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Winter College on Optics: Fundamentals of Photonics - Theory, Devices and Applications

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Photonics in surface cleaning processes (I)

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Photonics (Laser) in surface cleaning

CONFERENCE I

- Historical notes
- Principles of laser cleaning
- Laser systems
- Monitoring methods
- Some examples

CONFERENCE II

An exotic application: Solving a thorny problem using laser ablation

Collaboration Mexico-Cuba

IMRE-UH, Cuba

Tampico

Havana

CICATA-IPN, Mexico

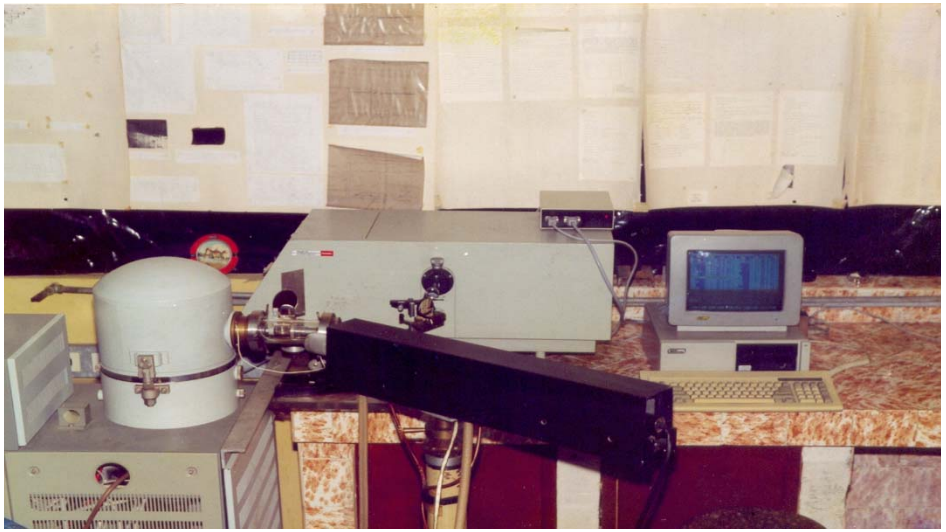
Research areas related with topic of conference

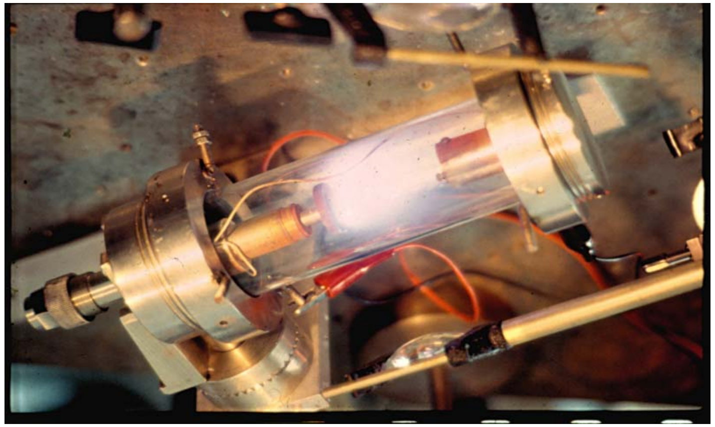
- Development of lasers and laser instruments - 1986
- Pulse Laser Deposition – 1987
- Laser cleaning and surface treatments – 1993
- Laser Induced Breakdown Spectroscopy - 2006

Development of laser instruments

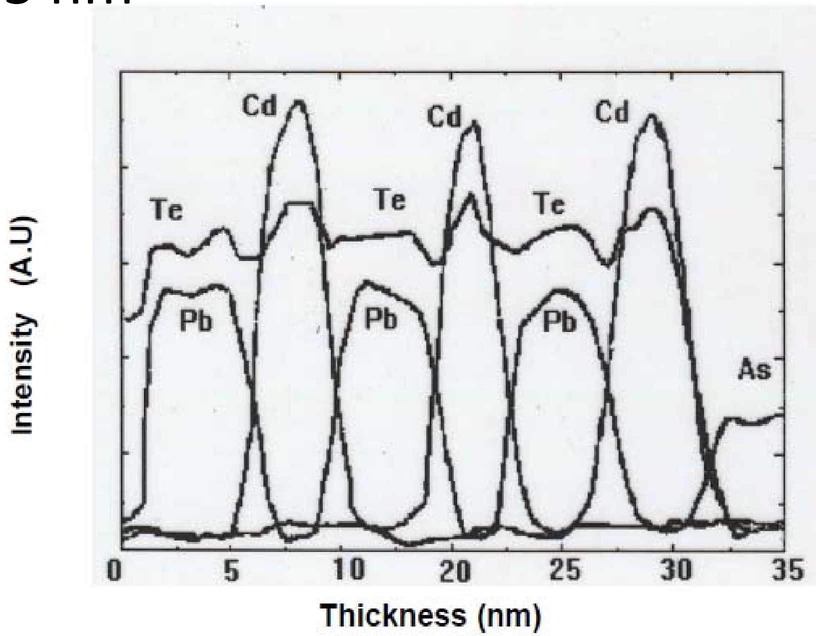
•Solid-state lasers for materials processing, medical aplications and others)
•Dielectric mirrors
•Laser rods (under development)

Pulsed Laser Deposition





Multilayer PbTe – CdTe, thickness 5 -25 nm



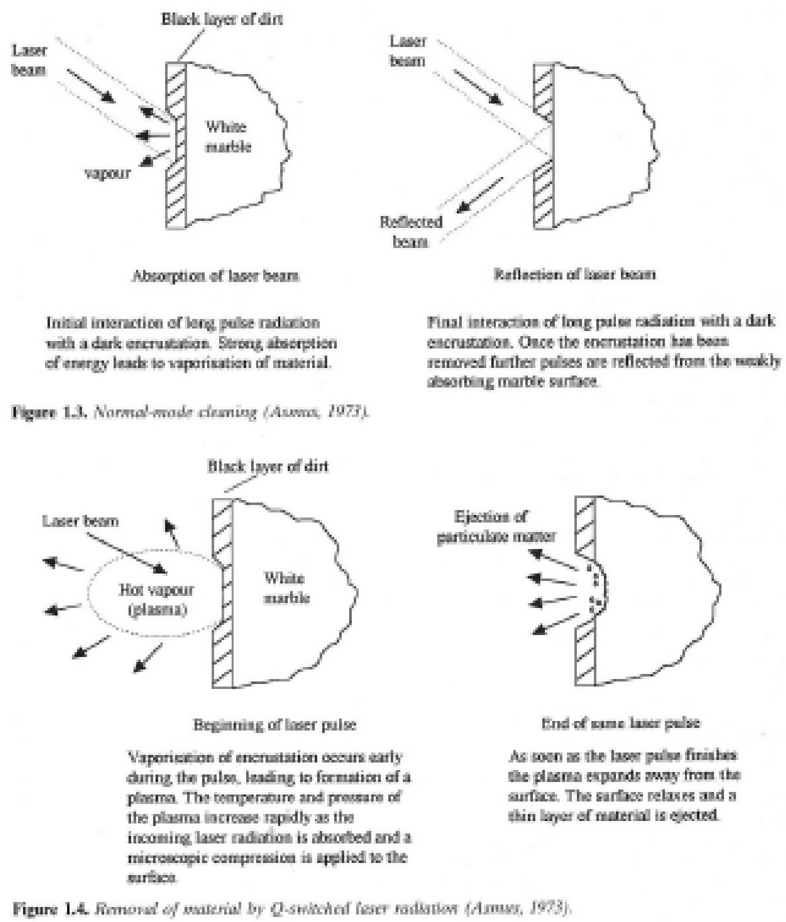
Laser Induced Breakdown Spectroscopy (LIBS)

- Compositional determination of Artworks
- Food products (fish, cactus, prickly pear)
- LIBS for tobacco quality determination
- Low cost and compact lasers as excitation source emitting in burst-mode regime

LASER CLEANING
Historical notes

- **The Beginning**: Laser Cleaning of Stone
- In the 1970ies in Venice, Frari Church, John the Baptist (sculpture of Donatello)
- There was the intention to make an holographic image, and incidentally first cleaning tests with a ruby laser were carried out.

- One of the first laser cleaning projects at the beginning of the1980ies was carried out by J. Asmus and G. Calcagno at the portal of the cathedral of Cremona in Italy
- Tool: Nd:YAG laser, 1064nm, normal mode
- Repetition frequency 1 pulse per second and therefore very slowly



- Description of the laser activity during cleaning as described by John Asmus

Advantages of laser cleaning

- **Selectivity**. It is possible to remove layers of dirt without removing any original material from the surface of the object.
- **Non-contact -** There is no mechanical contact with the surface. This allows extremely fragile surfaces to be worked on.
- **Localized action** – A laser beam can be precisely directed using a visible aiming beam and the exposure conditions can be optimized for removal.
- **Low substrate impact** – The substrate is unaffected by the exposure, while conventional cleaning can easily lead to irreversible damage. The relief can be preserved.

Advantages of laser cleaning

- **Environmental friendly**
  The only waste generated is the dirt ejected from the surface. There is no use of hazardous chemicals.

- **Versatility and reliability**
  Laser has successfully been used to remove dirt and other coatings from a wide range of materials including: marble, limestones, sandstones, terracotta, alabaster, textile, canvas, aluminium, bone, ivory and many others.

Principles of laser cleaning

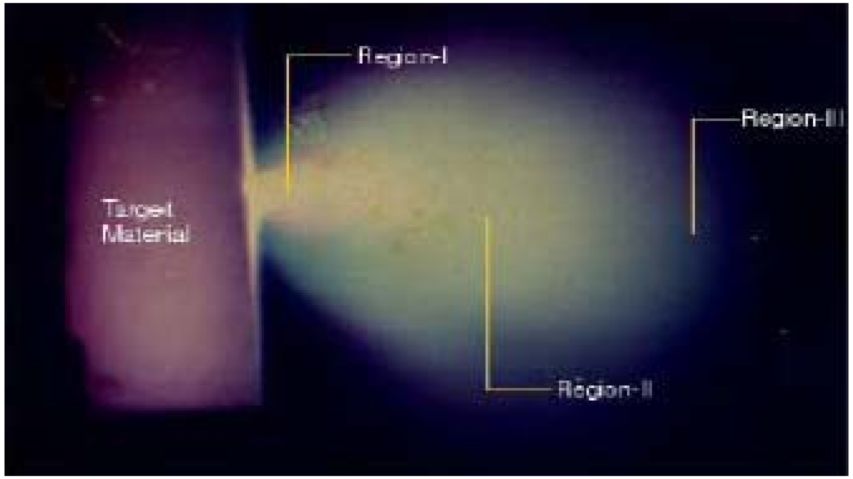
Laser ablation

- **Laser ablation** is the process of removing material from a solid (or occasionally liquid) surface by irradiating it with a laser beam.
- At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates.
- At high laser flux, the material is typically converted to a plasma.
- Usually, laser ablation refers to removing material with a pulsed laser, but it is possible to ablate material with a continuous wave laser beam if the laser intensity is high enough.

Laser ablation

- The depth over which the laser energy is absorbed, and thus the amount of material removed by a single laser pulse, depends on the material's optical properties and the laser wavelength and pulse length. The total mass ablated from the target per laser pulse is usually referred to as **ablation rate**.
- Laser pulses can vary over a very wide range of duration (milliseconds to femtoseconds) and fluxes, and can be precisely controlled. This makes laser ablation very valuable for both research and industrial applications.

The plasma during laser ablation



•The first region is the hottest area of the plasma in which the continuous emission of electrons dominates
•The second region contains an ionized plasma where recombination processes cause intense optical emission
•The third region contains mostly electrons which are the species that move faster

Laser ablation

- Laser ablation is a strongly non-linear process occurring when the irradiation fluence (pulse energy per unit area: $F_0 = E/A$) or in some cases intensity (peak power per unit area: $I_0 = P/A$) overcomes a critical threshold, which is an intrinsic property of the material structures under irradiation.

- In the domain of interest fluence and intensity are usually expressed in mJ/cm^2 or J/cm^2 and MW/cm^2 or GW/cm^2 , respectively.

Absorption and scattering

- The incidence of a laser beam on a material is accompanied by absorption and scattering phenomena producing attenuation and spatial redistribution (diffusion) of the beam energy.

- In the case of a layer of dielectric material (as for examples black crust, whitewashes etc.), it is useful distinguishing among back scattered, absorbed, and forward-scattered radiation and to introduce the reflectance ($R=E_r/E$), absorbance ($A=E_a/E$), and transmittance ($T=E_t/E$) parameters of the material layer

$$R+A+T=1$$

When irradiating thick or very absorbing materials $T \approx 0$, but in practical cases of adjacent material layers, often the transmittance must be taken into account in the energy balance.

The flux of energy, which propagates into the material, *F*, undergoes to a typical exponential attenuation law along the optical axis, *z*:

$$F(z) = F_{\alpha}\, e^{-\mu z}$$

where $F_a=(1-R)F_0$ and μ is the effective absorption coefficient, whose reciprocal represents the *optical penetration depth* $\delta = 1/\mu$, also named optical extinction length.

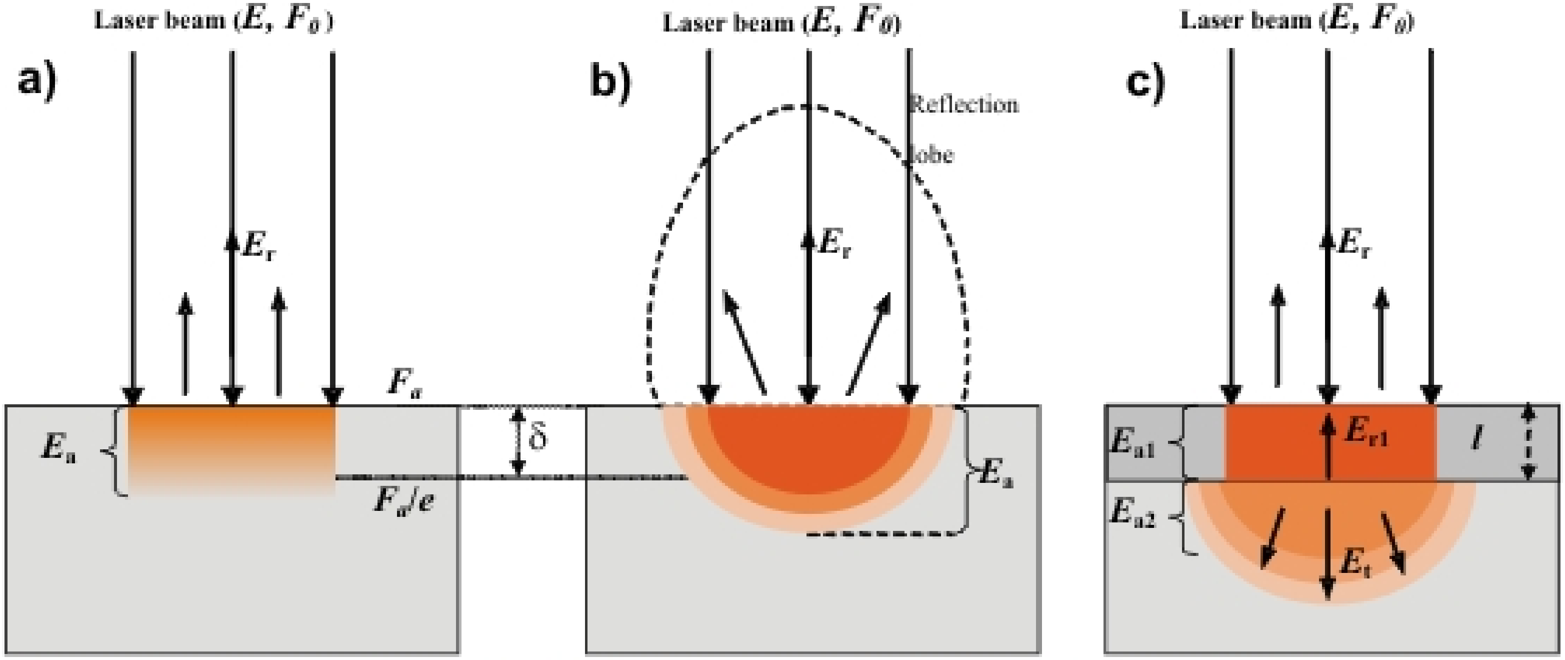


Fig. 2.1.1: Representation of energy redistributions in laser-material interaction: absorbing material (a), diffusing material (b), and the adjacent absorbing and diffusing materials layers (c). E_r, E_a =reflected and absorbed energies.

Thermal heating

- In the most of the cases the absorbed energy E_a is dissipated through the thermal channel
- Only at high irradiation intensities or short UV wavelengths also the direct ionisation and molecular photodissociation can play an important role.
- Hence, the main direct effect of the laser irradiation is a temperature rise within and in proximity of the irradiated volume.

Thermal heating

- Theoretical estimations of the thermal distributions induced in homogeneous materials can be derived through the heat conduction equation

$$\Delta T(t,z) = \frac{\sqrt{D}}{K\sqrt{\pi}} \cdot \int_0^t I_a(t-t') \cdot \frac{e^{-\frac{z^2}{4Dt'}}}{\sqrt{t'}} dt'$$

- where K and D are the thermal conductivity and diffusivity of the material, respectively. D=K/ρCp, where ρ and Cp are the density and specific heat of the material.

- The last equation requires the knowledge of the temporal profile of the laser pulse. As a first approximation it can be often assumed as Gaussian in the nanoseconds range and top-hat for longer pulse durations. For this latter case the expression of the surface temperature assumes the well-known form:

$$\Delta T_{surf} = 2\frac{F_a}{K}\left(\frac{D}{\pi\tau}\right)^{\frac{1}{2}}$$

where τ is the laser pulse duration (FWHM).

- As a general behaviour this equation states that **the surface temperature increases when the pulse duration decreases**, which is particularly important in the cleaning of metal artefacts

- As an example, the figure reports the temperature rise at gold-air interface for Gaussian profiles and Fa = 150 mJ/cm^2. The temperature peak decrease from 454 °C to 148 °C when the pulse duration increases from 6 ns to 100 ns

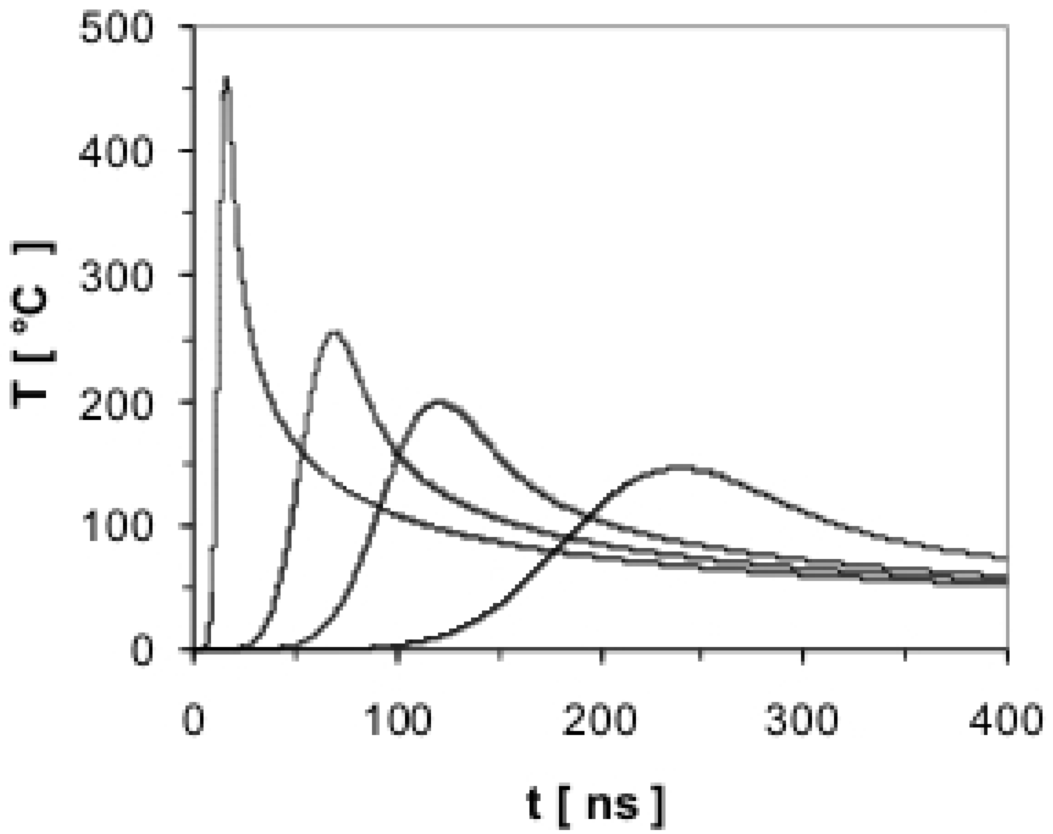


Fig. 2.1.4: Examples of temperature transients associated with Gaussian pulses of different duration.

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Photo-acoustic effects

- Pulsed irradiation can generate acoustical transients, which propagates into the irradiated materials.
- The basic mechanisms can be very different depending on the physical properties and laser parameters.
- For solid absorbing materials laser intensities of order of 10^6-10^8 W/cm^2 the photo-acoustic effect is usually originated by the thermoelasticity.

- All the materials in different levels exhibit a volume variation when heated, which is reversible within specific temperature and pressure range, i.e. thermoelasticity domains.

- The parameter characterizing the effect is the thermal expansion coefficient, β, representing the relative volume variation produced by unit temperature variation.

- Laser irradiation with short pulse duration generates fast thermal transients within the irradiated volume and hence associated pressure rises.

- This produces a pressure wave, which propagates into the medium with a quasi-sonic speed.

Ablation channels

At fluences below the minimum one for vaporisation the only possible ablation mechanisms are of photomechanical type, apart from the special case of VUV wavelengths, where the direct molecular bond breaking can provide a relevant contribution.

- The main channels are based on pressure confinement , where the impulsive ejection is generated by the high-pressure gradient at the interface, and primary spallation occurring when the laser matter interaction process exerts a strength larger than the specific breaking load of the material.

- These channels are very interesting for laser cleaning applications because they involve moderate temperatures and are very efficient. In real cases of inhomogeneous multilayer stratifications, the mechanisms of the photomechanical ablation gets rather more complex.

- Above the vaporisation threshold only fast thermal explosion induced by laser pulses in the nano-seconds range is the most properly called laser ablation,

- in the present concern it is useful to extend the concept to plasma-mediated material removal, of importance in some specific high intensity treatment, and to quasi-continuum vaporisation produced by SFR and FR Nd:YAG lasers.

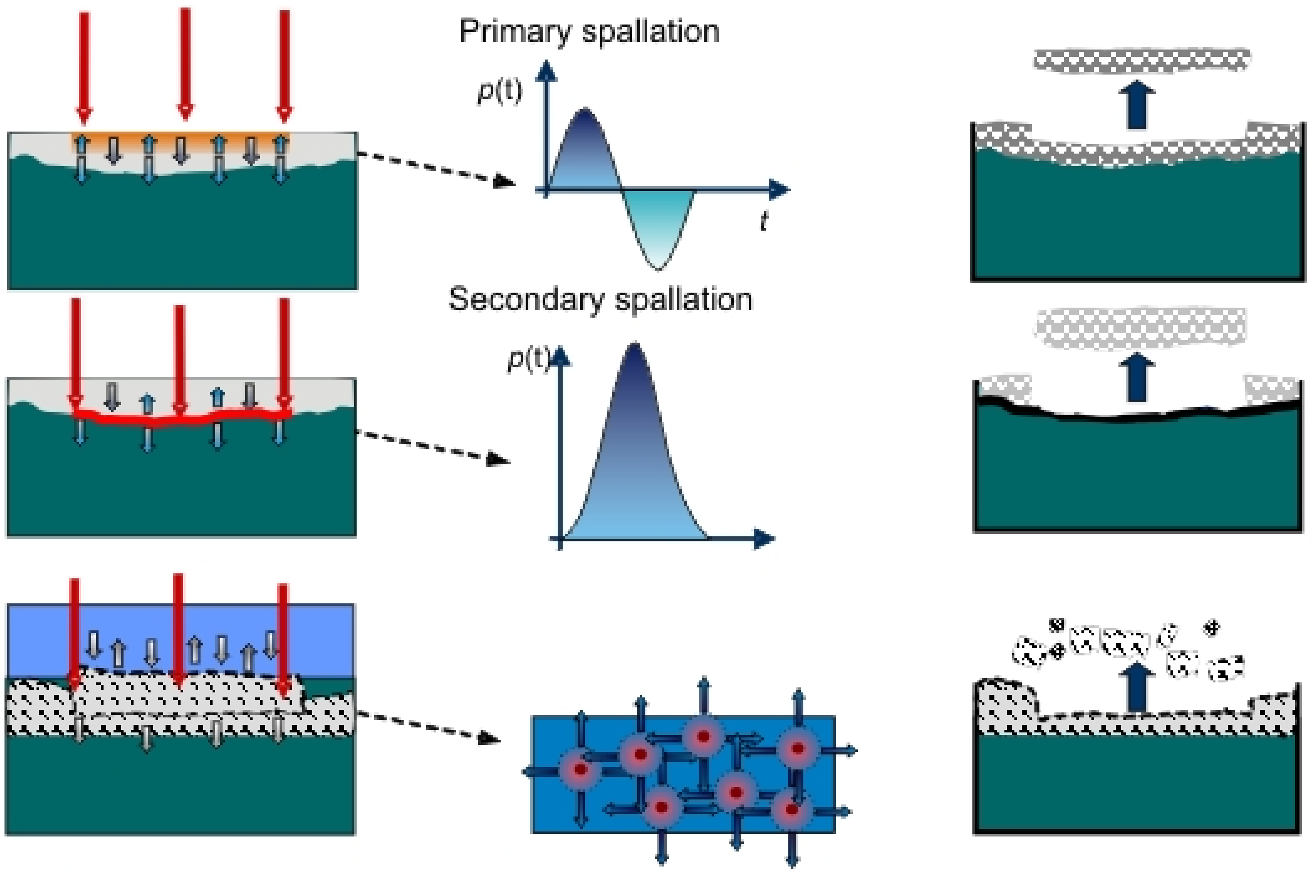

Fig. 2.1.8: Representation of possible spallation mechanisms. Primary spallation: produced by rarefaction peak. Secondary spallation: produced by laser heating and subsequent pressure development in proximity of the interface between two adjacent layers. Water-mediated spallation: similar to primary spallation, where water plays an important role in photomechanical and pressure wave propagation. A relatively strong fragmentation effect is expected in this latter case.

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Ablation threshold

- Laser ablation starts to be observed above the minimum fluence F_{th} named ablation threshold.

- Above this value the removal is almost linear up to the saturation fluence F_s, indicating where the efficiency is significantly reduced by dissipative phenomena as in particular ionisation and plasma formation.

Cleaning threshold

- For real stratifications it is useful to introduce concepts like cleaning fluence of cleaning threshold Fcl, which is the minimum laser fluence providing the desired cleaning result in self-terminated cleaning treatments.

Laser systems

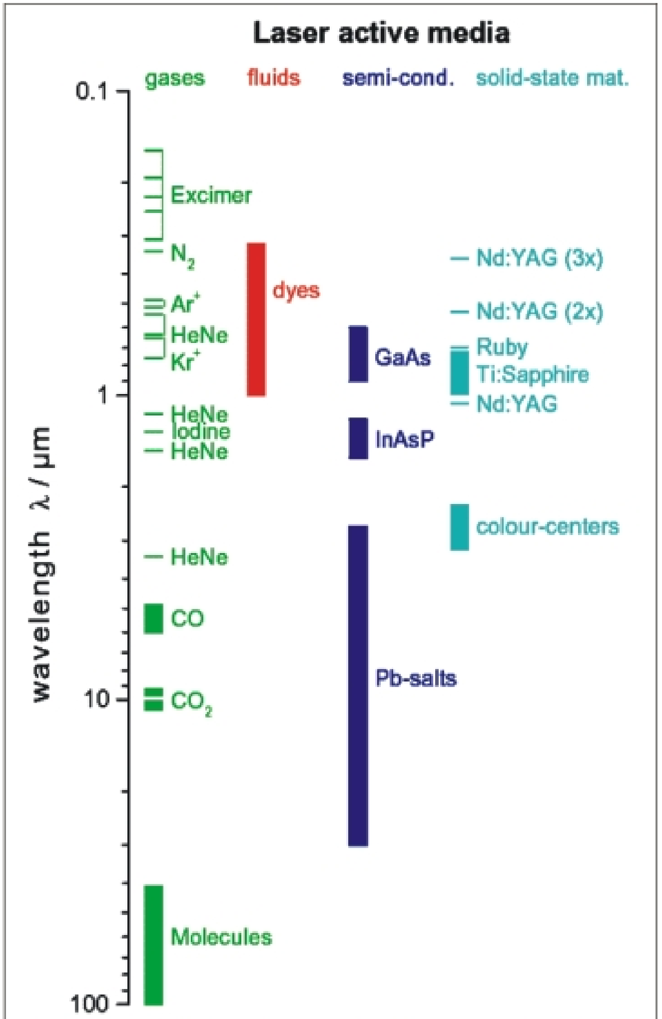


Fig. 1.1.7: Examples of the laser active media and the corresponding emission wavelengths of commercially available laser sources.

At present, the Nd:YAG lasers, and also the excimer lasers are most frequently applied for artwork conservation purposes.

However, in the initial phase of the research on artwork cleaning by laser the solid state ruby lasers were successfully used, too.

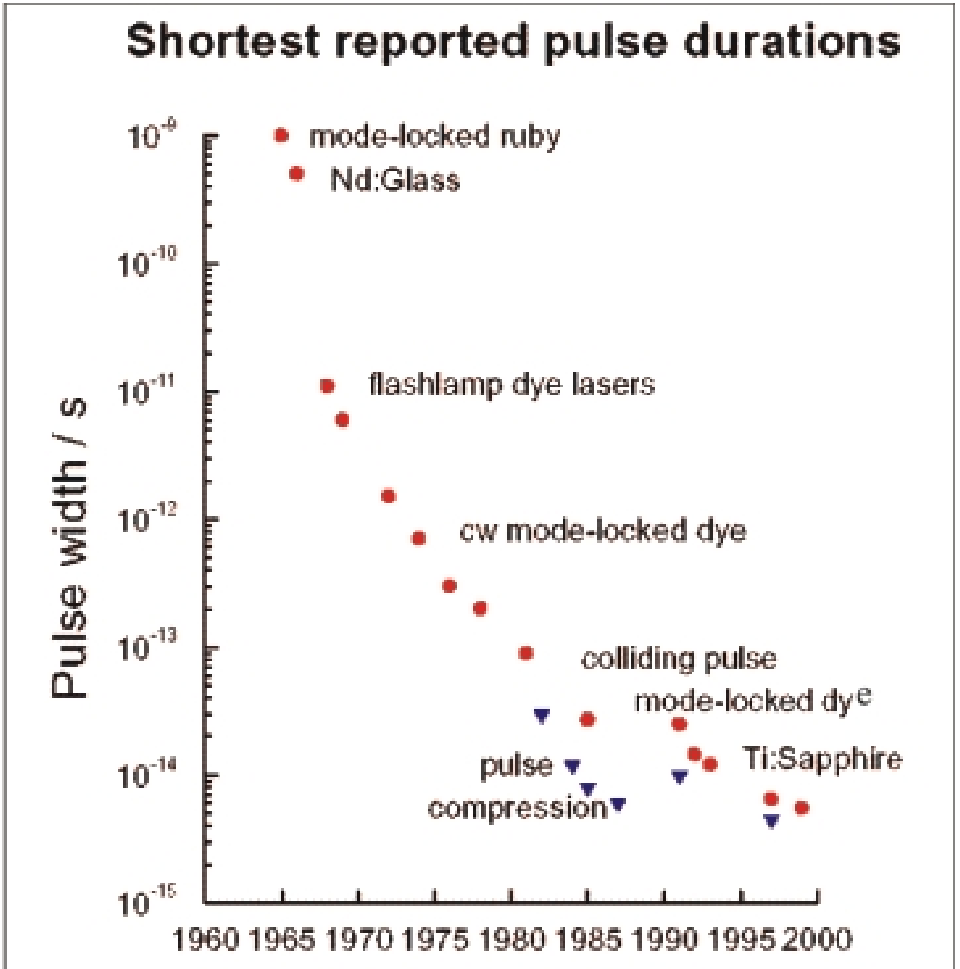


Fig. 1.1.8: The development of the short pulse laser techniques

The solid state Nd:YAG laser is the most popular for surface cleaning. This laser operates at the fundamental wave-length of 1064 nm and also the second, third and fourth harmonic at 532 nm, 355 nm and 266 nm can be obtained, respectively.

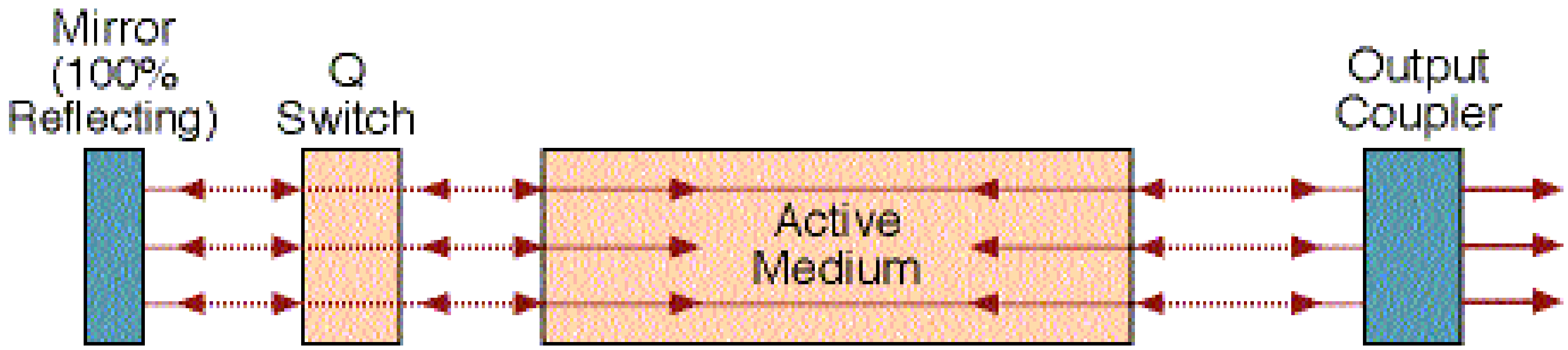
Some types of laser used in surface cleaning

Type of laser	Wavelentgh (nm)	Pulse energy (J)	Rep rate (pps)
Ruby	694	1	1
Nd:YAG	1064 / 532 / 355 / 266	1 / 0.7 / 0.3 / 0.1	1-200
CO2	10600	100 W (CW)	CW
Er:YAG	2094	0.5	20
Excimer	193 / 248 / 308	0.8	500

Nd:YAG laser

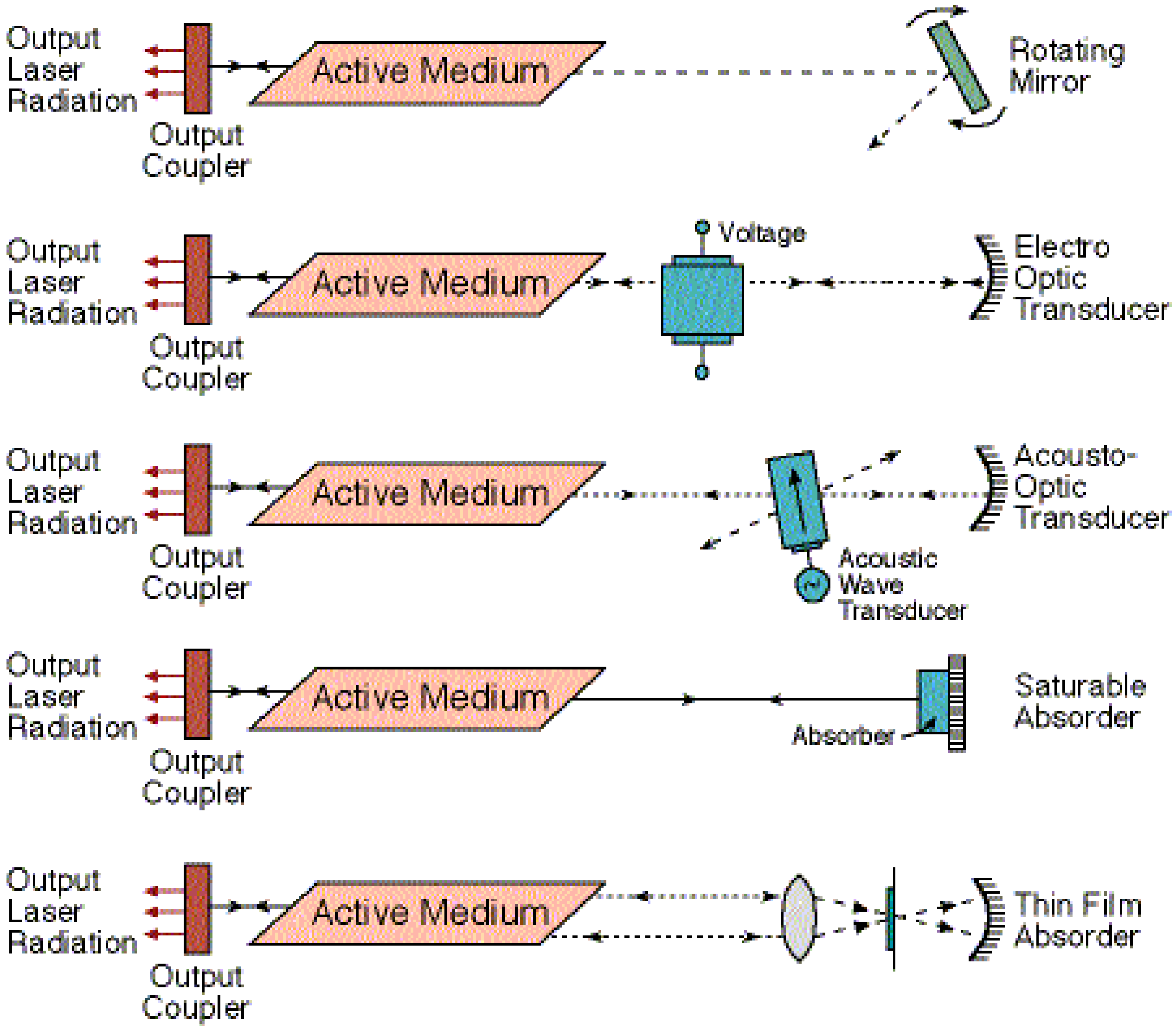
- For the pulsed regime operation, the repetition rates are in the range 10-100 Hz or even up to several kHz
- Pulse energies above 1 J can be routinely obtained at 1064 nm.
- The duration of non-processed pulses (free-running regime) are in the ms range, and shortening of the pulse duration by three orders of magnitude, i.e. down to several nanoseconds, is commonly achieved by means of the laser cavity Q-switching technique.
- As the pulse energy is temporally compressed in such a "giant" pulse, the Q-switched Nd:YAG laser emits peak powers (instantaneous power) in the range of 100 MW - 1 GW.

Q:Switching

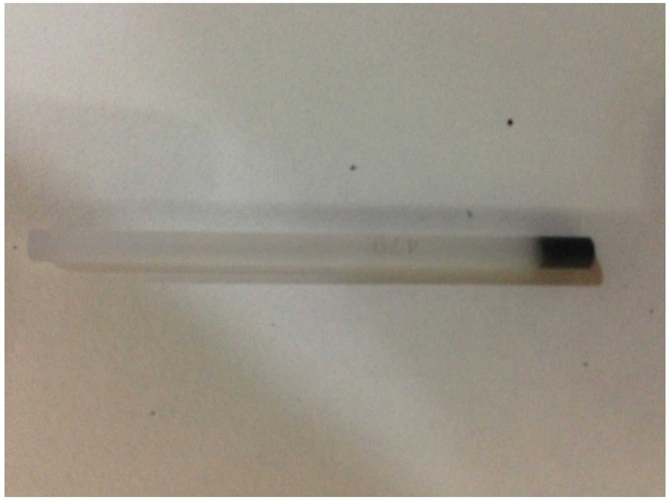


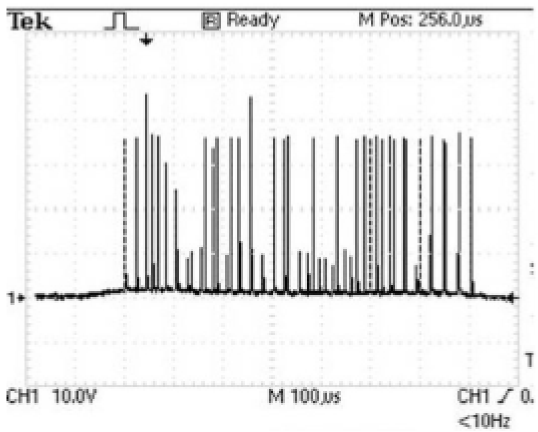
Q switch acts as a shutter that can be open suddenly inside the laser cavity.
When the switch is closed, the laser radiation can not move between the mirrors. Lasing can not occur, but the excitation continue to pump energy into the cavity.

Different Methods for Q Switch



Using saturable absorber in monolithic Nd:YAG laser cavity





Advantages:

- Compact
- No misalignment of mirrors


Laserblast
1000

An example: FotoClean Nd:YAG laser

Parameters:

- Max. average laser power: 80 W
- Pulse duration: 10 ns – 180 μs
- Spot diameter : 1,5 cm
- Max. pulse repetition rate: 100 pps
- Volume: 40 x 90 x 85 cm
- Weigth: 60 Kg

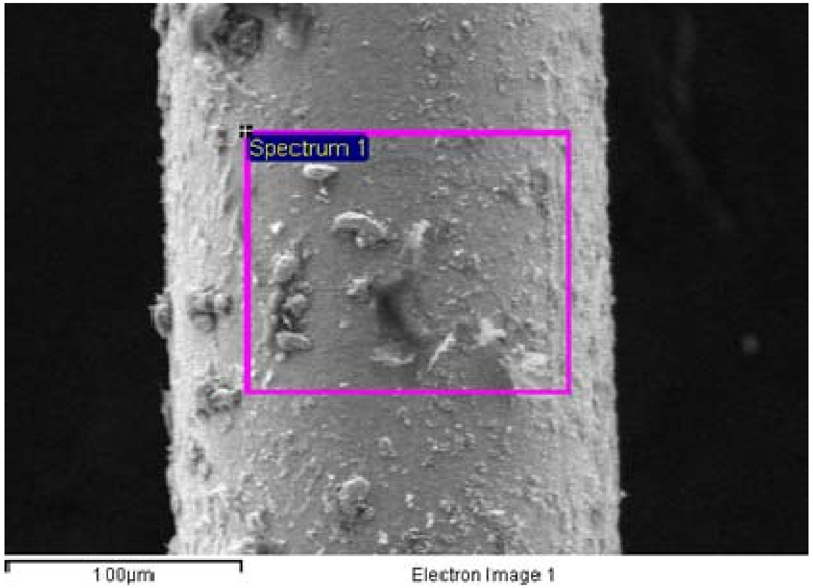
Case studies (an advance)

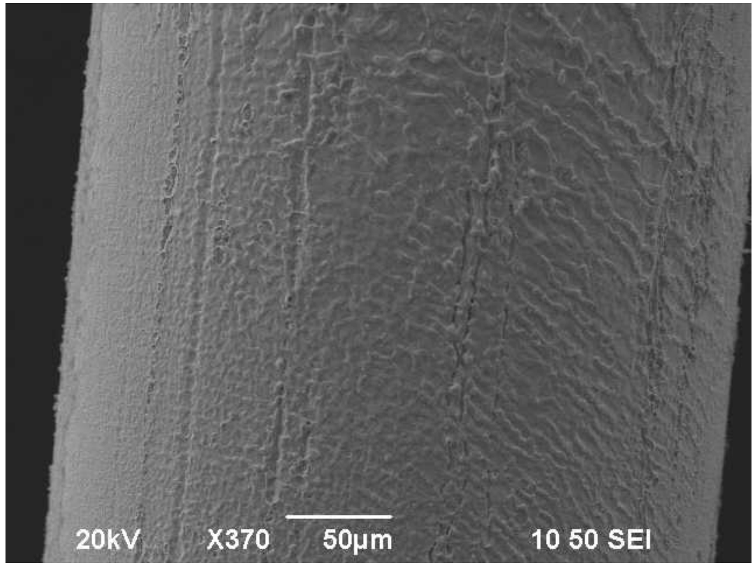
Laser cleaning of glass and ceramic isolators

Micro-cleaning of Tantalium capacitor electrodes

- 2 mm length
- 0.2 mm diameter
- Process speed: 10 capacitor per second
- Laser alignment
- Photo-acoustic sensor for process monitoring

Micro-cleaning of capacitor electrodes

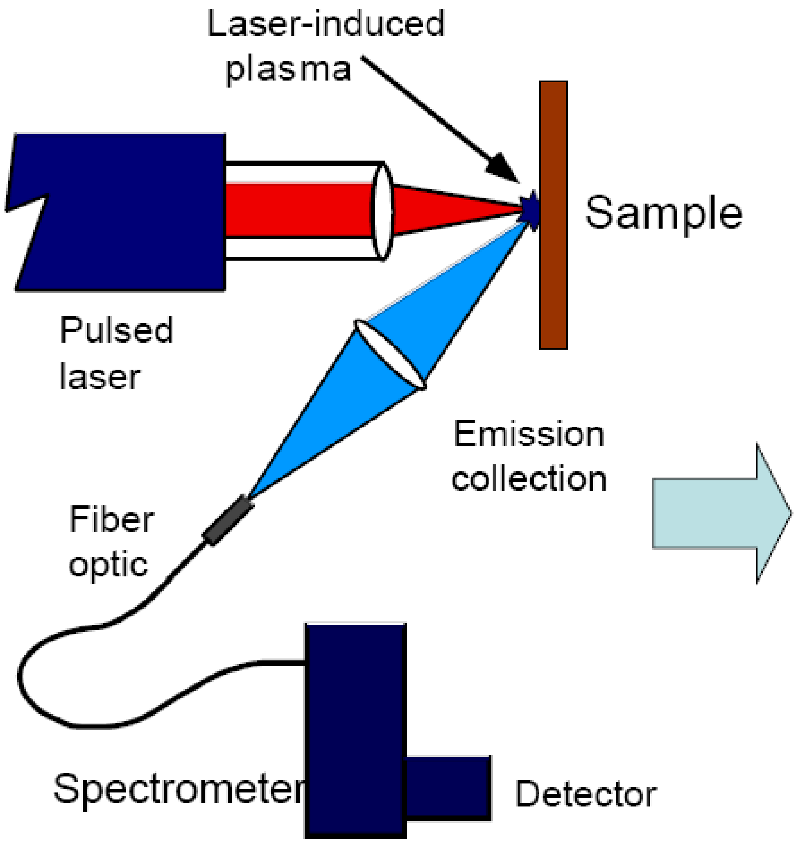


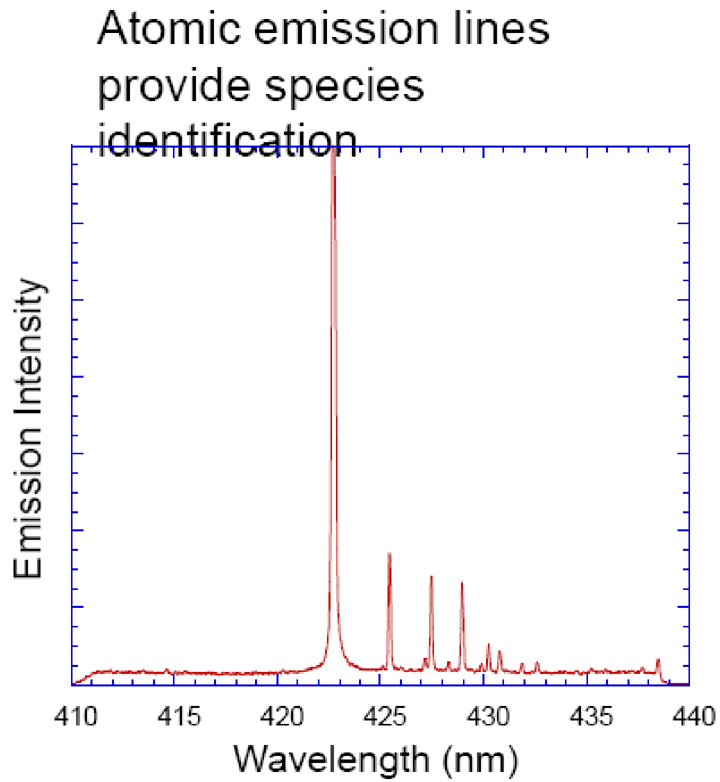


- Before and after laser cleaning

MONITORING METHODS

Laser Induced Breakdown Spectroscopy





- LIBS is an analytical technique that enables the determination of the elemental composition of materials on the basis of the characteristic atomic emission from a plasma produced by focusing a high-power laser on a material.

- LIBS has been used in a wide variety of analytical applications for the qualitative, semi-quantitative and quantitative analysis of materials

LIBS Advantages

- Express analysis
- No sample preparation
- Portable
- Sample size/amount needed: Less than one microgram
- External and clean excitación source: Laser

- The analysis by LIBS starts with the deposition of light energy in a small volume of material (less than 0.1 mm3) and within a short time period (5 - 20 ns).
- This rapid energy deposition is achieved by focusing a laser pulse on the surface of a solid target (the object analyzed) and results, through a series of processes, to material breakdown and generation of a micro-plasma plume.

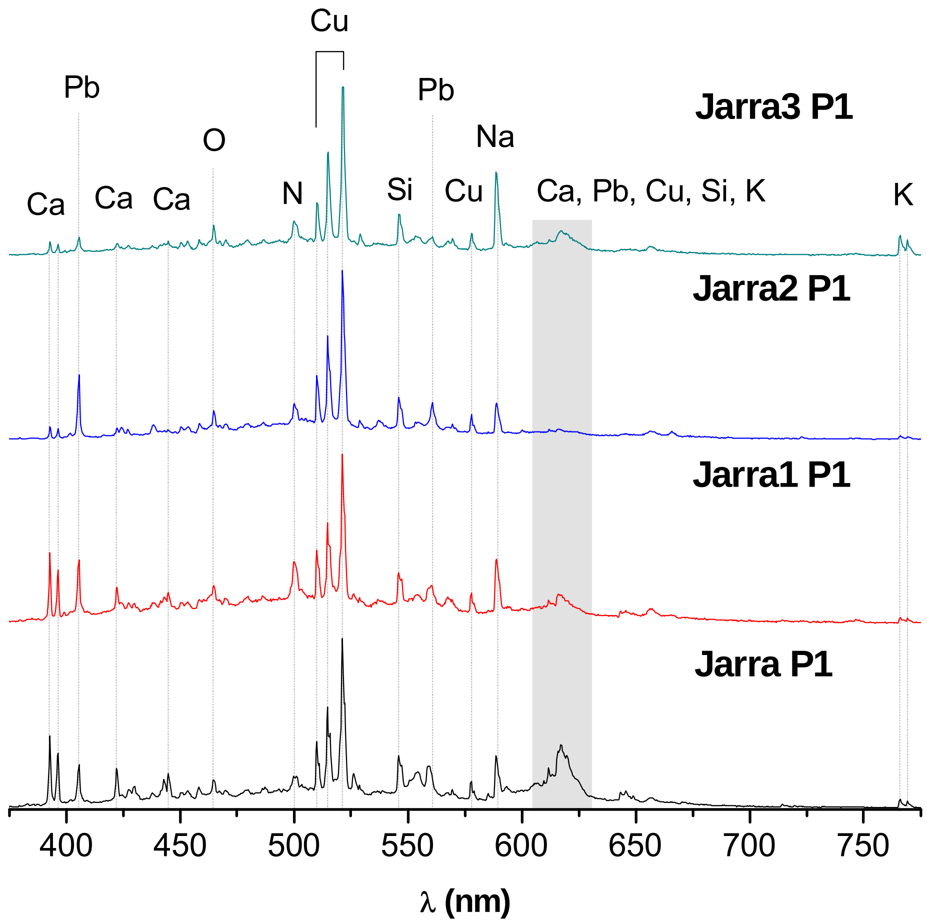
Monitoring of Laser Cleaning by LIBS

- Such control of laser cleaning can, in certain cases, be achieved by monitoring the optical emission resulting from material ablation.

- In essence, LIBS measurement is carried out simultaneously with the laser cleaning.

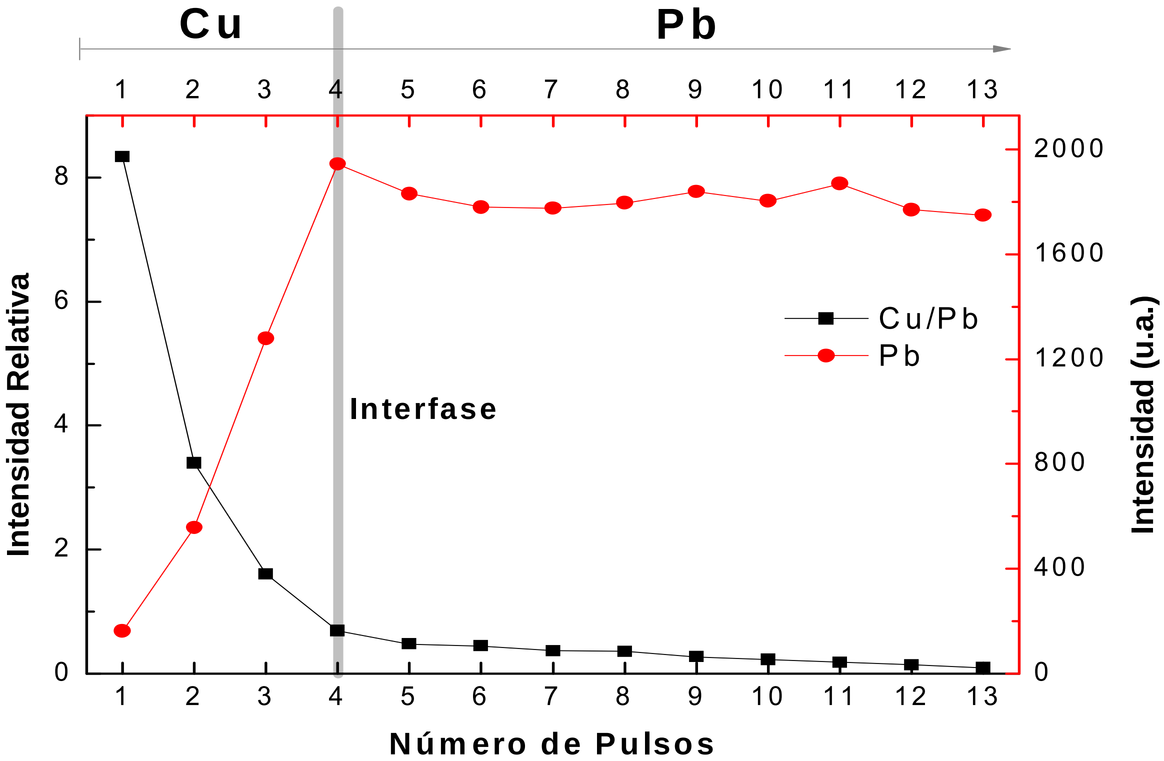
- If differences between the LIBS spectra of the contamination layer to be removed and the cleaned surface exist, then it is in principle possible to control the process of cleaning by a simple algorithm implemented on a computer.

LIBS compositional monitoring of metal artwork



LIBS spectra obtained for four different points on the metal jug.

Depth profiling



In-depth profiles for Ca(II) 392.83 nm, Pb(I) 405.56 nm, Cu(I) 521.24 nm, Si(II) 546.04 nm, Na(I) 588.67 nm and K(I) 765.93 nm as function of number of pulses

Monitoring laser surface cleaning by photo-acoustic (next conference)

Conclusions

- Laser cleaning is an efficient tool for precise removal of surface contaminant
- Using appropriate methods like LIBS or photo-acoustic is possible to control de removal process
- They are many well established applications as laser cleaning in artworks restoration,
- Novel applications are under development (next conference)


LABORATORIO
DE
TECNOLOGÍA

THANK YOU

Announcement:

Demonstrations of LIBS experiments in Adriatico Guest house in the night after dinner (no mandatory only for who interested)