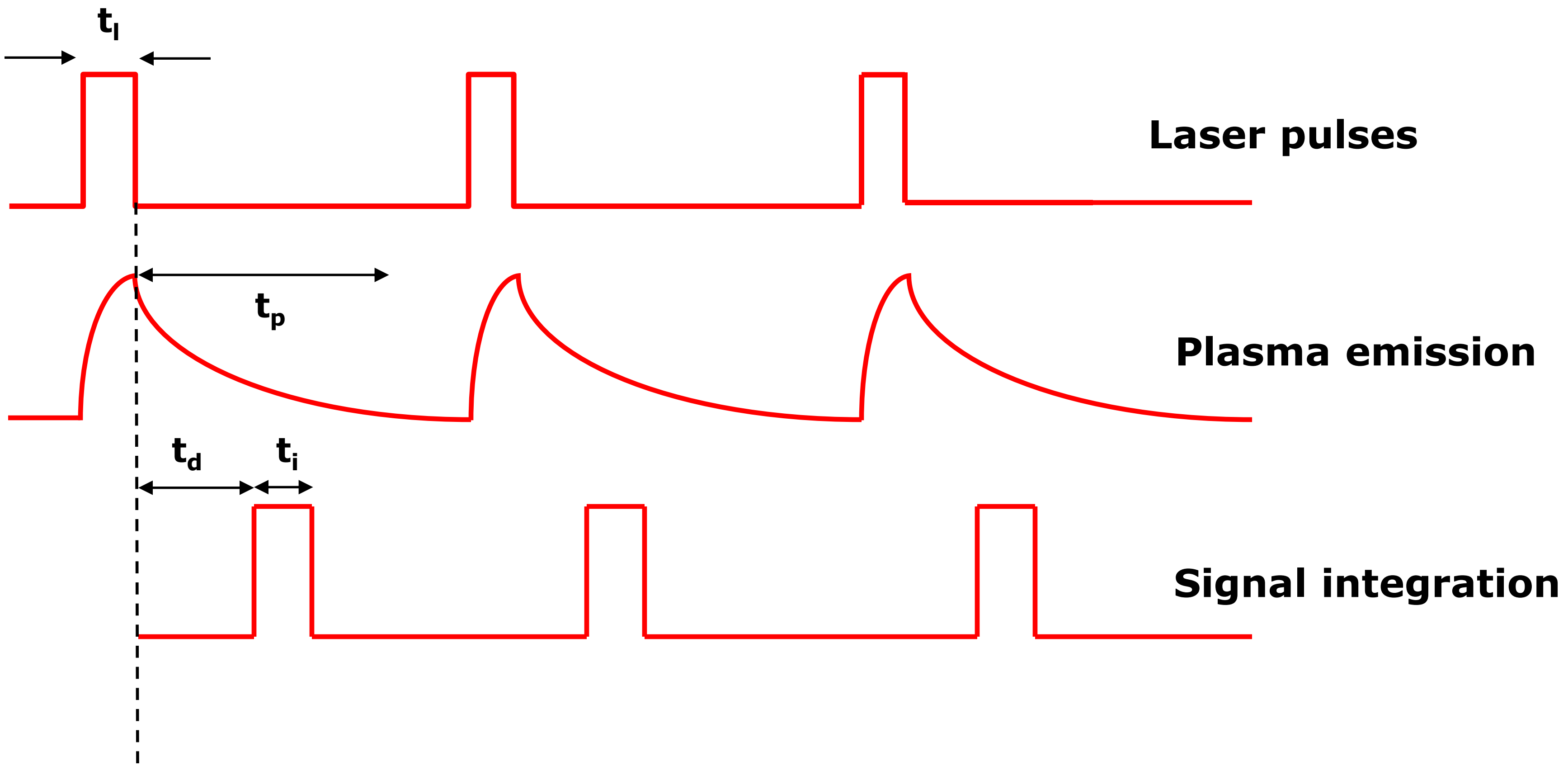
System	Spectrometer	Detector
A	Czerny-Turner 	i-PDA 
B	Czerny-Turner 	i-CCD 
C	Echelle 	i-CCD 
D	Compact Czerny-Turner 	Integrated CCD

Spectrometers and Detectors

Important parameters to consider when comparing LIBS instruments

- Sample, elements
- Spectral region considered and spectral bandwidth
- Plasma-to-spectrometer transfer optics
- Spectrometer type and luminosity
- Grating choice, spectrometer focal length
- Quantum efficiency of detector
- Photocathode material, pixel size
- MCP gain in intensified CCDs

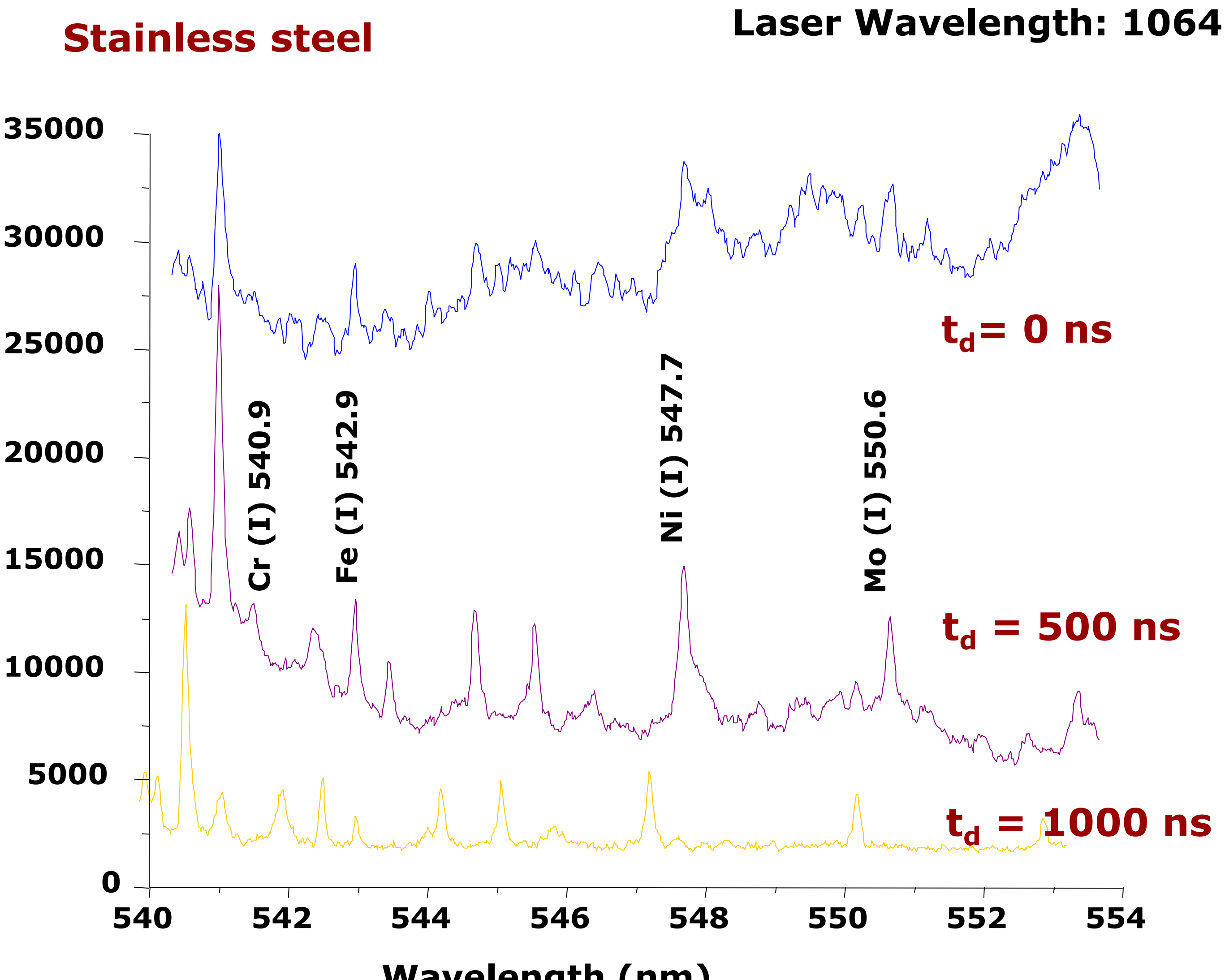
Time resolved LIBS



t_l : Temporal width of laser pulse
t_p : Plasma duration
t_d : Delay
t_i : Integration time

LIBS spectra

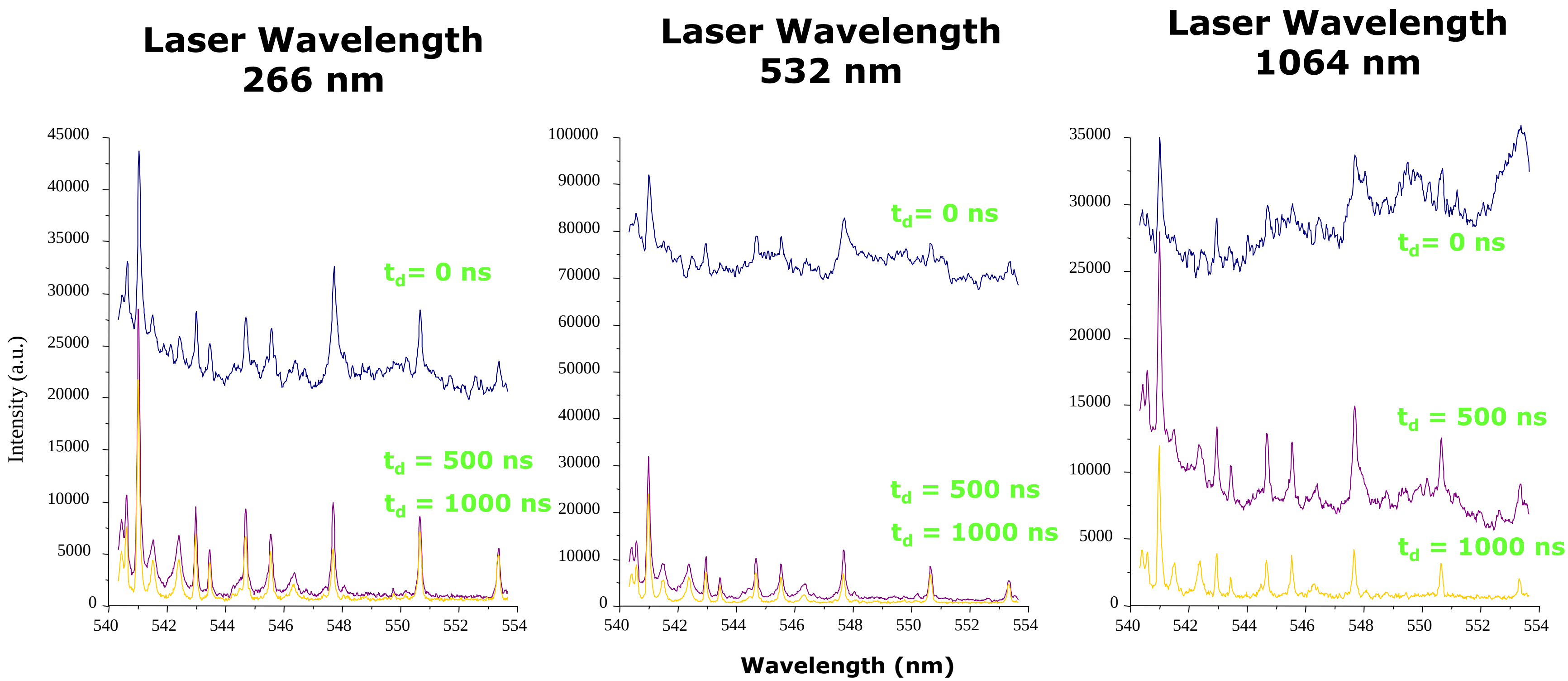
Stainless steel



* 25 laser shots
* Integration time: 500 ns

- Mostly continuum emission at 0 ns delay
- Continuum emission decreases with delay time
- The longer the delay, the narrower is the peak width
- Characteristics of emission related to plasma properties

Temporal behaviour of LIB Spectra

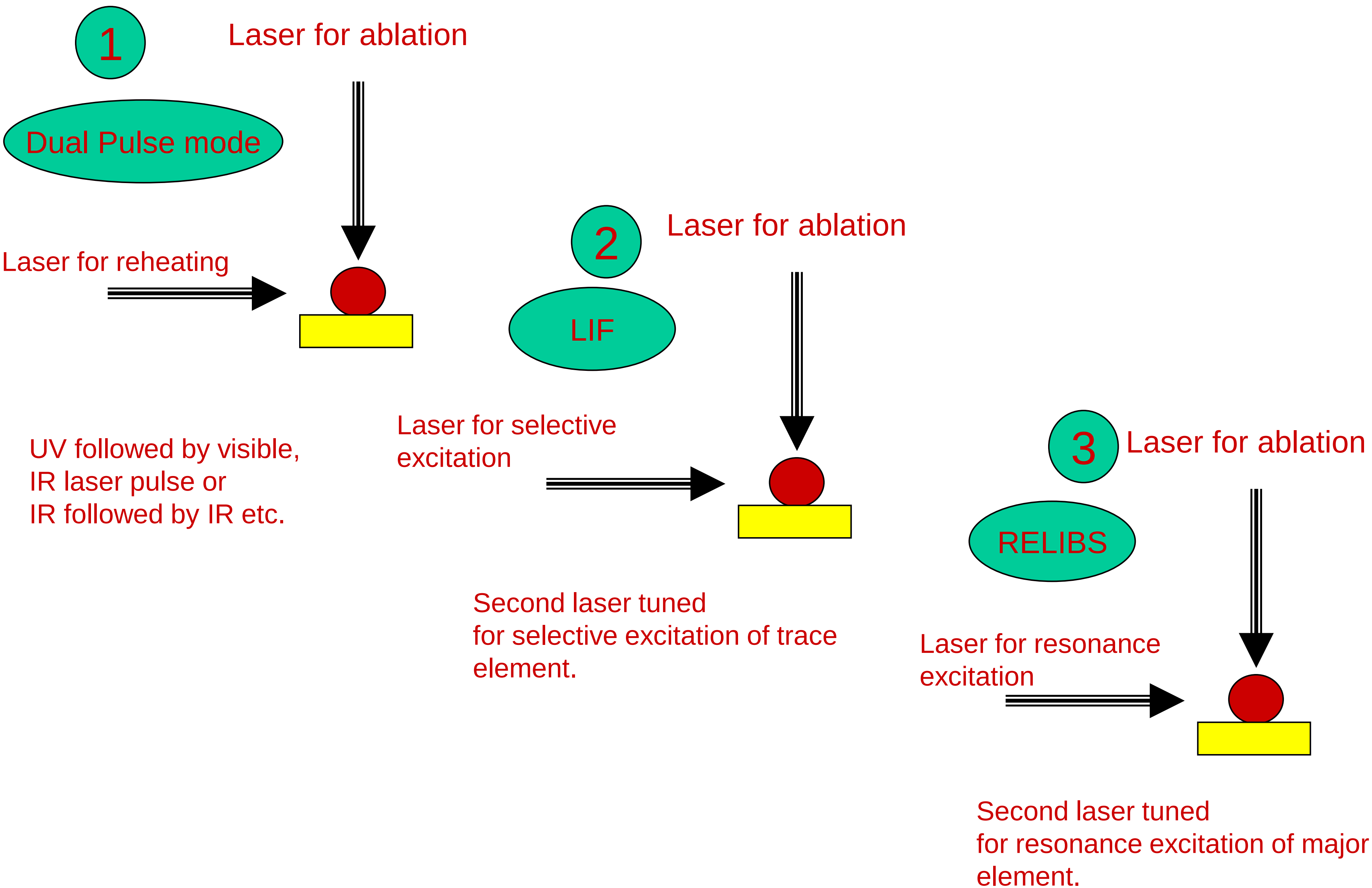


* 25 laser shots

* Integration time: 500 ns

* Linear reciprocal dispersion : 2.5 nm mm^{-1}

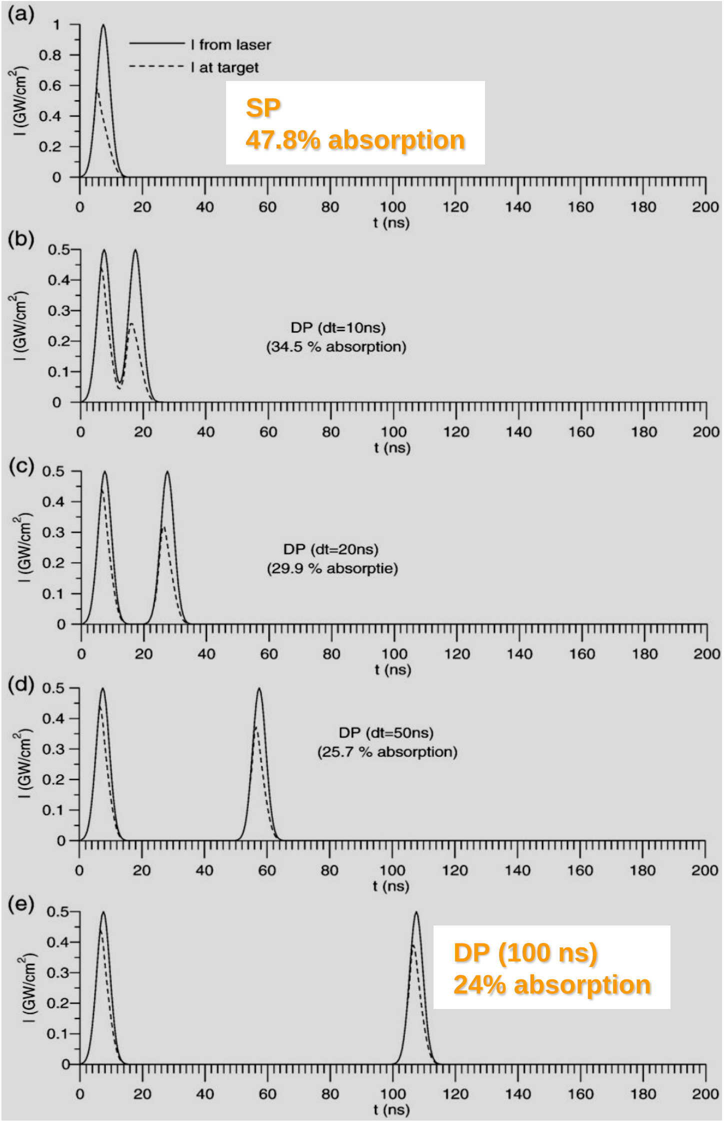
Approaches to enhance the LIBS sensitivity: Double-pulse LIBS



Dual Pulse LIBS

DP LIBS results in increased-

- **Plasma temperature**
- **Ion yield**
- **Plasma volume**
- **Ablated mass rate (in collinear mode)**
- **Line intensity**
  (larger enhancement for ionic than for atomic lines)
- **Detection power**
- **Molten phase lasts longer**
- **Reduced plasma shielding**



Modeling study in collinear-mode DP LIBS
A. Bogaerts, Z. Chen, D. Autrique, Spectrochim. Acta B, 63(2008)746

Selected limits of detection

Single pulse vs. dual pulse LIBS

		LOD (ppm)	
Element	Sample	Single pulse	Dual pulse
Al	Aqueous solution	18	20
C	Steel	80	7
Ca	Aqueous solution	0.013 – 0.6	0.04 – 0.8
Cr	Aqueous solution	0.04 – 300	1.04
	Steel	6– 10	7
K	Aqueous solution	4	1.2
Li	Aqueous solution	0.009	0.006
Mg	Aqueous solution	1–3	0.23
Mn	Steel	113	9
Na	Aqueous solution	0.007 – 2	0.0001 – 0.014
Ni	Steel	80	6
S	Steel	70	8
Si	Steel	80	11

Components and phenomena affecting LIBS analysis

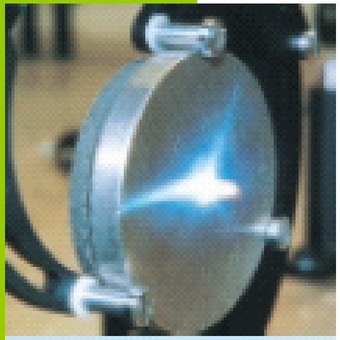
- **Sample** → Reflectivity, heat capacity, melting and boiling point, thermal conductivity, surface finish, etc.
- **Laser** → Pulse energy, duration, spot size, wavelength
- **Plasma** → Surrounding atmosphere (pressure, nature)
- **Spectrometer** → Resolution, spectral window…
- **Detector** → Resolution, timing, SNR…

LIBS analysis capabilities

A large range of matrices can be studied by LIBS

SOLIDS

- Metals
- Ceramics
- Semiconductors
- Polymers
- Pharmaceuticals
- Teeth
- Soils
- Minerals
- Bacteria on agar substrate
- Metals immersed in water
- Wood, paper
- Explosives



Laser spark on a solid surface

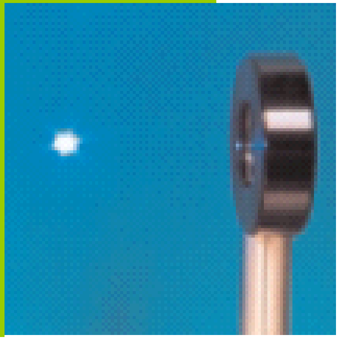
LIQUIDS

- Molten metals, salts and glass
- Industrial effluents
- Process liquids
- Pharmaceutical preparations
- Biological fluids
- Water (Environment)
- Colloids

Laser spark on a liquid surface

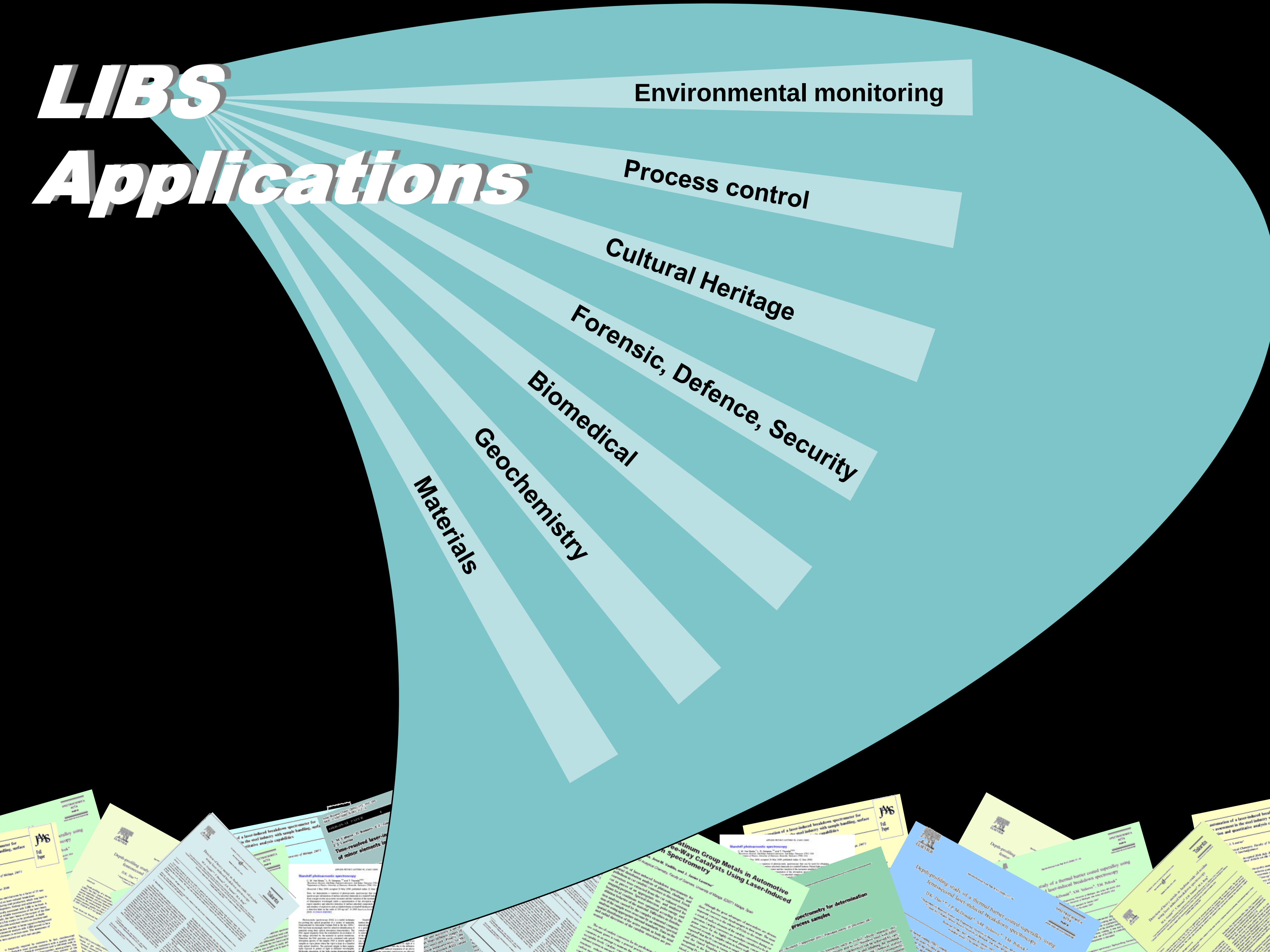
GASES

- Industrial exhaust streams
- Combustion environments
- Aerosols in ambient air
- Proof-of-concept for detection of chemical warfare agents



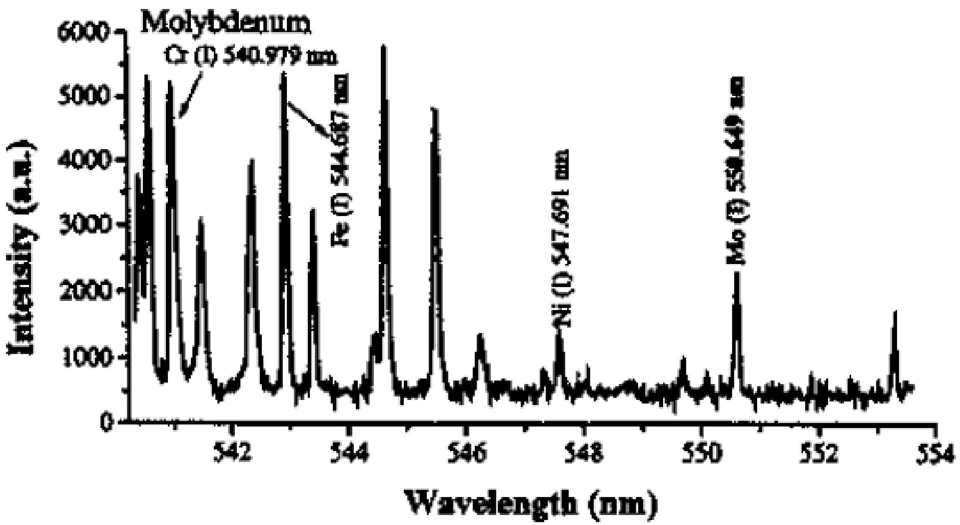
Laser spark in a gas

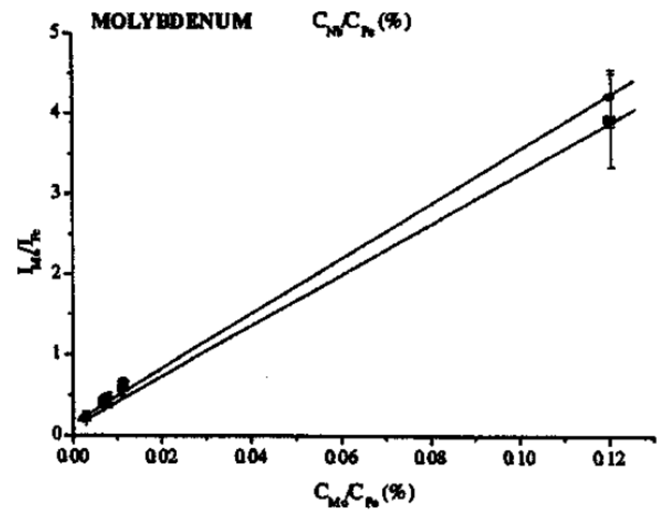
LIBS Applications

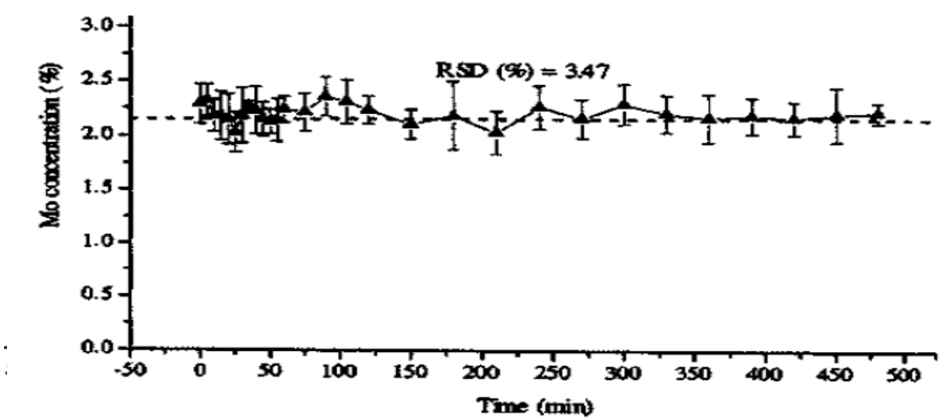


LIBS for bulk analysis

LIBS analysis of AISI 316 stainless steel







LIBS for bulk analysis

Effect of laser wavelength on precision and detection power

Analysis of AISI 304 stainless steel minor elements

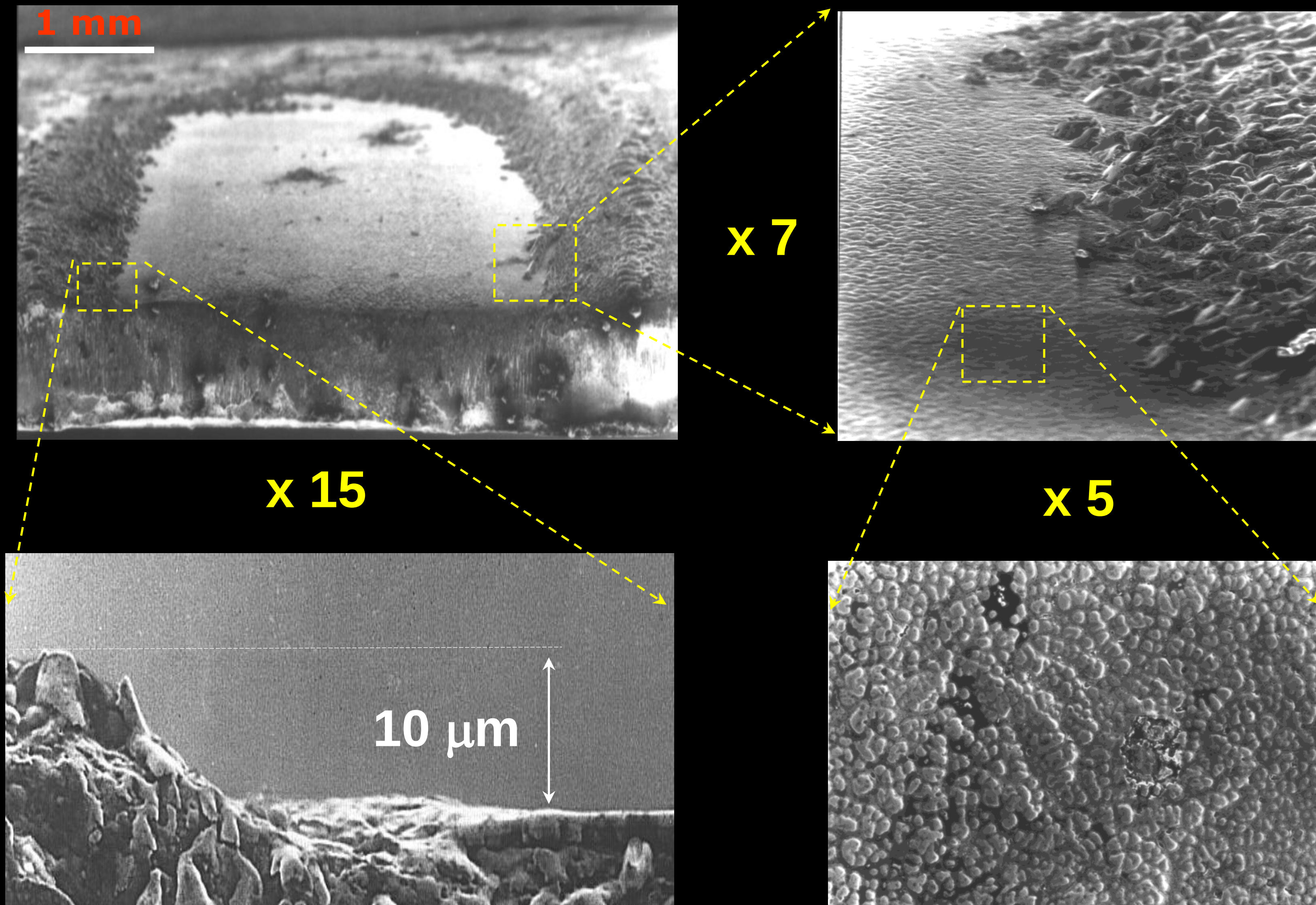
Table 4 Analytical figures of merit of the LIPS method for the analysis of AISI 304 stainless steel using internal standard. The data were obtained by accumulating ten laser shots and averaging fifteen replicate measurements each on a fresh sample position

Element	Wavelength (nm)	Breakdown at 266 nm			Breakdown at 532 nm		
		RSD_b[a] (%)	S/B[b]	C_{LOD}[c] (μg g^{-1})	RSD_b[a] (%)	S/B[b]	C_{LOD}[c] (μg g^{-1})
Si	288.157	2.6	5.8	78	2.0	4.6	77
Nb	405.894	2.8	6.6	54	2.5	5.4	56
Ti	334.900	3.1	7.1	24	3.5	7.1	26
Mo	550.649	2.5	7.7	61	2	7.9	144

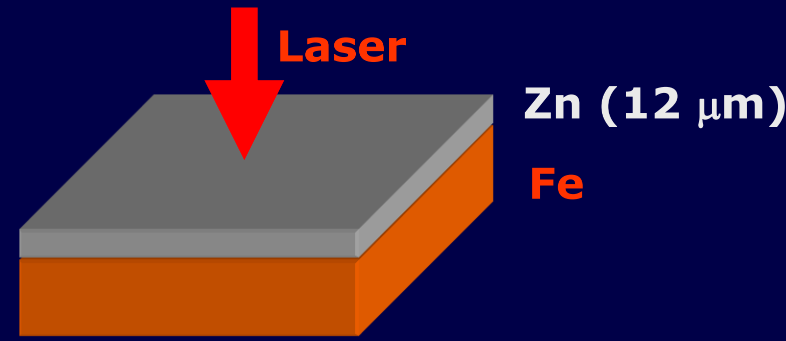
[a]Precision expressed as RSD (%) of the background for 15 replicate measurements
[b]Signal-to-background ratio for the concentration used in the C_{LOD}
[c]Limit of detection calculated from the equation: $C_{LOD}=(3\times C\times RSD_b)/S/B$ [31]

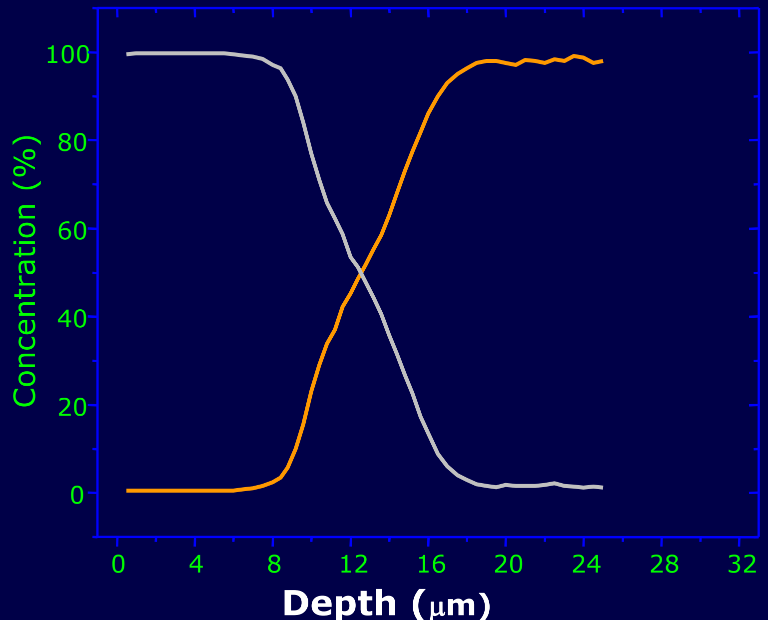
Depth profiling

Zn-coated steel; 4000 pulses XeCl (308 nm); 180 mJ pulse^{-1}; 1.98 J cm^{-2}



Zn-coated steel; 4000 pulses XeCl (308 nm); 180 mJ pulse^{-1}; 1,98 J cm^{-2}

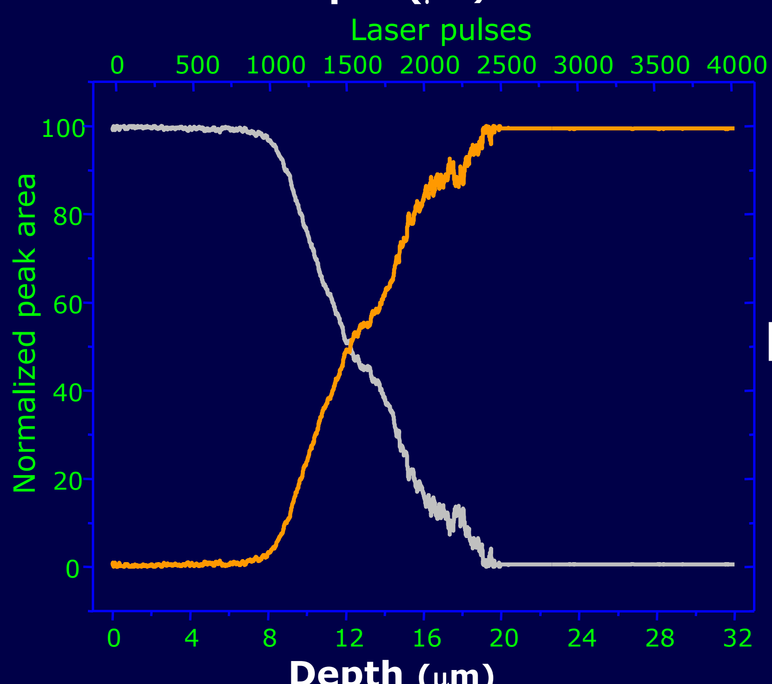




GD-OES

Zn (334.50 nm)

Fe (404.58 nm)



LIBS

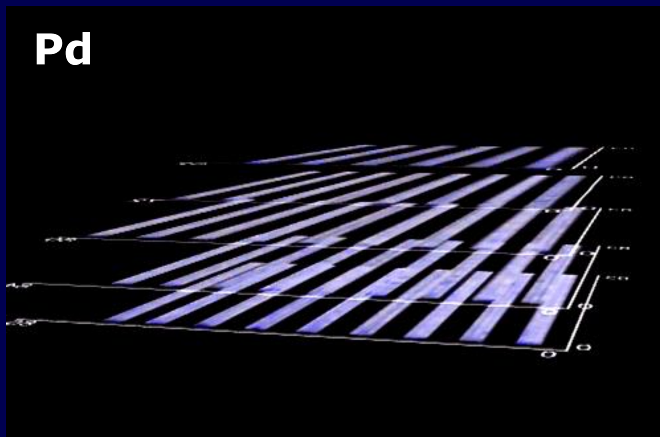
Ablation rate 2.5 nm pulse^{-1}

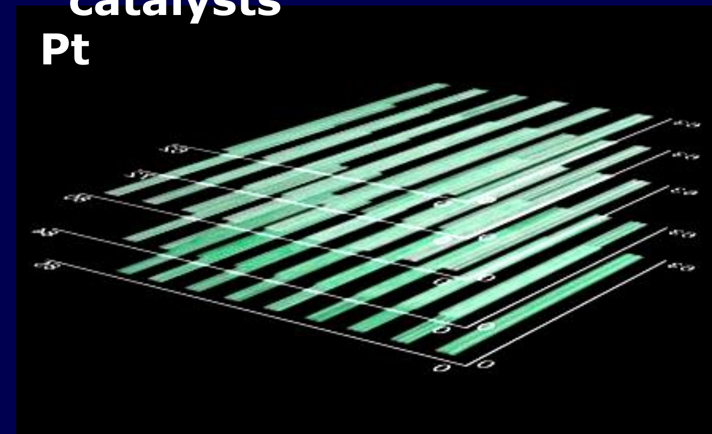
↓

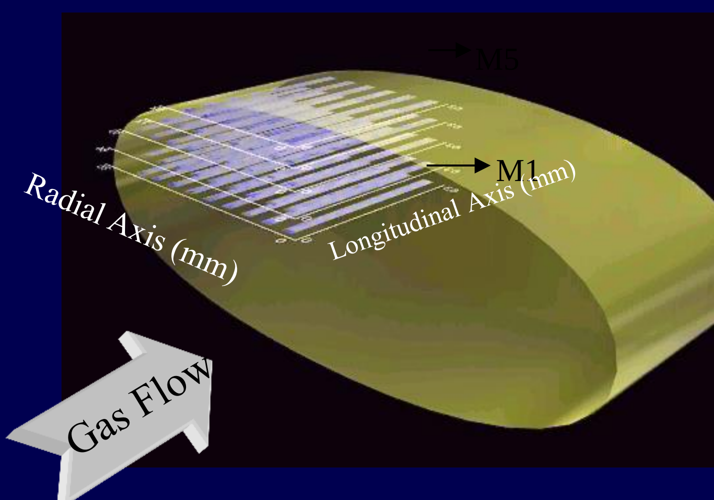
ng per pulse

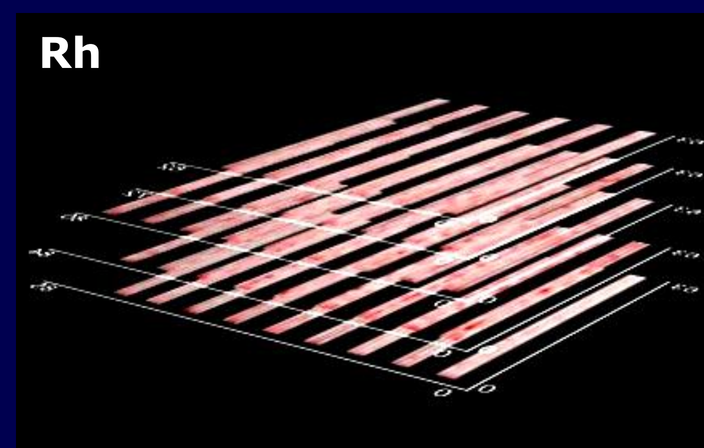
Chemical Imaging

3D-distribution of platinum group metals in automobile catalysts

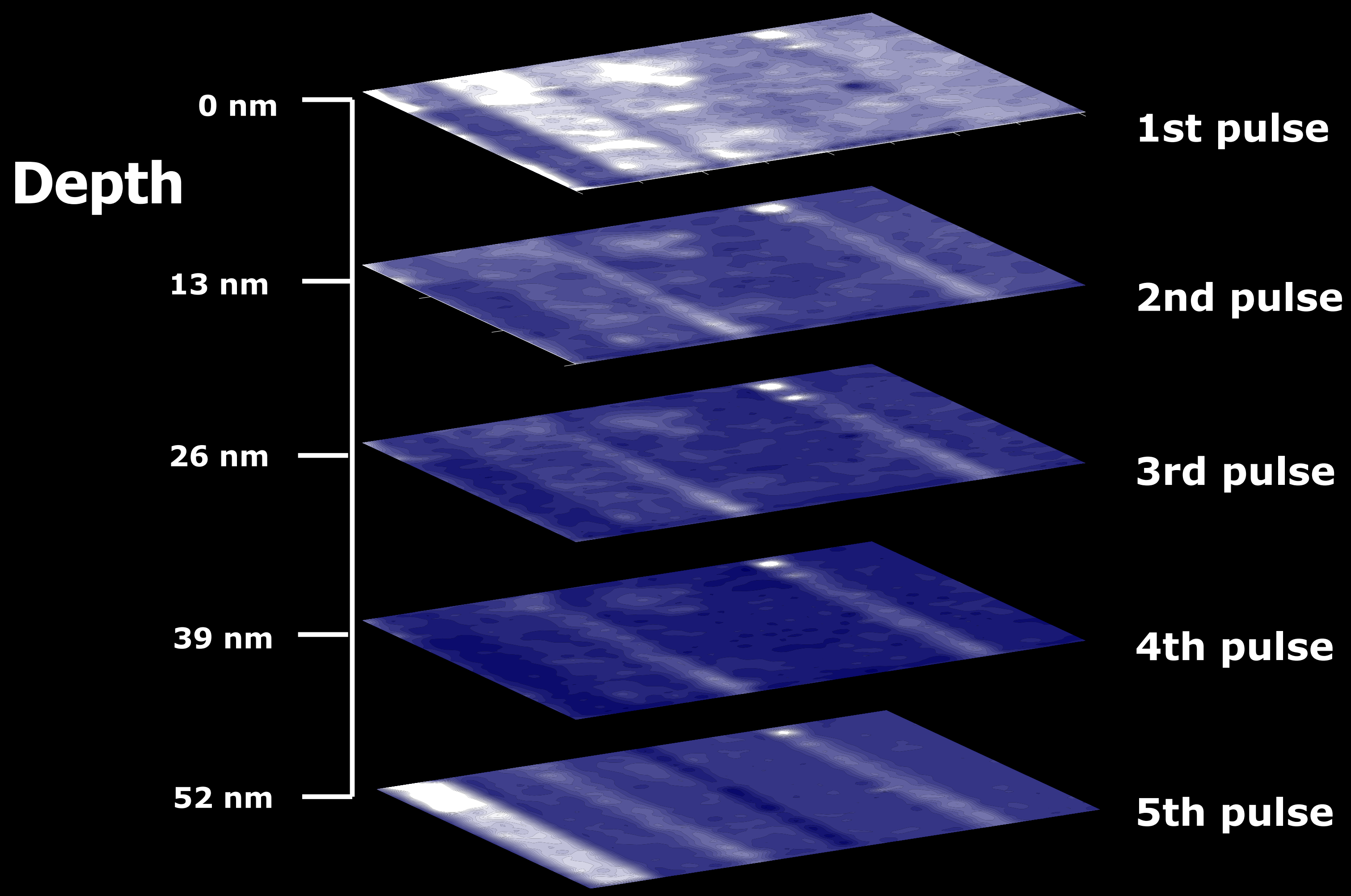




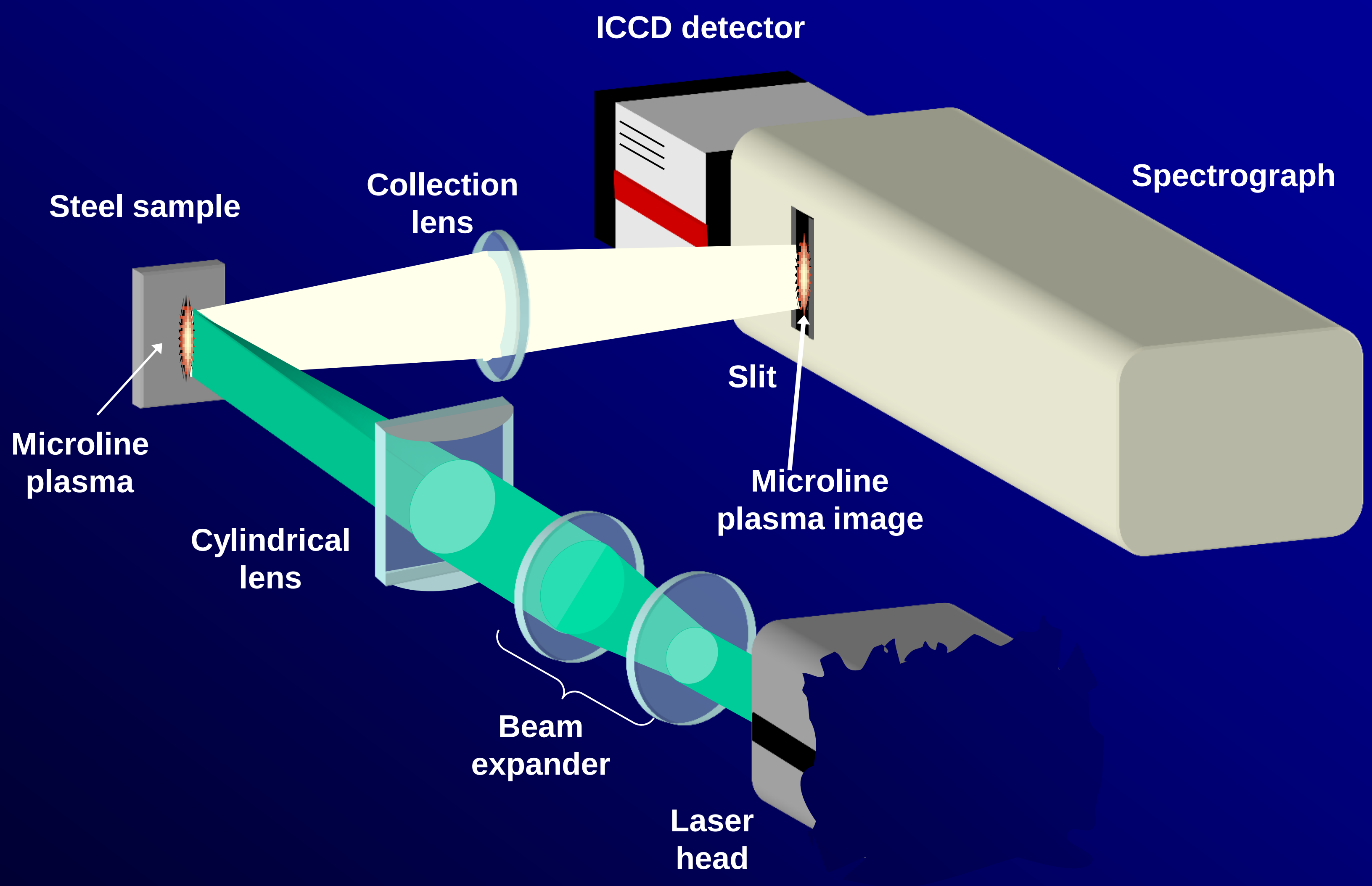




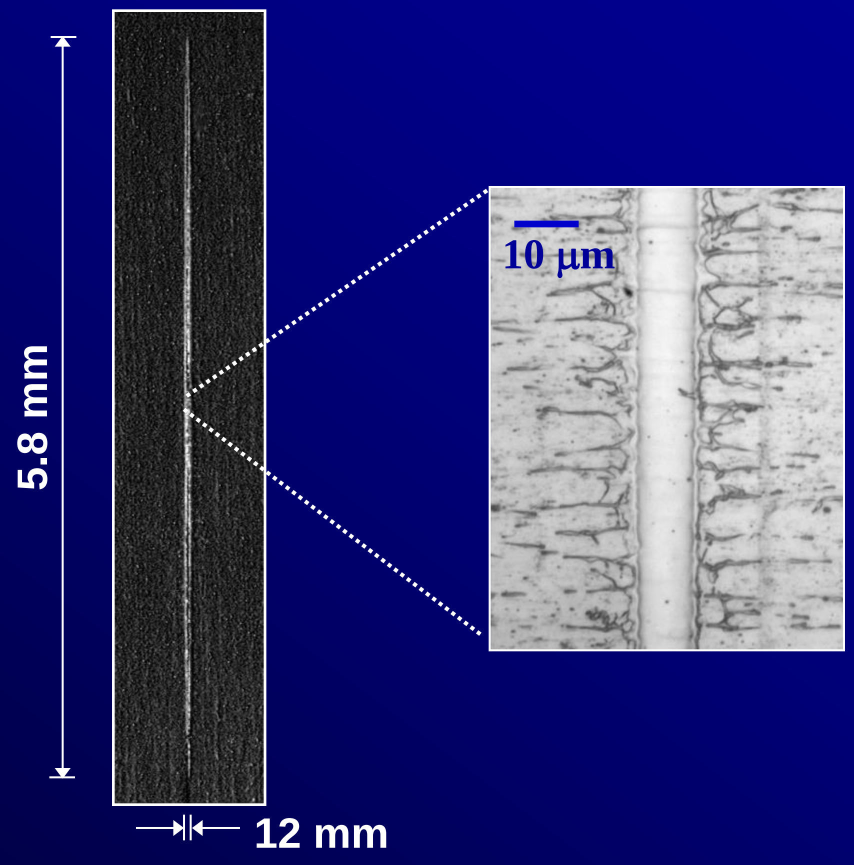
LIBS tomography: carbon impurities on silicon



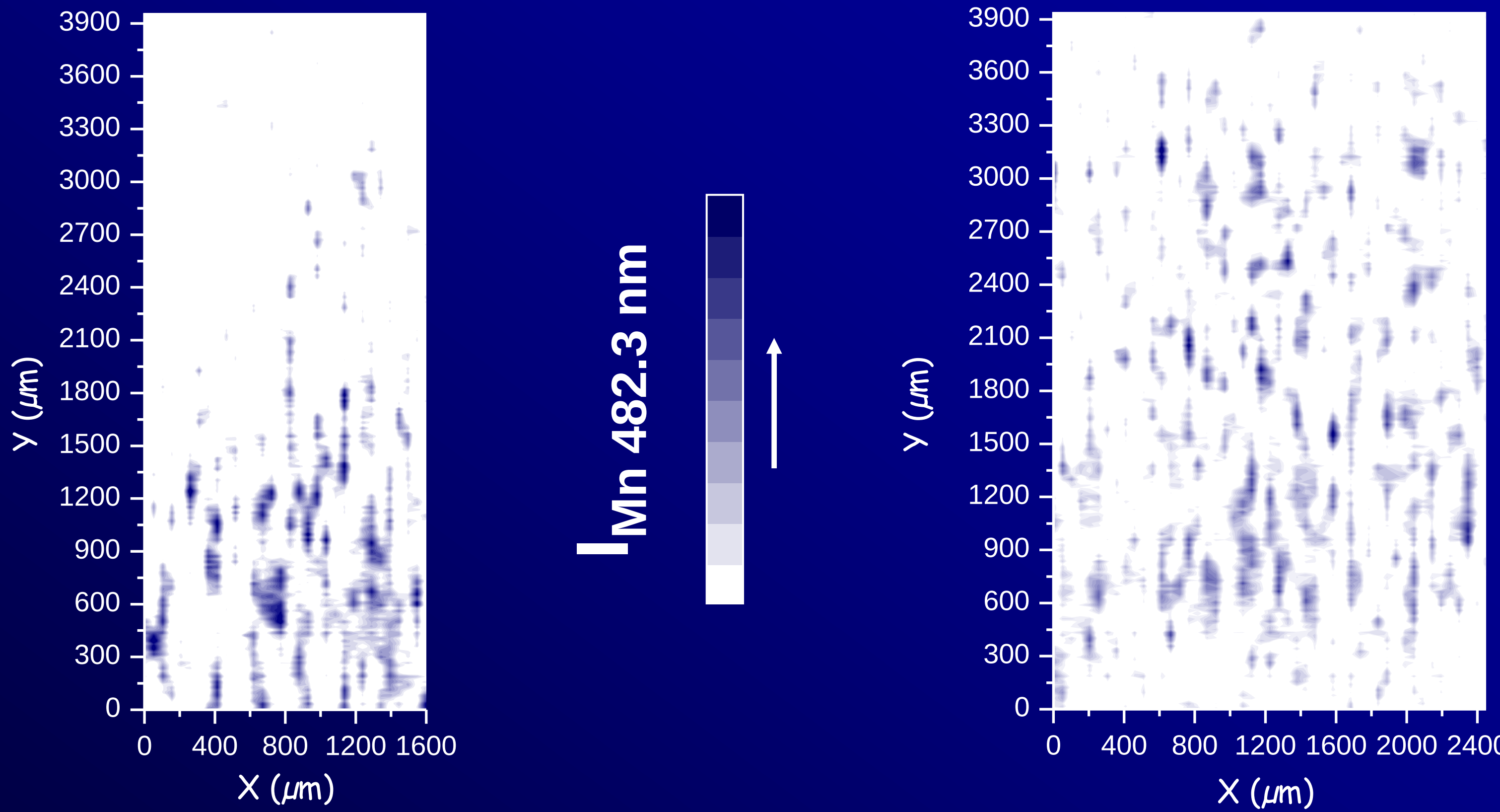
Large area mapping of inclusions in steel
Microline LIBS



Typical microline LIBS crater



Spatial distribution of MnS inclusions in AISI 303 stainless steel



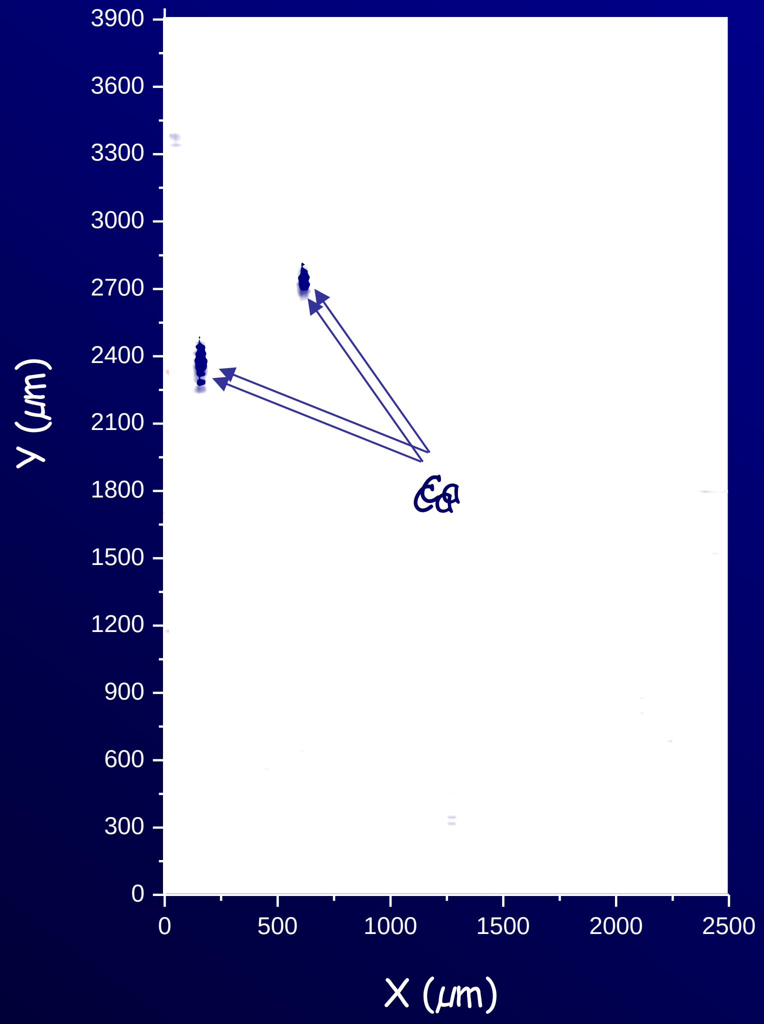
Experimental conditions

Number of pulses: 32
Mapped area: 3942 x 1600 μm^2
Lateral resolution: 50 μm, 16 μm
Sampling depth: 1 μm

Experimental conditions

Number of pulses: 49
Mapped area: 3942 x 2450 μm^2
Lateral resolution: 50 μm, 16 μm
Sampling depth: 1 μm

Ti and Ca inclusions in AISI 321 stainless steel



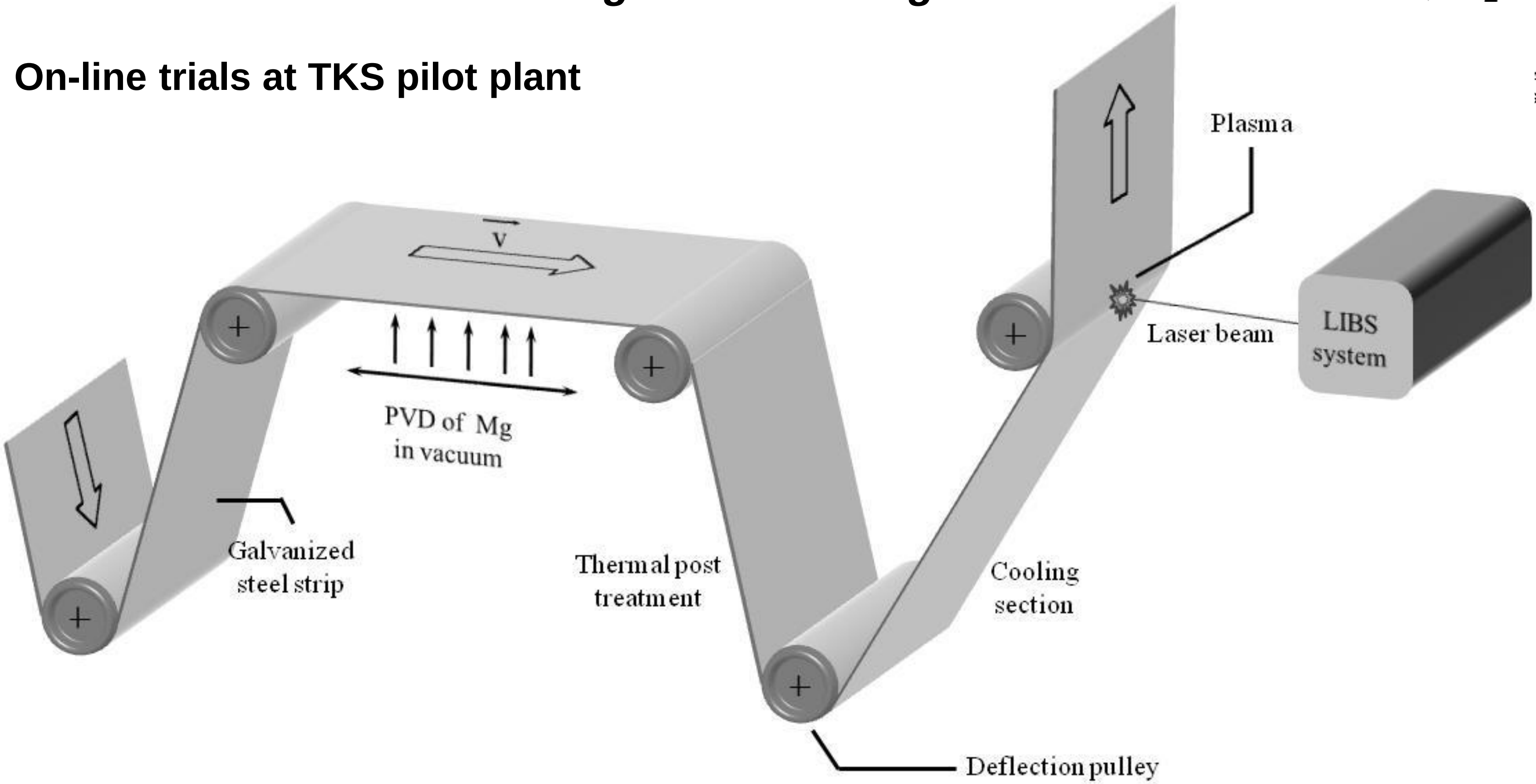
Experimental conditions

Number of pulses: 50
Mapped area: 3.9 x 2.5 mm^2
Lateral resolution: 50 μm, 16 μm
Sampling depth: 1 μm

Pulse rep rate: 2 Hz
Total acquisition time: 25 s

Room temperature and atmosferic pressure operation

On-line trials at TKS pilot plant



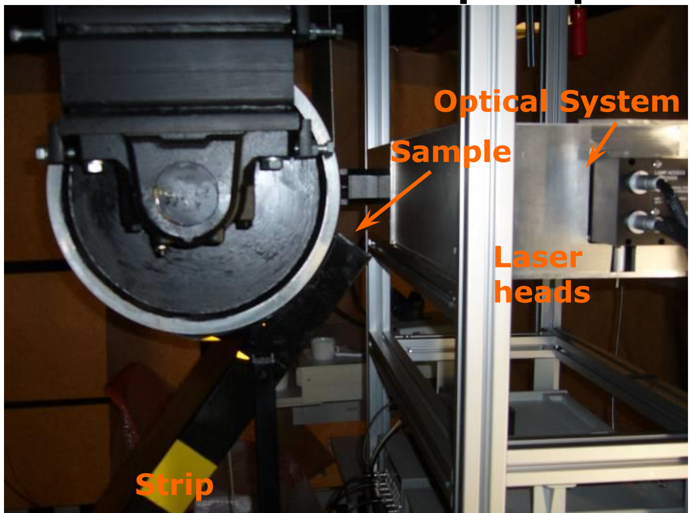
Experimental TKS-line conditions

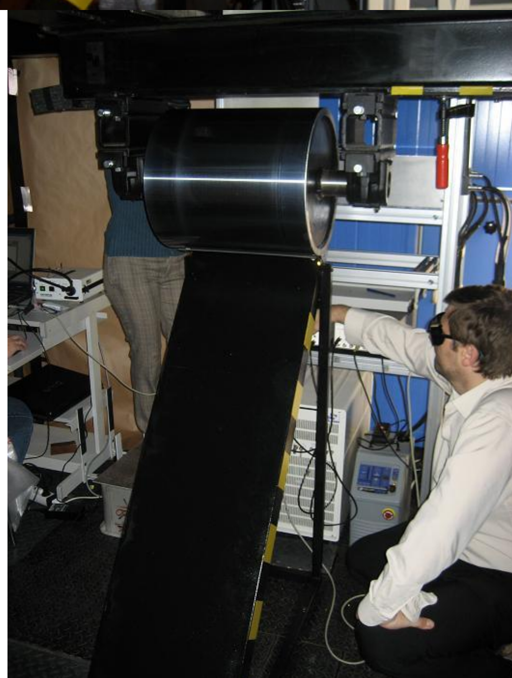
Low carbon steel, 2 µm Zn thickness (one side coating) and variable Mg thickness

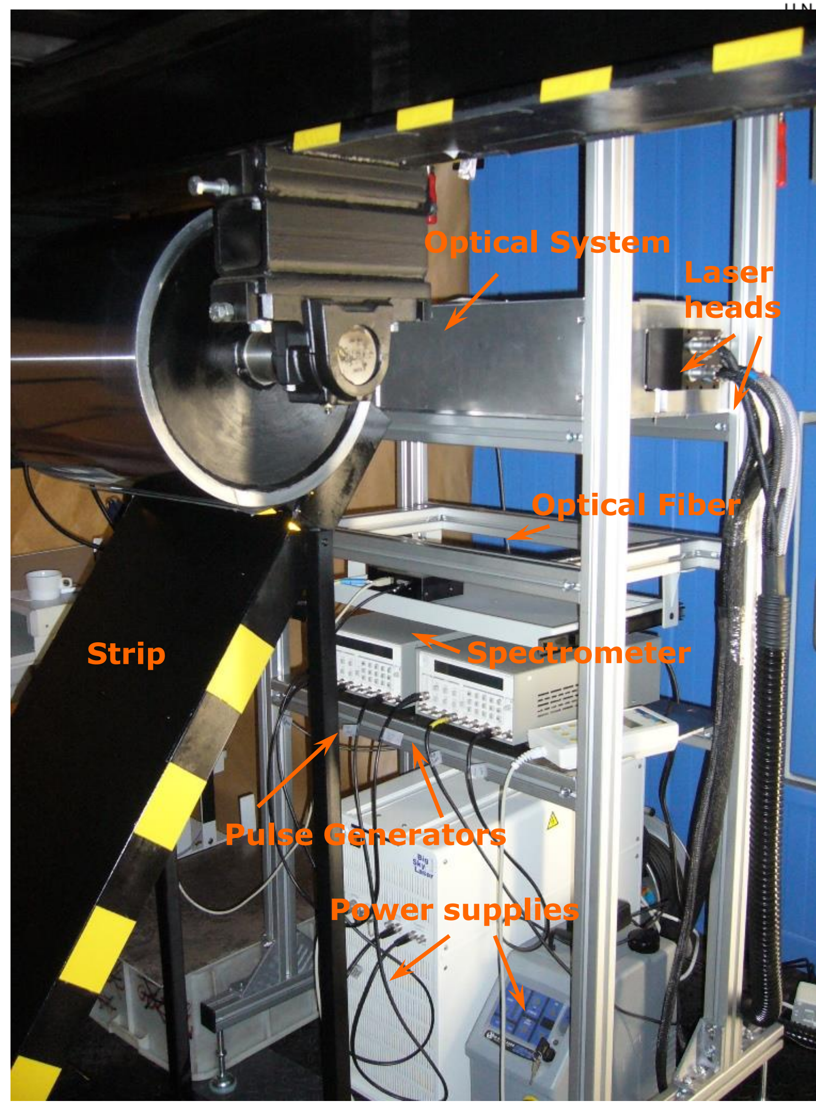
Strip velocity: 6-40 m/min
Strip width: 30 cm
Strip length: 1700 m
Strip thickness: 0.75 mm

Real-time measurement of coating thickness of galvanized steel

On-line trials at TKS pilot plant

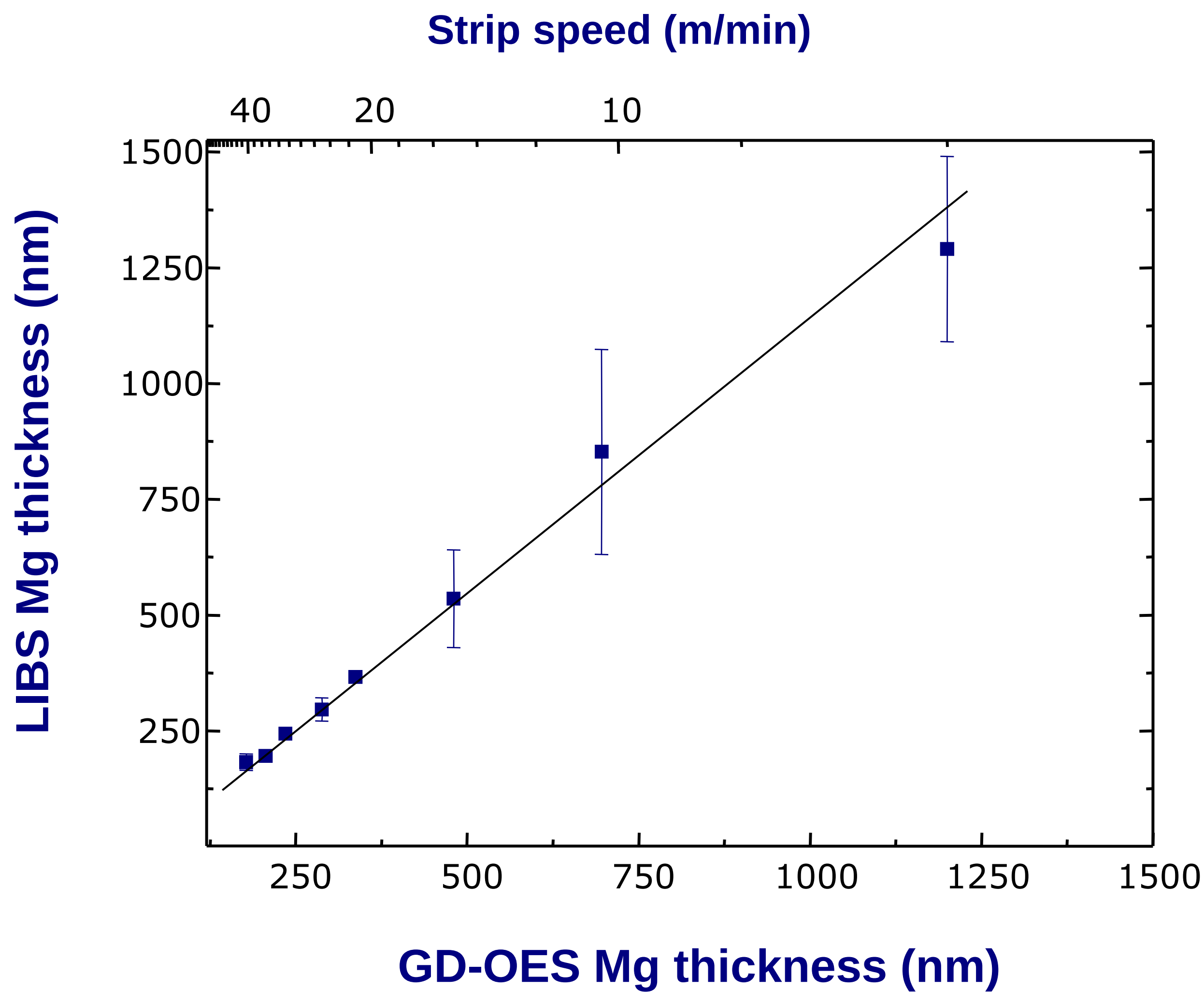






J. Ruiz, A. González, L.M. Cabalín, J.J. Laserna Appl. Spectrosc. 64 (2010) 318

Mg thickness: on-line LIBS vs laboratory GD-OES



J. Ruiz, A. González, L.M. Cabalín, J.J. Laserna Appl. Spectrosc. 64 (2010) 318

LIBS continuous monitoring and resolution of steel grades in sequence casting machines

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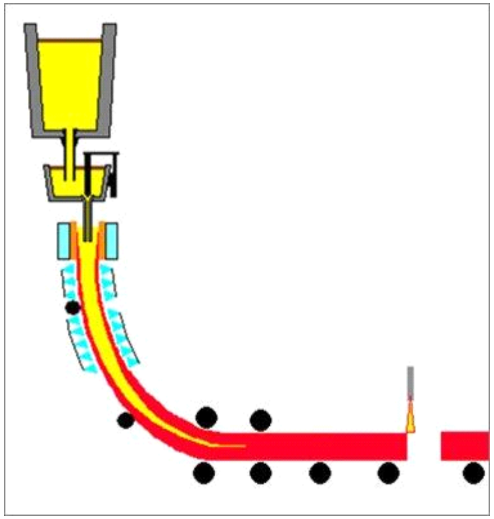
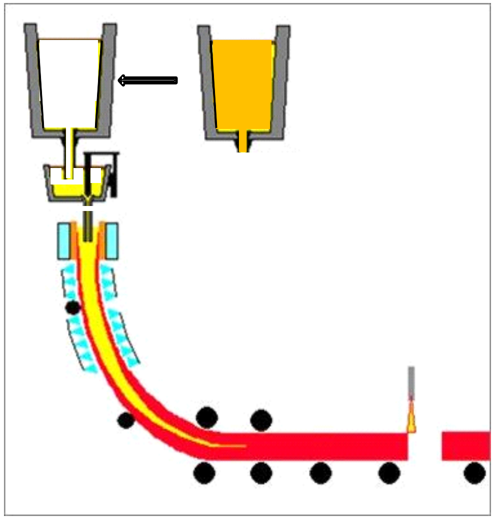
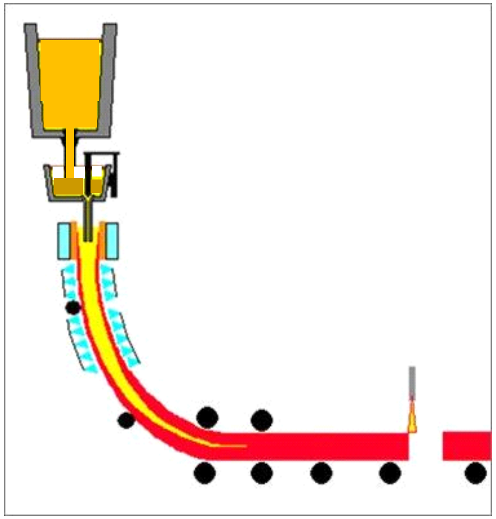
<u>1st step</u>: Casting 1st heat under steady state



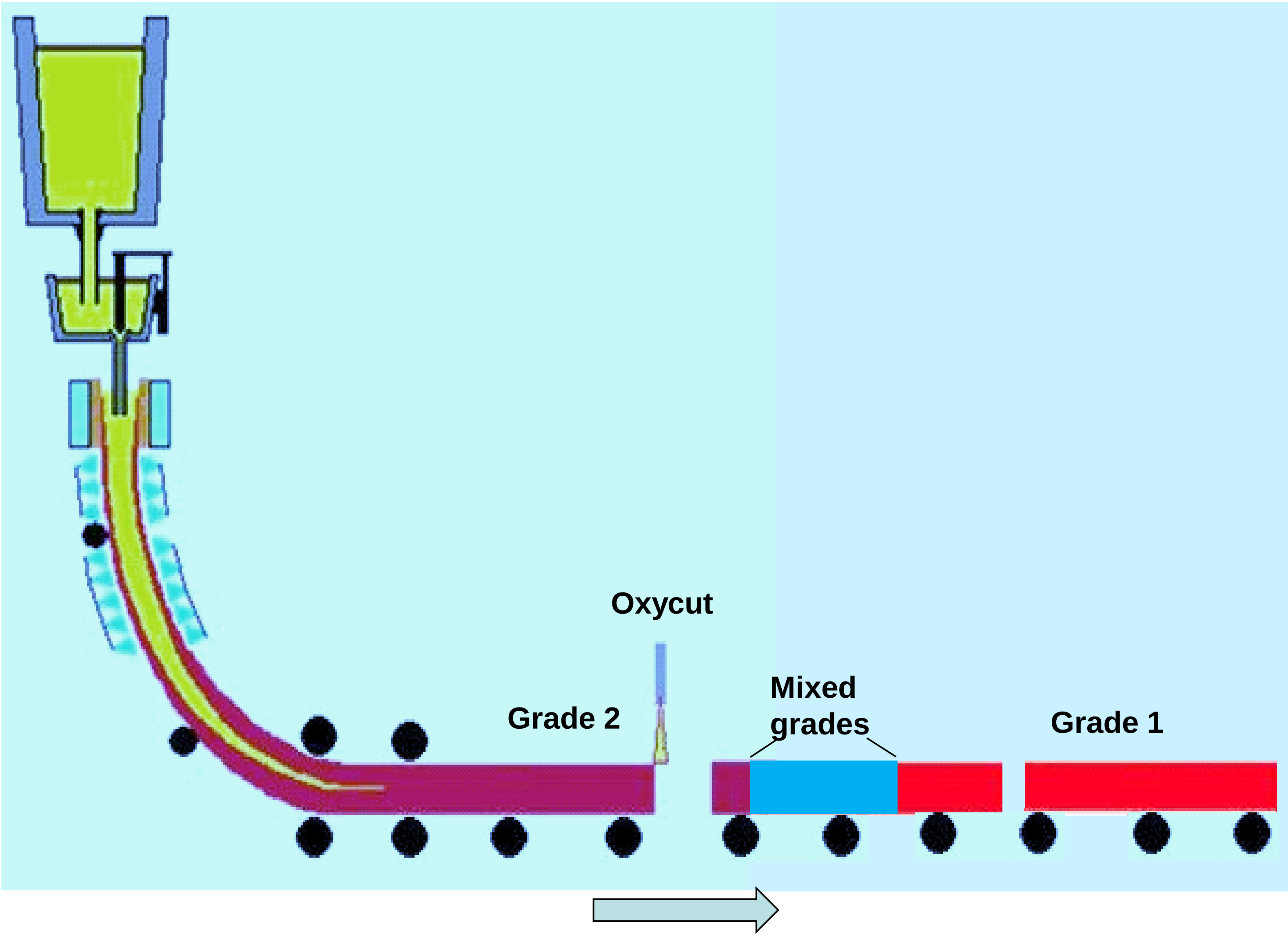
<u>2nd step</u>: Transition starting point



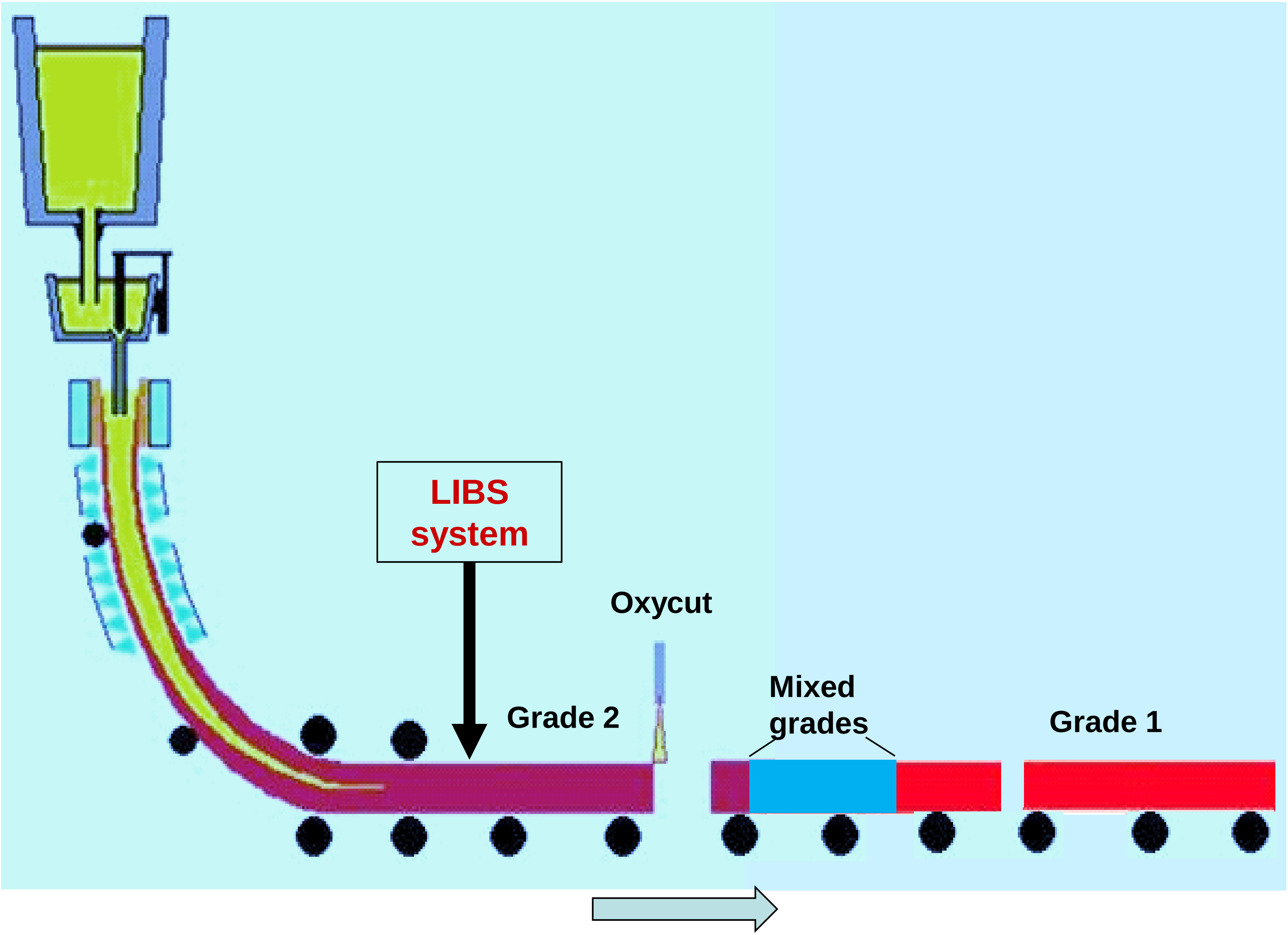
<u>3rd step</u>: Mix steel



LIBS continuous monitoring and resolution of steel grades in sequence casting machines



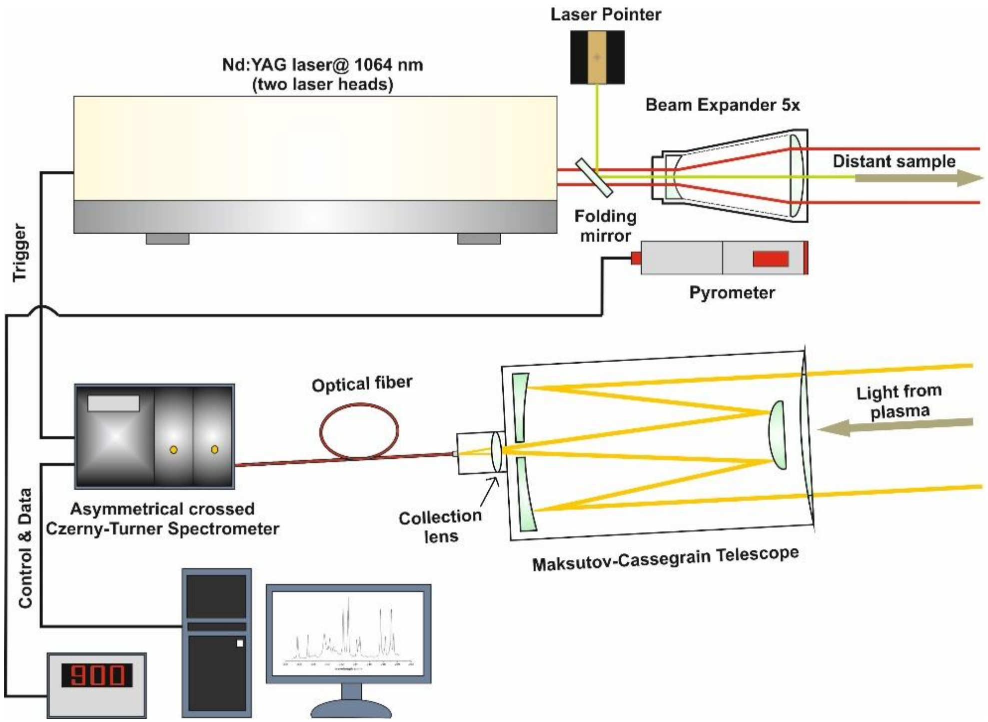
LIBS continuous monitoring and resolution of steel grades in sequence casting machines

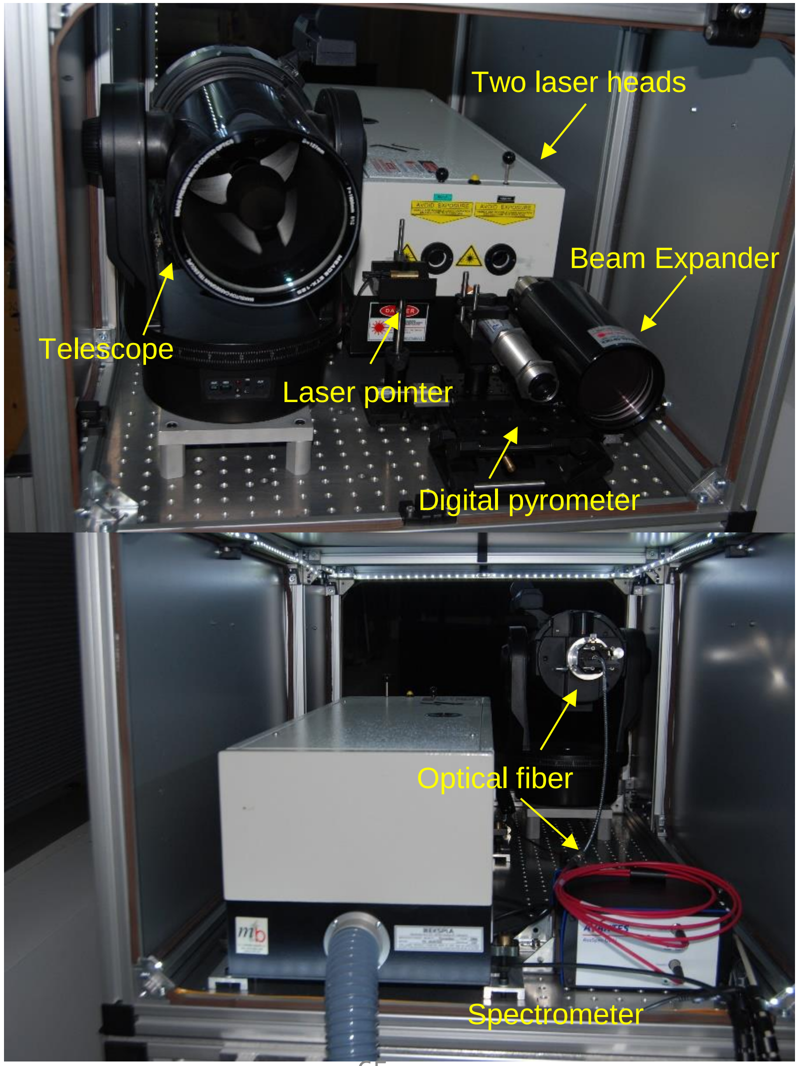


LIBS continuous monitoring and resolution of steel grades in sequence casting machines

UNIVERSIDAD DE MÁLAGA

LIBS instrument





LIBS continuous monitoring and resolution of steel grades in sequence casting machines

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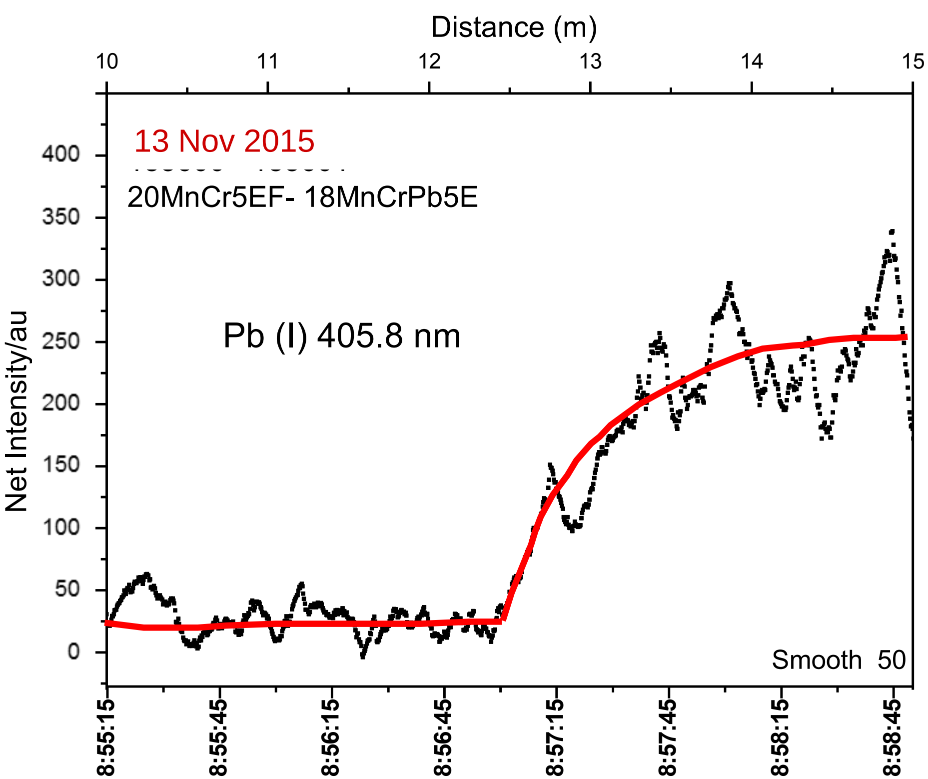
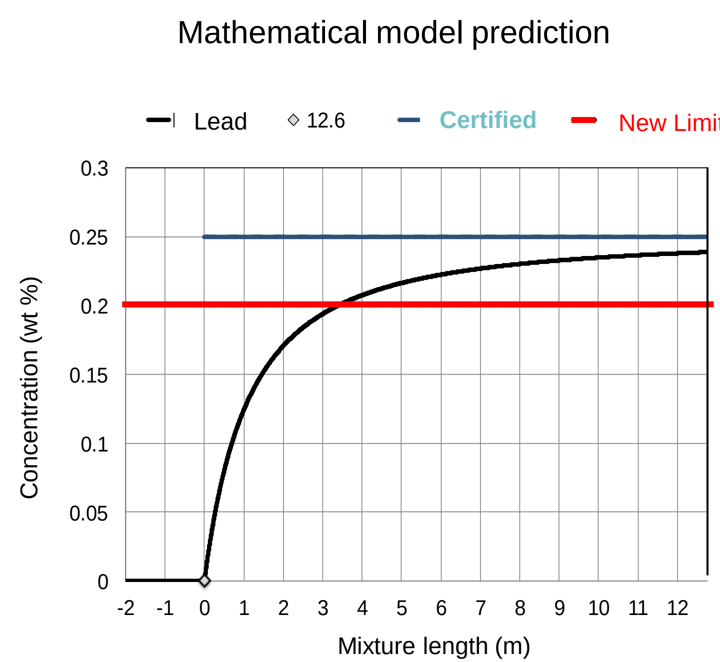
Sequence casting steels inspected and analyzed

GERDAU

Transition	Steel grades	Concentration, wt %	Speed (m/min)	Date (time)
4 183600-183601	20MnCr5EF-18MnCrPb5E	**Cr: 1.29 → 1.07** **Pb: 0.00 → 0.25**	**1.40-1.50**	13-11-2015 (18:57)





Industrial uses of LIBS analyzers

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DE MÁLAGA

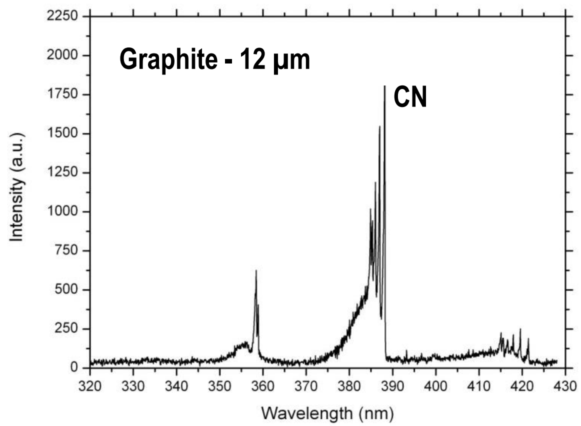
- **Al in Zn baths for deep-coating galvanizing baths 7/24**
- **As and Cd continuous monitoring in acid efluents 7/24**
- **Mg in mineral ore slurries 7/24**
- **In-line ash analysis**
- **Element recognition in Al recycling plants**
- **…**

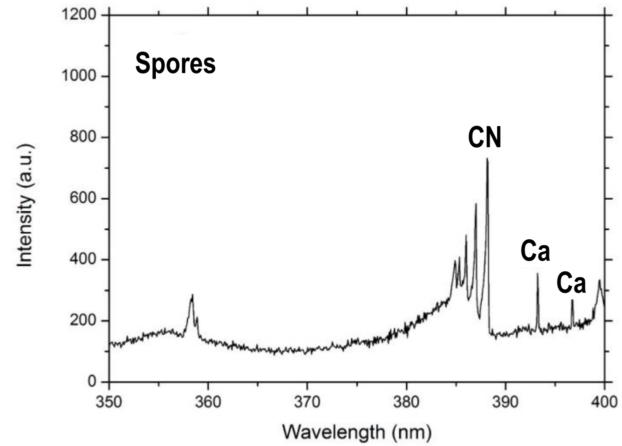
LIBS inspection of steel billets
at high temperature
for quality assurance

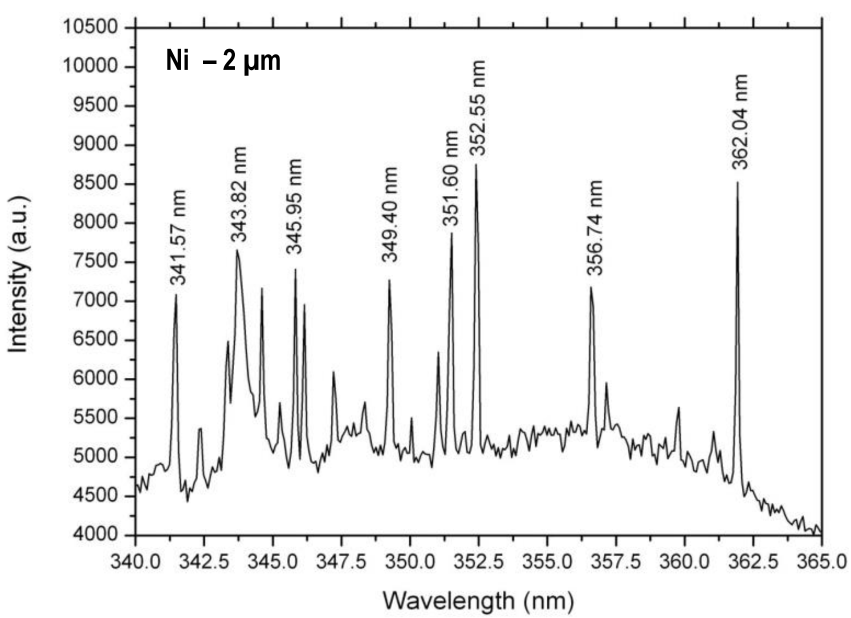
Acerinox Factory, Spain

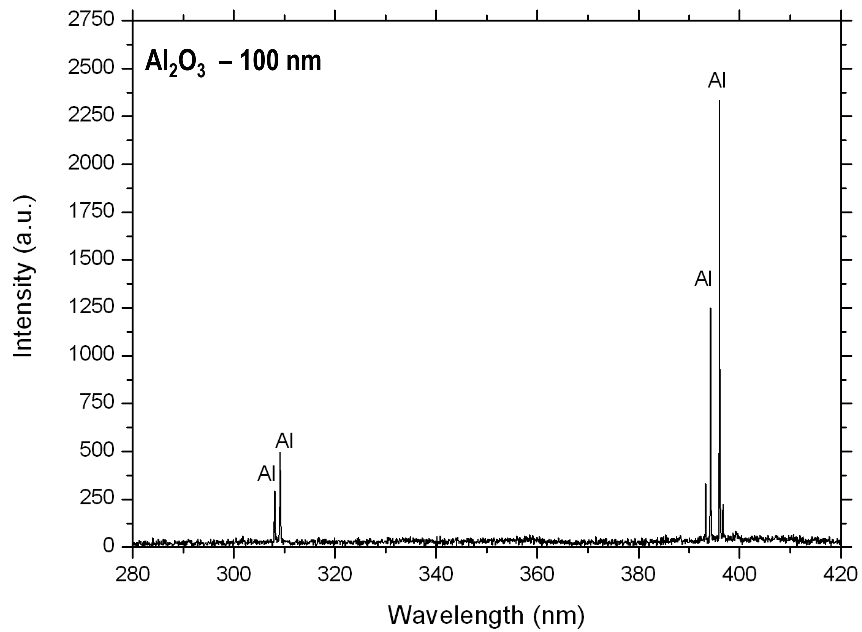
LIBS SPECTRA OF SINGLE TRAPPED PARTICLES

(single-shot spectra)

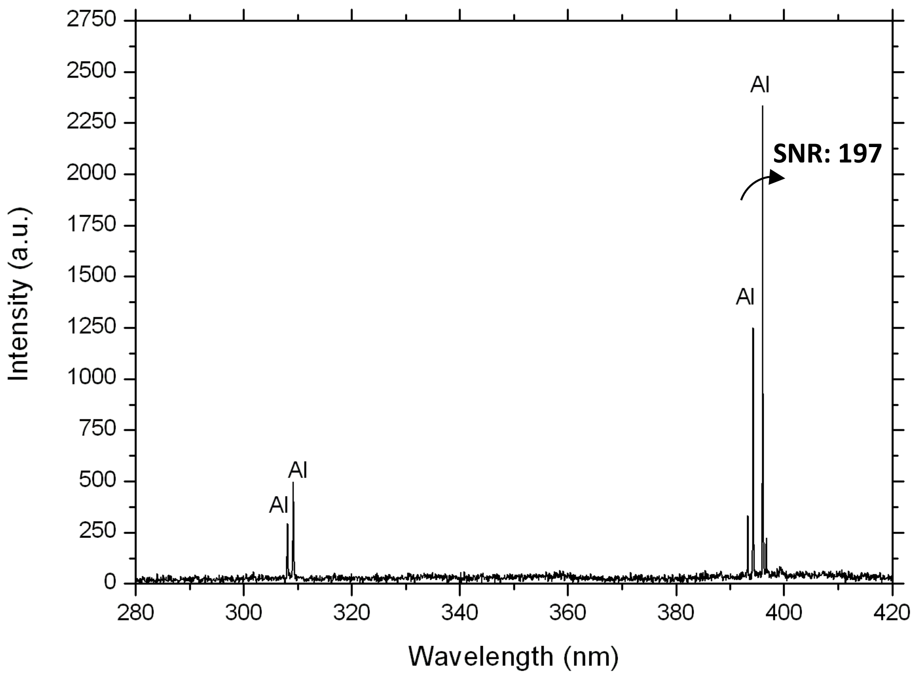








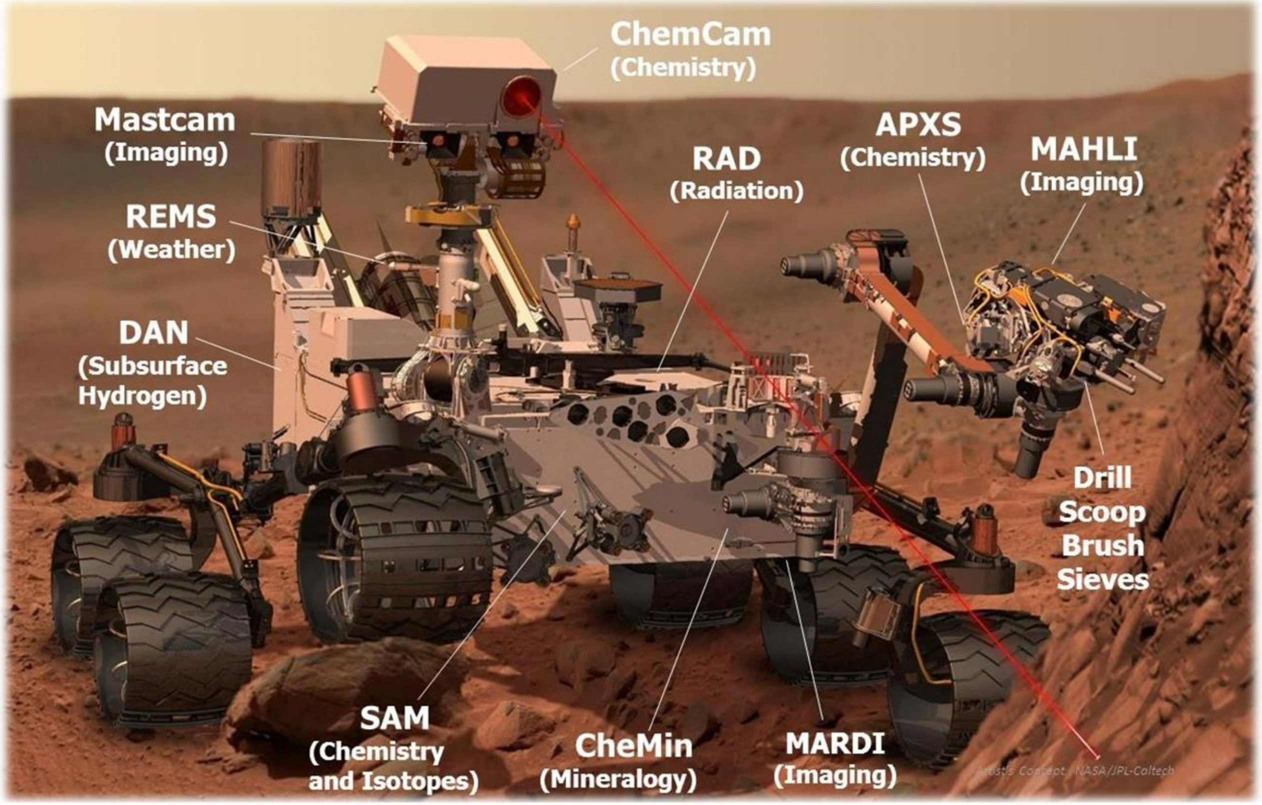
LIBS ANALYSIS OF SINGLE TRAPPED PARTICLES



Al_2O_3 particle – 100 nm
***Mass* - 17 fg**
FWHM – 0.2 nm (396 nm)
SNR (396 nm) - 197
Al LOD – 200 attograms

MARS SCIENCE LABORATORY - SCIENCE PAYLOAD

Cameras:	MastCam | MAHLI | MARDI
Spectrometers:	APXS | ***ChemCam*** | CheMin | SAM
Radiation Detectors:	RAD | DAN
Environmental Sensors:	REMS
Atmospheric Sensors:	MEDLI



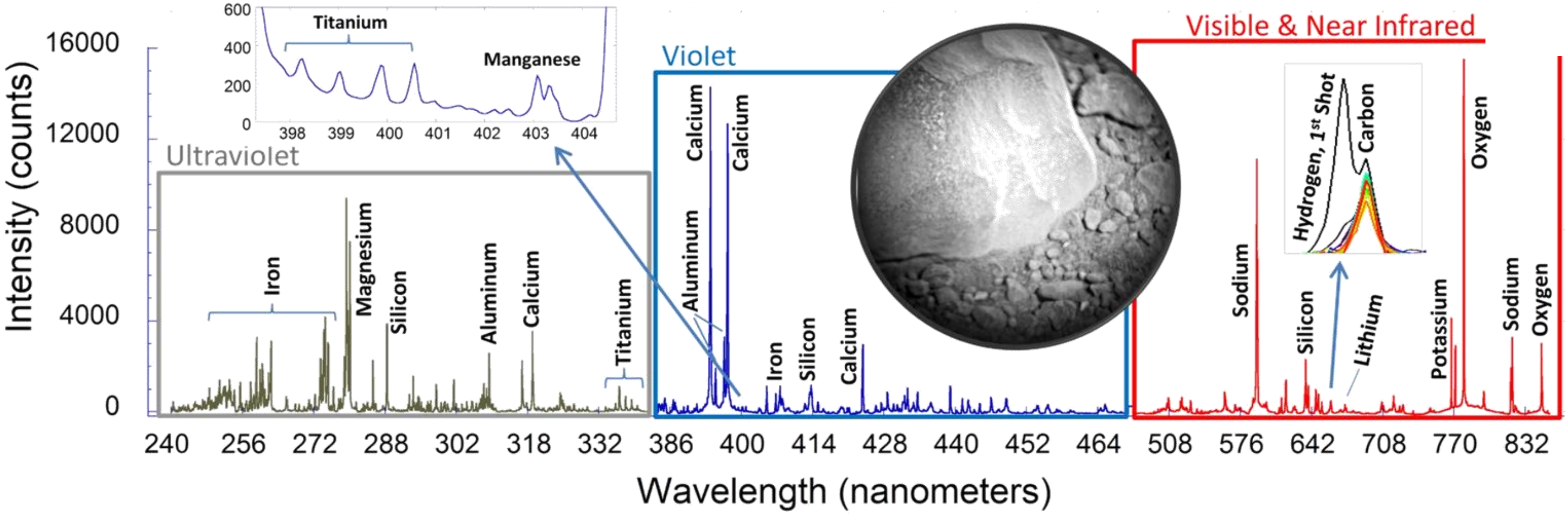
Remote Sensing (Mast)
ChemCam: Laser-Induced Breakdown Spectrometer & Remote Micro Imager
Mastcam: Color Medium and Narrow-Angle Imager

Contact Instruments (Robotic Arm)
MAHLI: Hand-lens Color Imager
APXS: X-Ray Backscatter Spectrometer

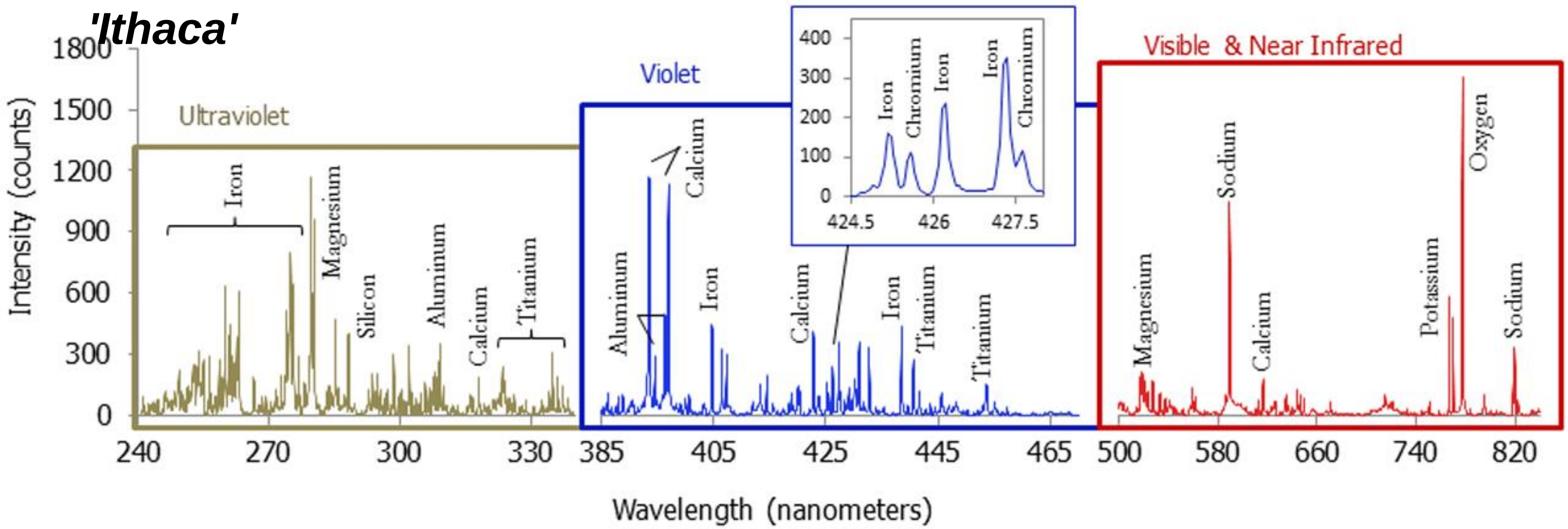
Analytical Laboratory (Rover Body)
SAM: Gas Chromatograph/Mass Spectrometer/ Tunable Laser Spectrometer
CheMin: X-Ray Diffraction

Environmental Characterization
MARDI: Descent Imager
REMS: Meteorological Monitoring
RAD: Surface Radiation Environment Monitor
DAN: Neutron Backscatter Subsurface Hydrogen Detection

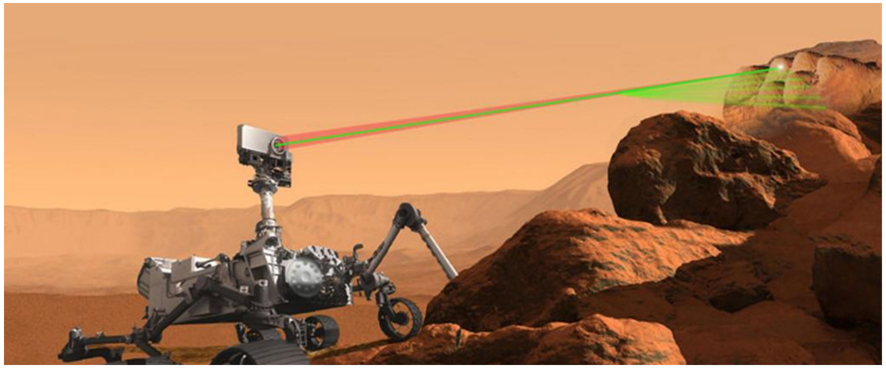
ChemCam 'Coronation' Spectrum:



ChemCam 'Ithaca' Spectrum:



LA NUEVA MISIÓN: MARS 2020



"Continuar la búsqueda de vida pasada, explorar las condiciones que permitan misiones tripuladas a Marte" y…

"Combinar la mineralogía, la textura y la química para analizar las rocas con precisión milimétrica"

PLAN DE LA MISION

Lanzamiento
Cohete Atlas
Julio/agosto 2020

Crucero/aproximación
8-9 meses
Llegada aprox. enero/marzo 2021

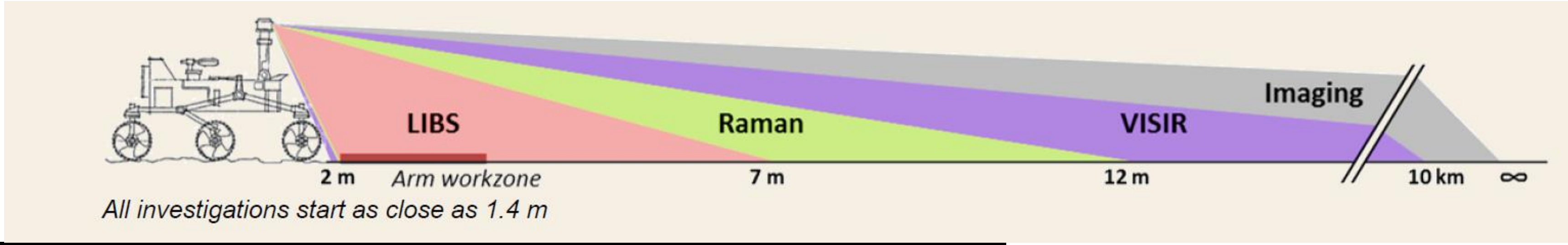
Entrada, descenso, aterrizaje
Idéntico sistema al MSL
Elipse de aterrizaje mucho más precisa (25 x 20 km)

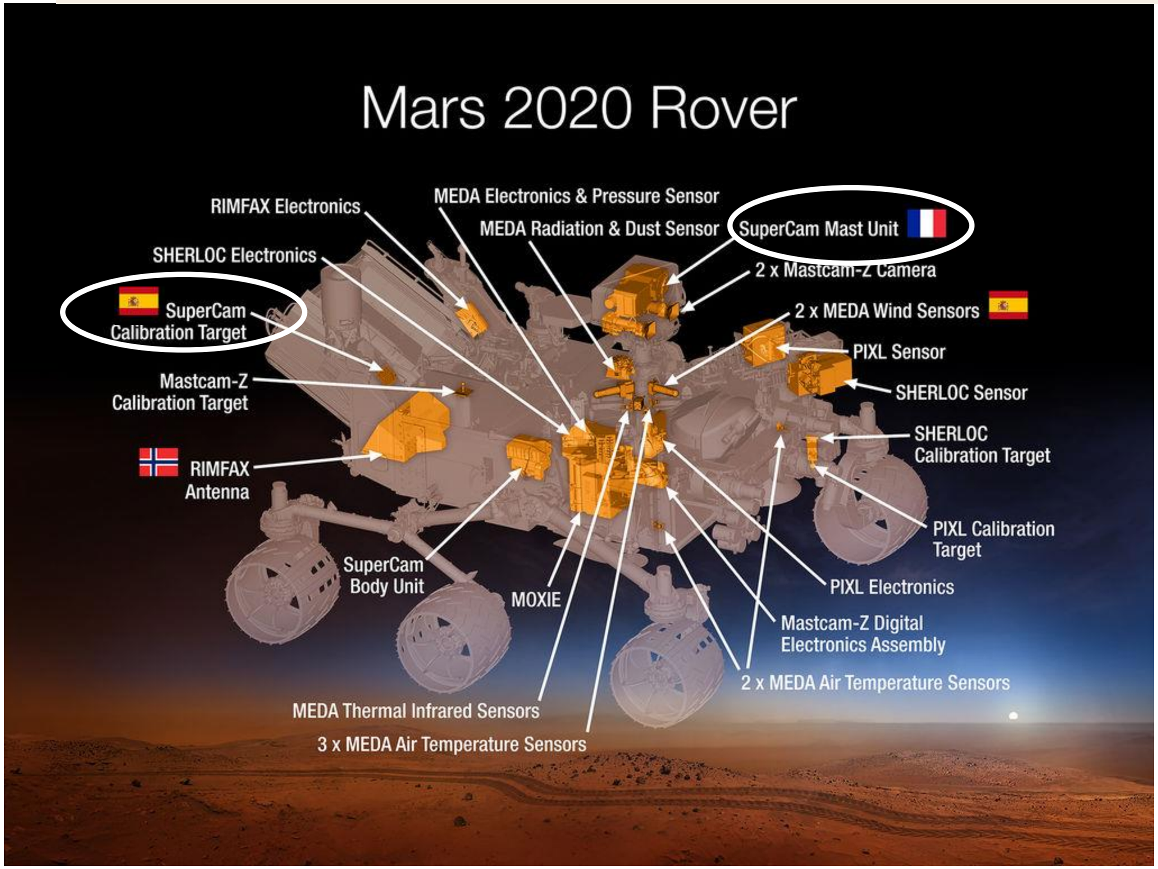
Misión en superficie
Un año de operaciones (669 días)
Mayor distancia de exploración
Mejores comunicaciones
Mayor capacidad de almacenaje de datos

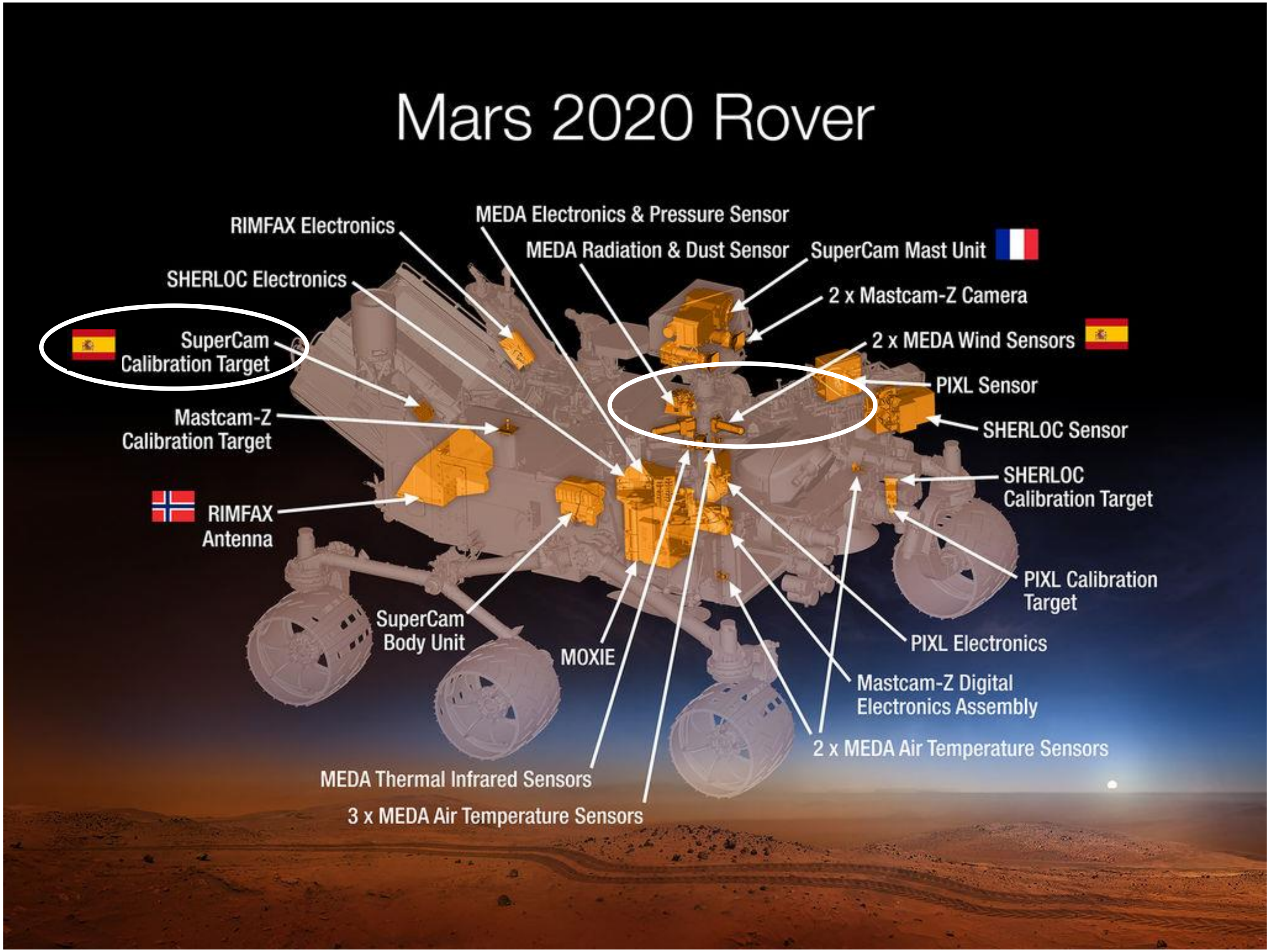
* EDL in work

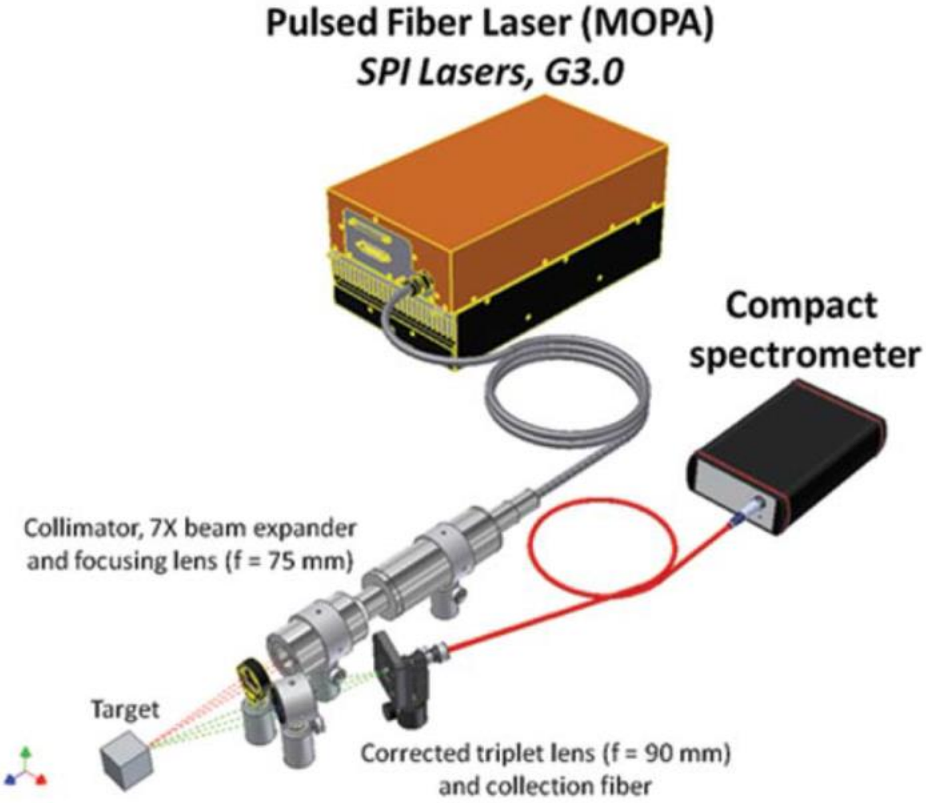
MARS 2020. The mission to the Red Planet

Supercam






Mars 2020 Rover
RIMFAX Electronics
MEDA Electronics & Pressure Sensor
MEDA Radiation & Dust Sensor
SuperCam Mast Unit
SHERLOC Electronics
2 x Mastcam-Z Camera
SuperCam Calibration Target
2 x MEDA Wind Sensors
PIXL Sensor
Mastcam-Z Calibration Target
SHERLOC Sensor
SHERLOC Calibration Target
RIMFAX Antenna
PIXL Calibration Target
SuperCam Body Unit
MOXIE
PIXL Electronics
Mastcam-Z Digital Electronics Assembly
2 x MEDA Air Temperature Sensors
MEDA Thermal Infrared Sensors
3 x MEDA Air Temperature Sensors



Courtesy: Mohamad Sabsabi, National Research Council, Canada

Commercial hand-held LIBS analyzers

- Identify a wide variety of metal alloys at the press of the trigger
- Measure elements, light and heavy in short time
- Test large or small samples such as shavings, turnings, granules, cables, etc.
- No x-rays and free from the regulatory constraints usually associated with x-ray analysers
- Simple point-and-shoot operation

Introduction to
Laser Induced Breakdown Spectroscopy

J.J. Laserna
Department of Analytical Chemistry
University of Málaga, Málaga, Spain

UNIVERSIDAD DE MÁLAGA

laserna@uma.es

http://laser.uma.es

Winter School on Underwater Sensing Science
Aberdeen Scotland UK 22 March 2017