CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

CSIC

"LASERS IN CONSERVATION; ANALYSIS AND DIAGNOSIS WITH LASER INDUCED FLUORESCENCE AND LASER INDUCED BREAKDOWN SPECTROSCOPY"

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Curso de Conservación del Patrimonio II,
Sevilla, Marzo 2007

Laser analytical techniques in Art/ Archaeology

- Laser Induced Fluorescence (LIF)
- Laser Induced Breakdown Spectroscopy (LIBS)
- Raman Spectroscopy/Microscopy
- Laser ablation TOF-MS
- Laser ablation ICP-MS

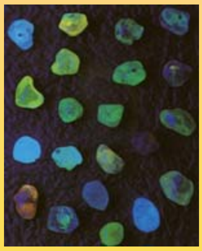
Laser Induced Fluorescence LIF

http://www.nationmaster.com/encyclopedia/Fluorescence

- **Basic principles**
- **Main features**
  - Versatile, non-destructive,
  - Applicable in situ,
  - Sensitive, capable of detecting organic and inorganic materials,
  - Microscopic and imaging implementation,
  - Performed *in situ* and in remote sensing

http://www.raphael-medieval.org

- **Instrumentation**
  - Excitation with continuous or pulsed laser sources,
  - Detection system
- **LIF in Art and Archaeology**
  - Pigments
  - Binding media and varnishes
  - Biological contaminants



http://www.diamondsourceva.com/Education/diamonds-fluorescence.asp

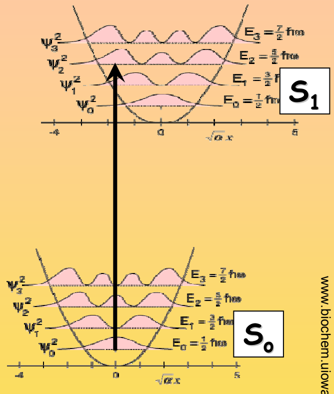
LIF Basic principles

- **Molecular emission spectroscopic technique: molecules that absorb UV light and enter into excited electronic states will eventually return to the ground electronic state. They can do this 'radiatively' or 'non-radiatively'.**
- **Molecules that return via radiative means (i.e. by emission of light) are said to 'fluoresce'.**
- **Fluorescence is effectively the opposite of absorption.**
- **Provides information directly related to molecular structure of materials on the illuminated substrate.**
- **Fluorescence is a 3-step process...**

www.biochem.uiowa.edu/courses/99241

LIF step 1

- Molecule starts in the ground vibrational state of the ground electronic state (S_o)
- Absorbs UV light and undergoes a ‘vertical transition’, this happens very fast (10^{-15}s)
- Enters an excited electronic state.
- The excited electronic state will almost always be a ‘singlet’ (‘S’): the excited electron retains its spin.



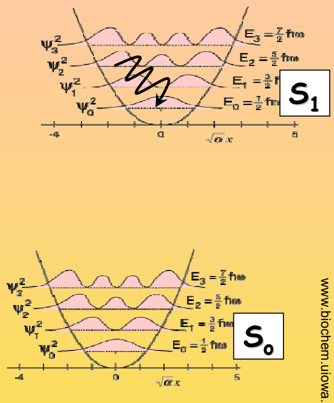
www.biochem.uiowa.edu/courses/99241

LIF step 2

- Molecule in an excited vibrational state of the 1st excited electronic state (S_1)...

  will rapidly return to ground vibrational state (~10^{-12} s)

  this process is ‘internal conversion’



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LIF step 3

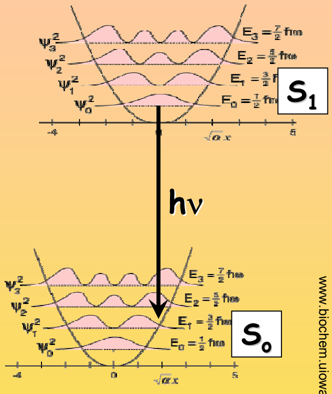
- Molecule reaches ground vibrational state of S_1...

  it will pause to consider its options (~10^{-8} s)
- Total time spent in the excited electronic state(s) is known as the 'fluorescence lifetime'
- Molecule returns to ground electronic state by:

  emitting radiation (fluorescence)

or

giving the energy to surrounding molecules (by collisions)



www.biochem.uiowa.edu/courses/99241

LIF: Fluorescence intensities

- Similarly to absorption, the molecule can return to a range of different vibrational energy levels
- Each will result in emission of a different wavelength of light
- The Franck-Condon principle allow us to understand the relative intensities of fluorescence emissions (as with absorption bands...)

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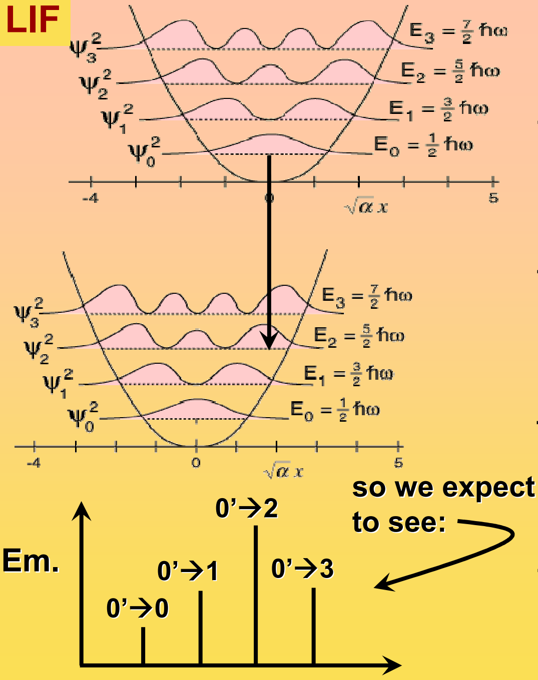
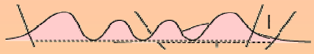
LIF



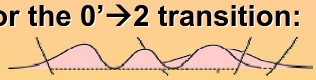
so we expect to see:

for the 0'→3 transition:



some overlap

for the 0'→2 transition:

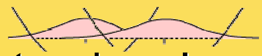


lots of overlap

for the 0'→1 transition:

some overlap

for the 0'→0 transition:



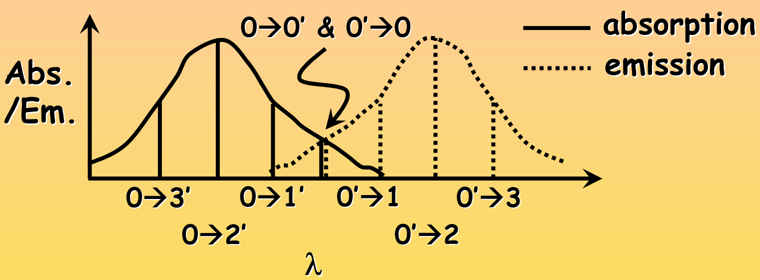
not much overlap

www.biochem.uiowa.edu/courses/99241

LIF spectra

We expect mirror image spectra

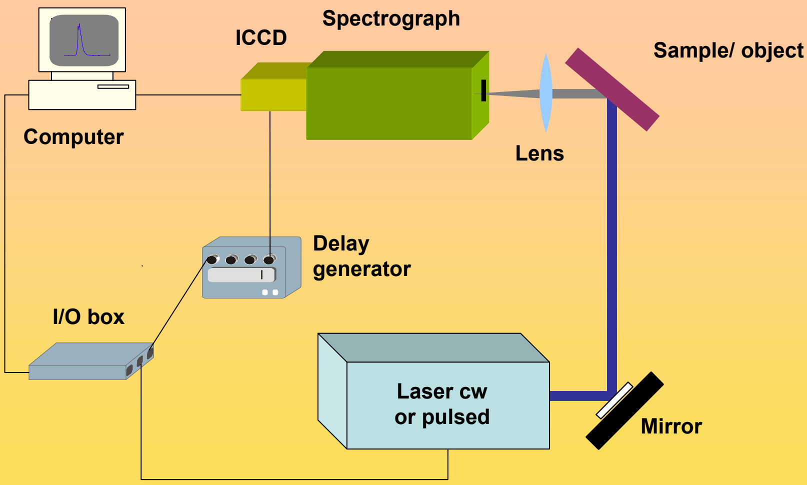
- We can combine our ideas about absorption and emission intensities into a single graph:



- in the above graph, 0→0' and 0'→0 transitions occur at the <u>same</u> wavelength
- general microenvironment effects can change this...

www.biochem.uiowa.edu/courses/99241

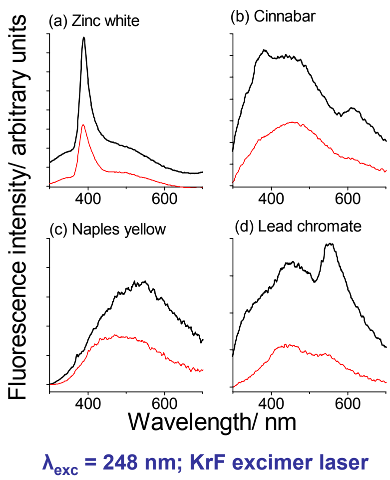
LIF set up



LIF spectra of model paint samples

R. Teule et al, J. Cult. Herit. 4 (2003) 209s.
Castillejo et al J. Cult. Herit. 4 (2003) 257s.

LIF spectra of unvarnished tempera systems

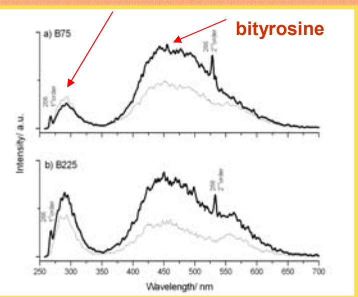


Castillejo et al Anal. Chem.2002, 74,4662-4671

LIF spectra from painting media

LIF spectra of gelatines

aromatic amino acid
residue tyrosine

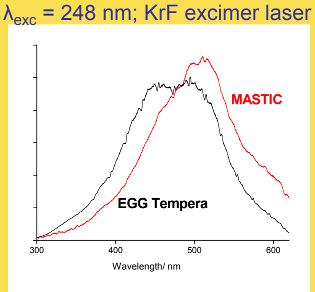


Castillejo et al, J. Phys. D 2005 submitted

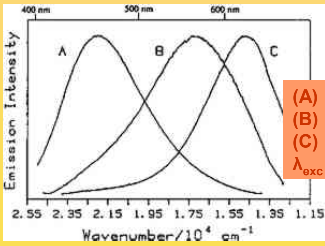
Fluorescence emission discriminates different types of organic paint media

LIF spectra of tempera and mastic

λ_{exc} = 248 nm; KrF excimer laser



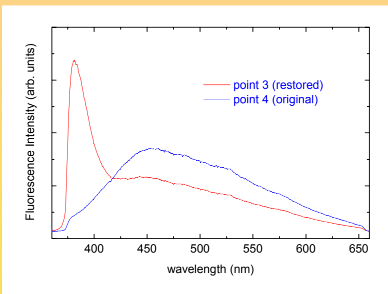
Emission from the **lipid** component of the paint



(A) casein,
(B) egg yolk
(C) linseed oil,
λ_{exc} = 363.8 nm

JAIC 1991, 30, 89 to 104

LIF spectra of 18th century oil painting



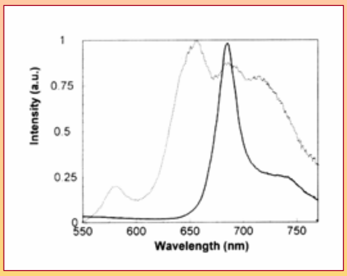
Fluorescence emission differentiates between retouching and original paint

λexc = 355 nm; Nd:YAG laser

Courtesy D. Anglos, IESL FORTH

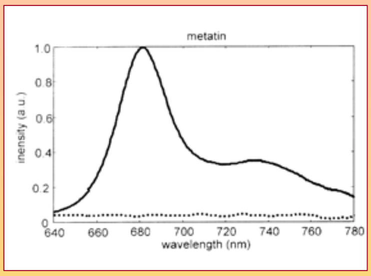
LIF of biodeteriogens on marble and stone

Exc : 488 nm; cw Ar ion laser



Fluorescence from green algae and cyanobacteria

Exc : 355 nm; Nd:YAG laser



Fluorescence from green algae on marble before and after treatment with biocide

Remote mapping of algae distribution and stone differentiation on cathedral facades using a laser radar

L. Pantani et.al. CNR-IROE, Florence, Italy; S. Svanberg et.al. LLT, Lund, Sweden

Fluorescence LIDAR

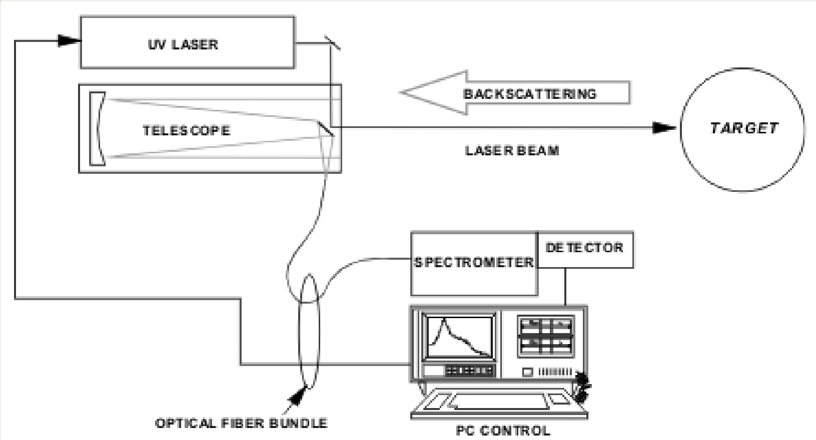


Figure 3.6.1: Block diagram of a fluorescence lidar.

LIF lidar imaging of historical monuments

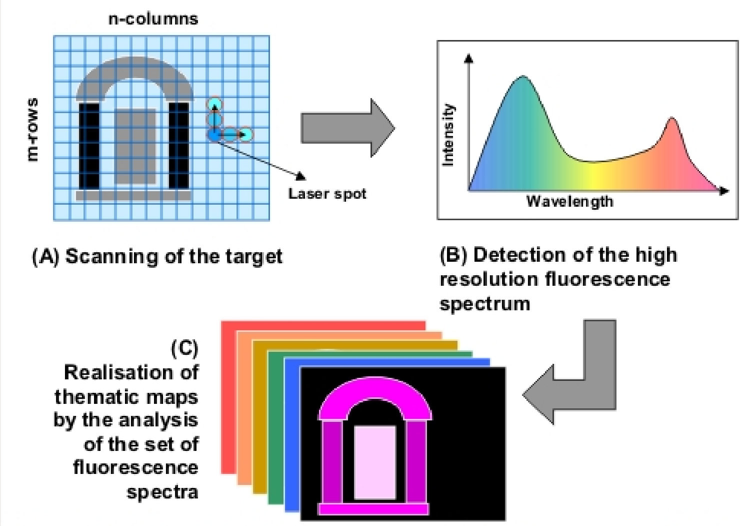
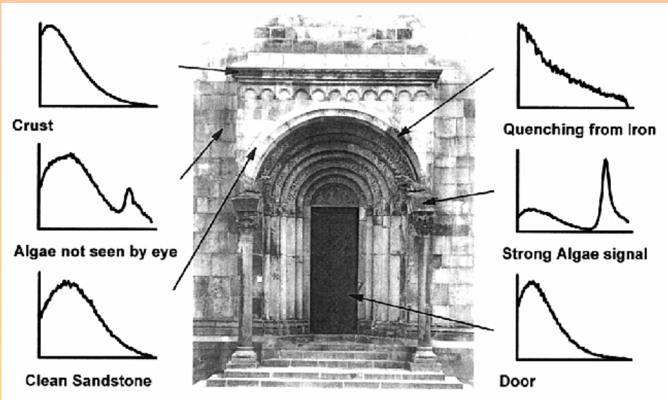


Figure 3.6.3: Basic principles of lidar hyper-spectral imaging on monuments [17].

LIF lidar imaging of historical monuments



Northern portal of Lund cathedral

Multispectral fluorescence imaging

Excitation: 355 nm

Distance: 60 m

Emission spectra recorded at different “points”

P. Weibring et al, Applied Optics **40**, 6111 (2001)

Fluorescence lifetime imaging, FLIM

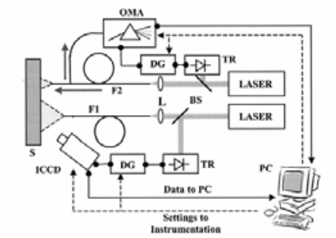


Fig. 1. Basic schematic of the fluorescence experimental setup: LASERs, pulsed N_2 lasers; BS, beam splitter; L, focusing lens; F1, silica fiber; F2, silica fiber bundle, ICCD, time-gated intensified camera; TRs, optical trigger circuits; DGs, delay generators; S, sample; PC, personal computer.

1 April 2004 / Vol. 43, No. 10 / APPLIED OPTICS

Fig. 4.5.1: Picture of a damaged painted surface.

© Comelli et al., *in: "Handbook on the Use of Lasers in Conservation and Conservation Science", 2006.*

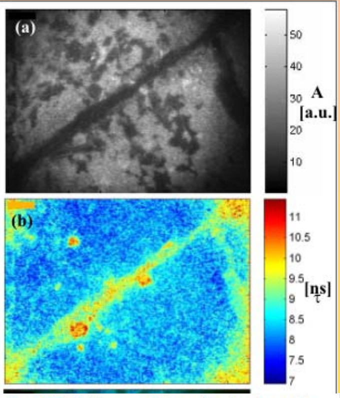


Fig. 4.5.2: FLIM maps of the painted surface of Figure 4.5.1; (a) amplitude; (b) lifetime; (c) HSV.

© Comelli et al., *in: "Handbook on the Use of Lasers in Conservation and Conservation Science", 2006.*

Fluorescence lifetime imaging, FLIM

FLIM on Michelangelo's David

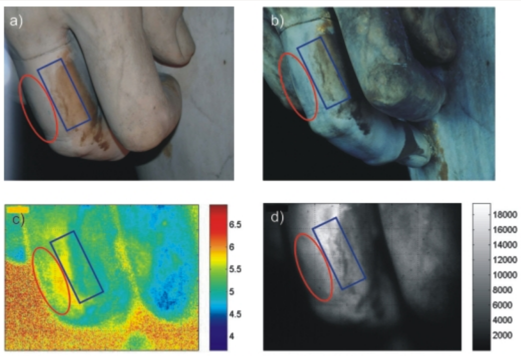
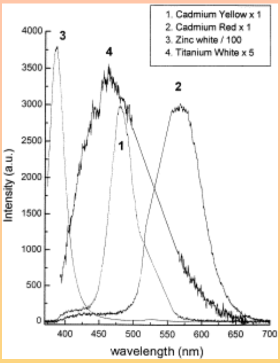


Fig. 4.5.6: a) VIS light image of the fingers of the right hand. b) UV image; c) fluorescence lifetime map and d) fluorescence amplitude map of the same area.

© Comelli et al., *in: "Handbook on the Use of Lasers in Conservation and Conservation Science", 2006.*

Different types of overlaid materials identified: wax residues, concentrated in small drops or permeated into the marble surface; salt deposits, mainly composed of gypsum, calcium oxalates and particulate matter; organic contaminants (not precisely identified), concentrated in small areas or spots.

LIF of artworks

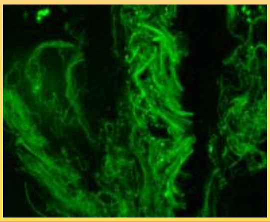


Borgia et al, Appl. Surf. Scie. 127-129 (1998) 95.

Drawbacks: broad bands, not enough analytical capacity

Increased by:

- **Lifetime measurement**
- **Imaging**
- **Multiphoton excitation with fs lasers**



Three-photon laser scanning confocal microscopy image of fibrin in blood vessels, http://www.cas.ucf.edu/chemistry.

Multiphoton excitation for high resolution mapping of substrates, much smaller probed volume than that in one photon excitation. Well-demonstrated advantage in the characterization of cells and tissues. Foreseen to be equally powerful in characterization of artworks

Laser Induced Breakdown Spectroscopy (LIBS)

- **Basic principles**
- **Main features**
- **Instrumentation**
- **LIBS in CH analysis**

LIBS

Basic principles

Atomic emission spectroscopy providing elemental analysis information

Focusing of pulsed laser on solid surface

- Atomisation/ ionization and excitation
- Detection of atomic/ ionic fluorescence

$$I_\omega^{ik} = N \frac{h\omega}{8\pi^2} \frac{g_i A_{ik} e^{-(E_i/k_B T_e)}}{Z(T_e)}$$

Main features

- Elemental analysis information (qualitative, quantitative)
- Practically non-destructive
- Sensitivity, Specificity
- High spatial resolution, Depth profiling
- Applicable in-situ (no sampling or sample preparation)
- Speed of analysis
- Compact, transportable instrumentation
- Work on site

Transportation of archaeological objects and samples is subject to strict regulations

LIBS

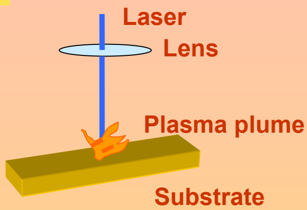
Basic principles

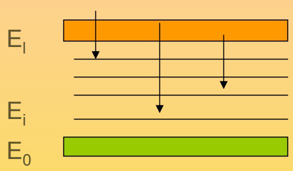
Temporal regimes of LIBS

1. 0-10 ns.
Plasma ignition:
Thermal or
multophoton ionization

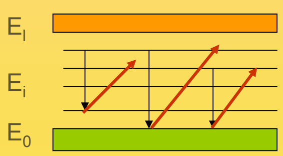
2. Some 100 ns:
Recombinación

3. Some μs:
Relaxation





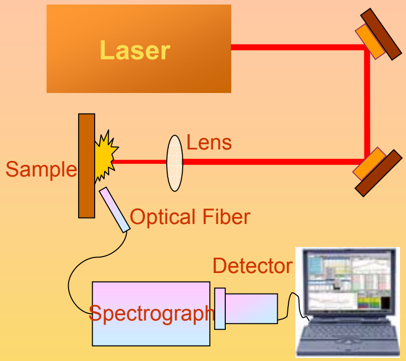
Unspecified emission

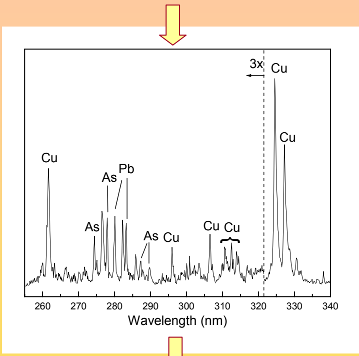


Atomic and molecular emissions

Laser-Induced Breakdown Spectroscopy (LIBS)

Spectral information from *micro-plasma* generated when a *laser pulse* probes the sample/object surface



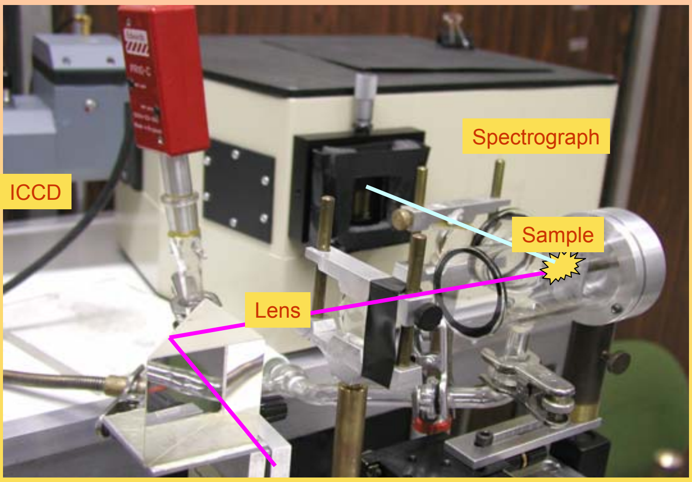


Characteristic Spectral Lines → Which elements?

Line Intensity → How much of each?

Courtesy D. Anglos

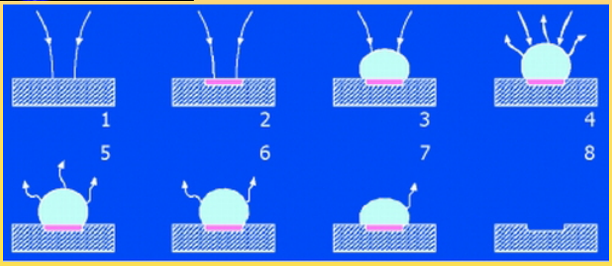
LIBS set up



Effects of LIBS analysis on object surface

Ablation plumes, ablation craters

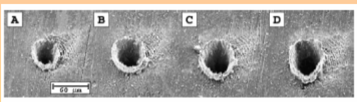
355 nm laser ablation plume on CaF_2



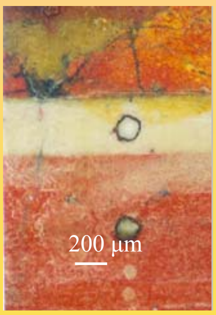
Effects of LIBS analysis on object surface

Ablation craters

On Steel, 800 nm, 140 fs laser



K. L. ELANDet al., APPLIED SPECTROSCOPY 55, 2001

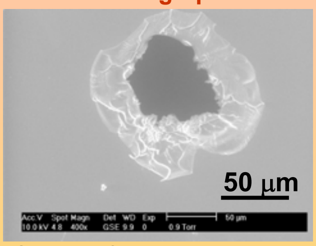


D. Anglos, IESL, FORTH

Craters formed on painting in a depth profiling study

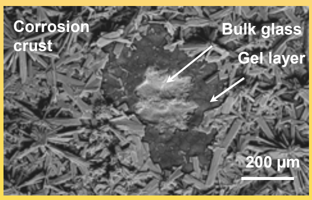
50 laser pulses (355vnm, 10ns) at each spot

SEM micrographs



Gelatine film 1064 nm, 6 ns

Oujja et al, J.Phys. submitted, 2005

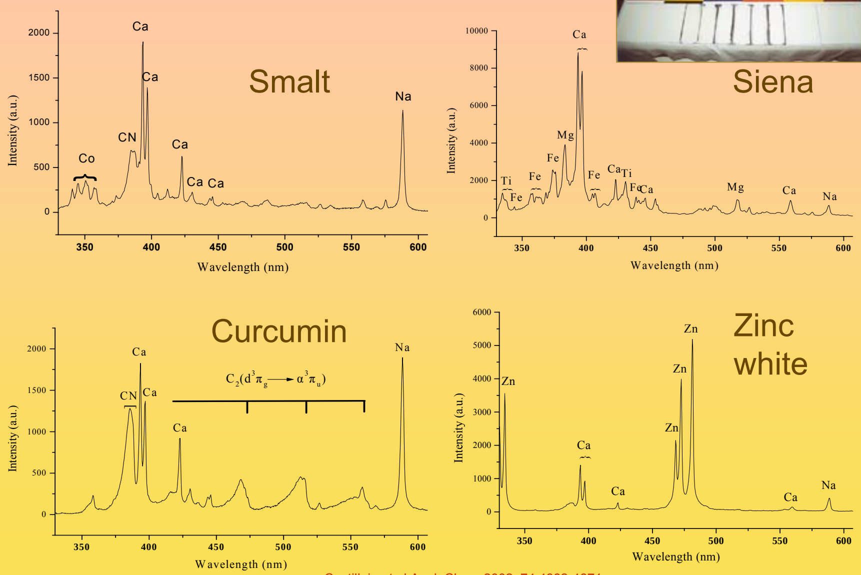


Corroded glass, 266 nm nm, 6 ns

Carmona et al, Spectrochim Acta, B 2005

LIBS spectra of model paint samples

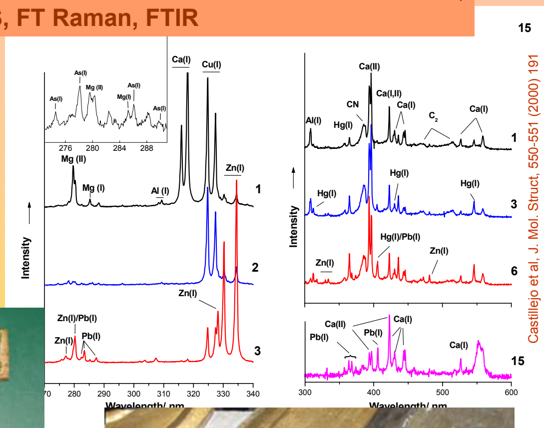
λexc = 248 nm; KrF excimer laser



Castillejo et al Anal. Chem.2002, 74,4662-4671

Análisis LIBS de pigmentos en policromías en subtrato lígneo

Identificación de materiales mediante LIF, LIBS, FT Raman, FTIR



Castillejo et al, J. Mol. Struct, 550-551 (2000) 191

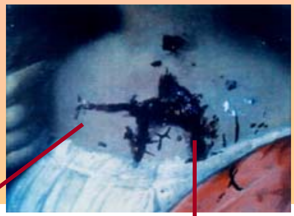
Catedral de Teruel, Mudéjar ss 13.

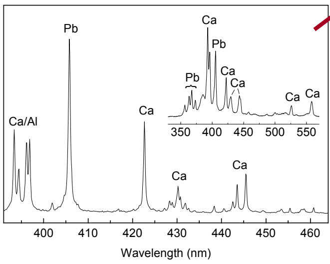
Capilla del Castillo de Mesones de Isuela, Zaragoza Mudéjar-Italiano, Gótico, s. 14

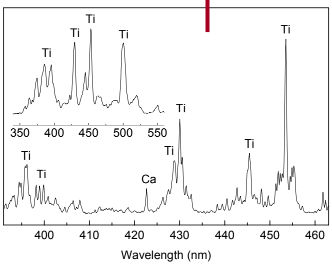
Iglesia de Escatrón, Zaragoza, Policromía Rococó

Identificación por LIBS de pigmentos en tabla al óleo del s. XVIII

Copia de "La Bella", Palma Vecchio, s. XVIII.







Pigmento original:
blanco de plomo ($Pb(OH)_2 \cdot 2PbCO_3$)

Retoque: blanco de titanio (TiO_2)

Appl. Spectrosc. 55 (2001) 186A

Laser cleaning of terracotta decorations of the Portal of Palos of the Cathedral of Seville.

- **Determine optimum laser cleaning conditions whithout substrate damage.**
- **Analysis of materials and chemical modifications induced by laser irradiation (Colorimetry, LIBS and Raman microscopy).**

Before restoration **After**

Tympanum of portal
Terracotta decorations were severely soiled and appeared covered by thick layers of black dirt, strongly attached to the surface, and constituted by soot from urban emissions and some organic matter.

Castillejo et al.
Journal of Cultural Heritage 2005

Laboratory study on terracotta sample

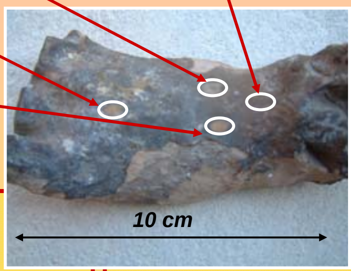
Raman
G: gypsum $CaSO_4 \cdot 2H_2O$
A: anhidrite $CaSO_4$

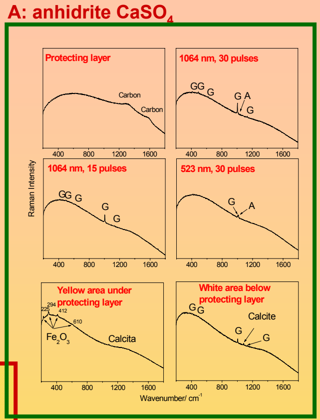
Z-c: 532 nm, 103 mJ, 30 p

Z-d: 266 nm, 61 mJ, 200 p

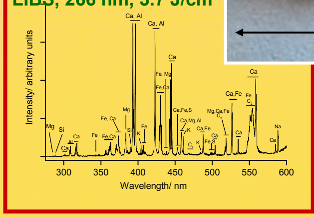
Z-a: 1064 nm, 102 mJ, 30 p

Z-b: 1064 nm, 102 mJ, 15 p

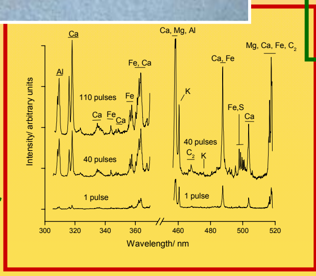




LIBS, 266 nm, 3.7 J/cm²



LIBS on protecting layer



Castillejo et al, J. Cult. Herit. October 2005.

Laser cleaning of terracotta decorations of the Portal of Palos of the Cathedral of Seville.

- Irradiation at 1064 nm with a Q-switched Nd:YAG laser was more effective than the harmonic wavelengths of 532 or 266 nm.
- LIBS and Raman microscopy gave information on the composition of terracotta and identified the presence of a protective layer made of gypsum and calcite.
- As detected by Raman spectroscopy, laser irradiation caused the elimination of the carbon component of the soiling layer and the appearance of an anhydrite component in the laser irradiated gypsum layer applied over the terracotta substrate for protective purposes.
- Local heating of the surface caused by laser irradiation at 1064 nm, the laser wavelength used for restoration of the portal, might be responsible for a process of partial dehydration of gypsum into anhydrite

LIBS analysis of pottery

Terra Sigillata fine tableware produced in Roman times and characterized by a red sintered slip.

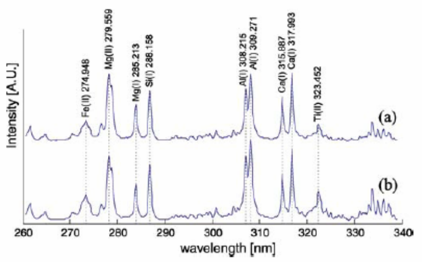


FIGURE 1 LIP spectra in the region from 260 nm to 340 nm obtained by 355 nm-laser irradiation on (a) Hispanic sample, H5 and (b) Gaulish sample G3

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Applied Physics A
Materials Science & Processing

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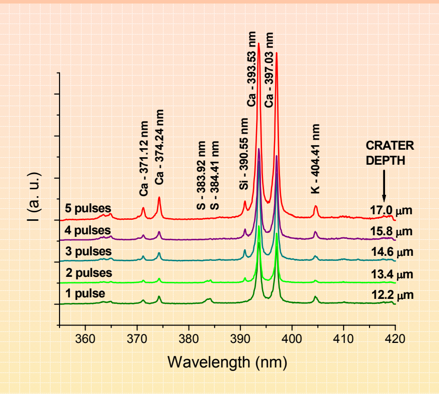
LIPS and linear correlation analysis applied to the classification of Roman pottery Terra Sigillata

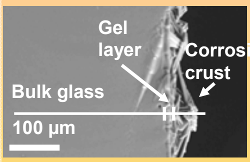
Dpto. Enseñaria Industrial II, Universidade da Coruña, 15403 Ferrol, A Coruña, Coruña, Spain

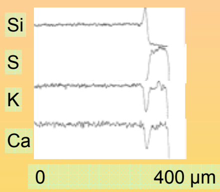
Ascription of the provenance of ancient pottery

Identificación de capas de corrosión en vidrios históricospor LIBS



SEM and EDX analysis





Good agreement LIBS- SEM/EDX

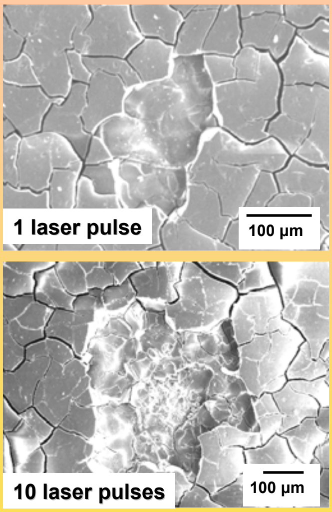
Layer identification:

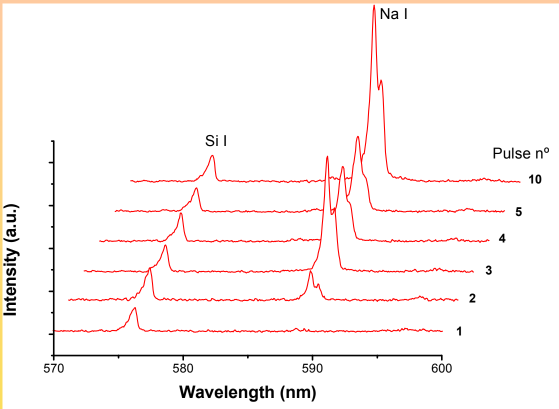
- Corrosion crust, sublimated with the first pulse, gypsum ($CaSO_4 \cdot 2H_2O$) and syngenite (K2Ca(SO_4)2·$2H_2O$) crystals.
- Gel layer, cracked area, destroyed after the the second pulse, indicates the presence of Si.
- Bulk glass unaltered in the following pulses.

Carmona et al, Spectrochim Acta, B 2005

Identification of corrosion crusts in historic glasses by LIBS

SEM micrographs of glass with acid –based corrosion layer





LIBS spectra after succesive laser pulses on same area

Carmona et al, Spectrochim Acta, B submitteB 2006

LIBS-lidar

Remote imaging laser-induced breakdown spectroscopy and remote cultural heritage ablative cleaning
S.Svanberg and col.

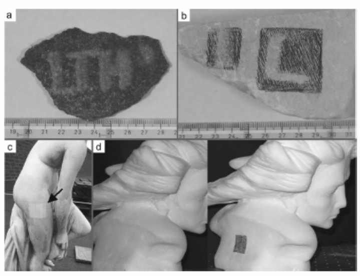


Fig. 4. Remote laser ablative cleaning of, a, mortar; b, alabaster; c, a replica of an Italian statue with the arrow indicating the 100 cm^2 cleaned area; d, a statue made of Carrara marble after and before cleaning.

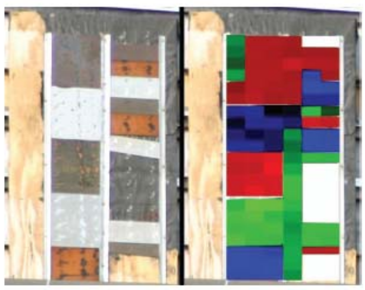
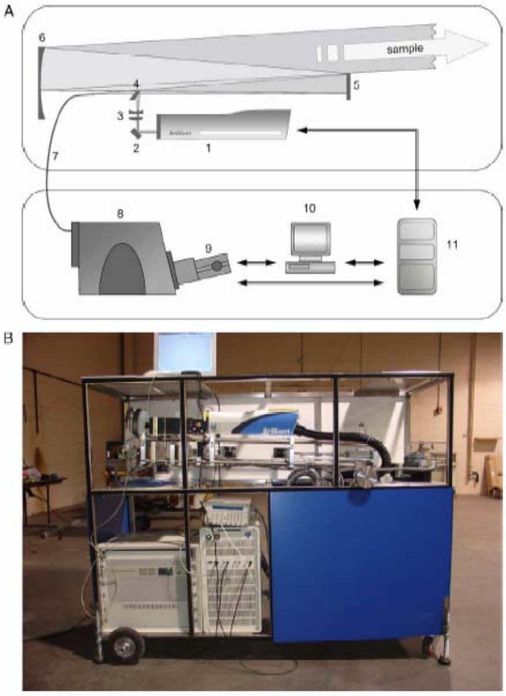


Fig. 3. LIBS imaging of metal plates, with the target on the left and a false-color coded identification image on the right with copper (red), aluminum (green) and iron (blue). The classification has good correspondence to the spots where the laser has hit the target. The big plates on the left are (from top to bottom) copper, stainless steel, brass, aluminum, and iron. The stainless steel is classified as iron and the brass as copper, as they contain large amounts of these substances. The vertical profiles holding the plates are made of aluminum and are classified accordingly. Note that the pixels are much larger than the spot size and that the scanning resolution is quite low. The beam scanning has been slightly tilted, and the middle spot in the upper rows does not hit the aluminum profile but instead hits the metal plates. White parts correspond to nonmetallic surfaces.

OPTICS LETTERS / Vol. 30, No. 21 / November 1, 2005

LIBS-lidar



Spectrochimica Acta Part B 61 (2006) 88 – 95

LIBS-lidar

Design, construction and assessment of a field-deployable laser-induced breakdown spectrometer for remote elemental sensing
J. Laserna and col.

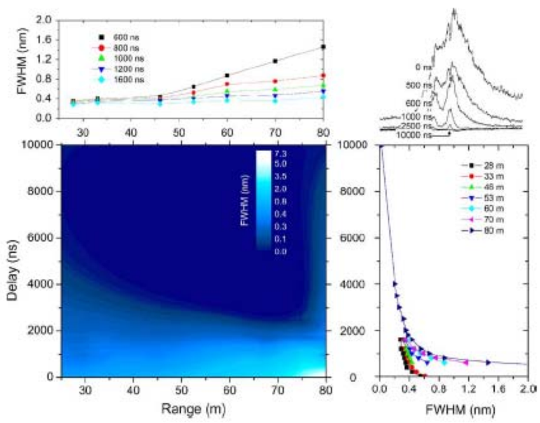
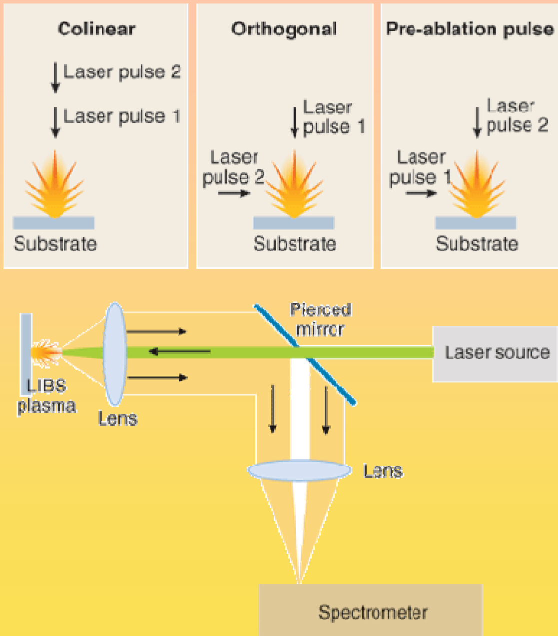


Fig. 5. Behavior of the 396.152 nm Al(I) line width versus acquisition delay and working range. On the top-right, the line profiles at different acquisition delays for a 80-m range have been plotted.

Spectrochimica Acta Part B 61 (2006) 88 – 95

New developments in LIBS

Improving sensitivity, reducing matrix effects by double pulse LIBS



Laser Focus World, Feb 2006

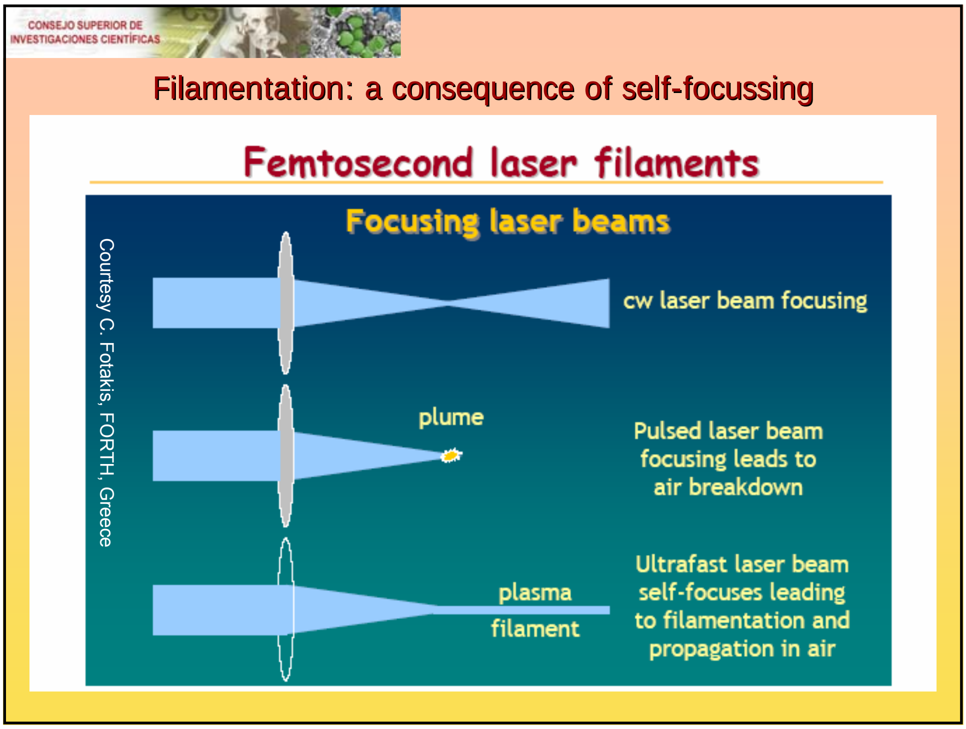
New developments in LIBS

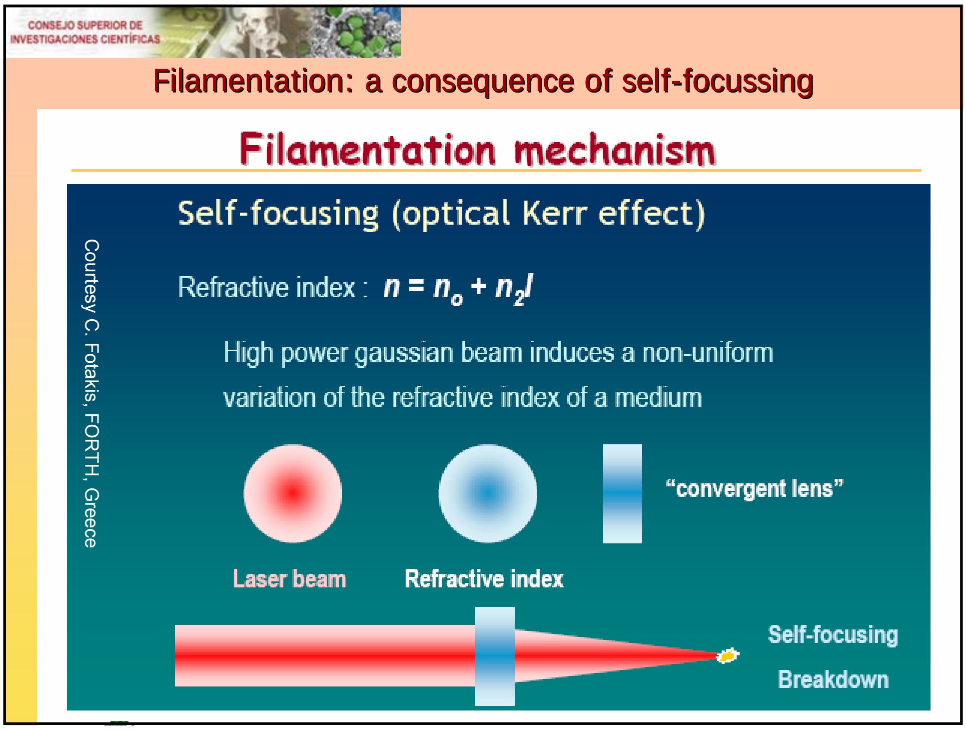
Femtosecond LIBS

The fs advantage for LIBS

- Shorter thermal diffusion lengths allow controlled material removal with rates of less than 10 nm per shot
- fs lasers suitable for fast in-depth profiling of multilayered samples in sub-μm range.
- Implementation of temporal pulse shaping and optimisation procedures for an improvement of the properties of the ablated material for different analytical techniques.

Aluminium target. Comparison ns - fs


CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
Filamentation: a consequence of self-focussing
Femtosecond laser filaments
Focusing laser beams
cw laser beam focusing
plume
Pulsed laser beam focusing leads to air breakdown
plasma filament
Ultrafast laser beam self-focuses leading to filamentation and propagation in air
Courtesy C. Fotakis, FORTH, Greece


CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS
Filamentation: a consequence of self-focussing
Filamentation mechanism
Self-focusing (optical Kerr effect)
Refractive index : $n = n_o + n_2 I$
High power gaussian beam induces a non-uniform variation of the refractive index of a medium
"convergent lens"
Laser beam
Refractive index
Self-focusing
Breakdown
Courtesy C. Fotakis, FORTH, Greece

Filamentation: a consequence of self-focussing

Filamentation mechanism

But :

Ionization of air counteracts self-focusing : $n \rightarrow n - n_p$

"divergent lens"

$n_p = n_e(I) / n_{cr}$

A self-sustained filament is formed

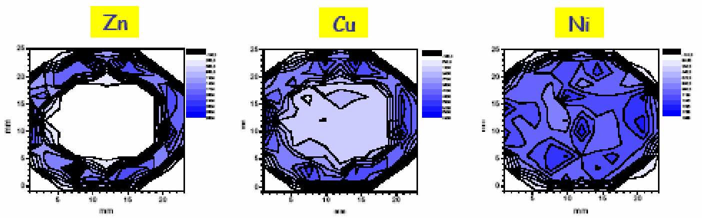
Propagation in air is possible for several kilometers

Courtesy C. Fotakis, FORTH, Greece

Remote and in-situ analysis

Mapping with fs-LIBS

Compositional mapping of EURO coin from a distance of 10 m away



Remote elemental mapping of large surfaces can be achieved with very good spatial resolution determined by the filamented beam diameter

C. Fotakis, IESL - FORTH

LASER INDUCED BREAKDOWN SPECTROSCOPY AND FLUORESCENCE

- LIF and LIBS are advanced tools for analysis and diagnosis in conservation.
- LIF is non-destructive and provides information on the molecular composition.
- LIBS is micro destructive, tells about elemental constituents. Possible stratigraphic analysis.
- Developments/ needs:
  - Incorporation of advanced laser analytical and diagnosis techniques to the scenario of artwork conservation (fs, multipulse, remote LIBS).
  - Cheap, compact, integrated systems for in situ, remote analysis and diagnostics.

CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS

CSIC

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