LIBS for deep sea applications

Javier Laserna

Departamento de Química Analítica
Universidad de Málaga

http://laser.uma.es

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

LIBS goes everywhere…

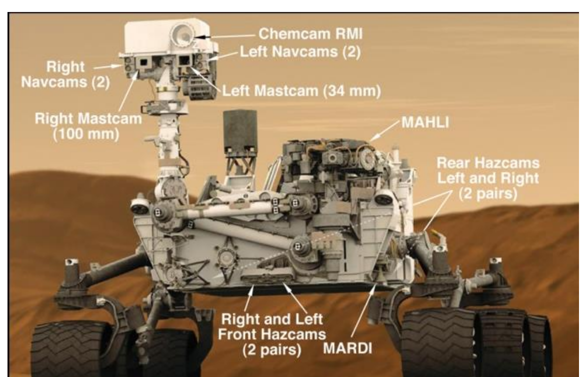
Desert

Tunnels

LIBS

Factories

Urban environment



Planets

Underwater analytical technologies

UNIVERSIDAD DE MÁLAGA

- ► **Raman spectroscopy** S. White et al. Geochem. Geophys. Systems 2006
- ► **X-Ray fluorescence** J. Harten et al. J. Marine Chem. 2008
- ► **Mass spectrometry** S. Short et al. J. Am. Soc. Mass Spectrom. 2001
- ► **LIBS**

Bow Railing of the *Titanic*
Courtesy*: National Geographic Society*

focal point review **Appl. Spectrosc. 2012**

UNIVERSIDAD DE MÁLAGA

XIN ZHANG
KEY LAB OF MARINE GEOLOGY AND ENVIRONMENT INSTITUTE OF OCEANOLOGY,
CHINESE ACADEMY OF SCIENCES,
7 NANHAI ROAD,
QINGDAO, SHANDONG 266071, PR CHINA

WILLIAM J. KIRKWOOD, PETER M. WALZ, EDWARD T. PELTZER, AND
PETER G. BREWER
MONTEREY BAY AQUARIUM RESEARCH INSTITUTE,
7700 SANDHOLDT ROAD,
MOSS LANDING, CA 95039

A Review of Advances in Deep-Ocean Raman Spectroscopy

Initial reports of underwater sparks

UNIVERSIDAD DE MÁLAGA

H. Konen and H. Finger, Z. Elektrochem. 15 (1909) 165

W. Lee Smith, P. Liu, and N. Bloembergen – Superbroadening in H2O and D2O by self-focused picosecond pulses from a YAlG:Nd laser, Physical Rev. A, 15 (1977) 2396

D. Cremers, L. Radziemski, T. Loree - Spectrochemical analysis of liquids using the laser spark, Appl. Spectrosc. 38 (1984) 721

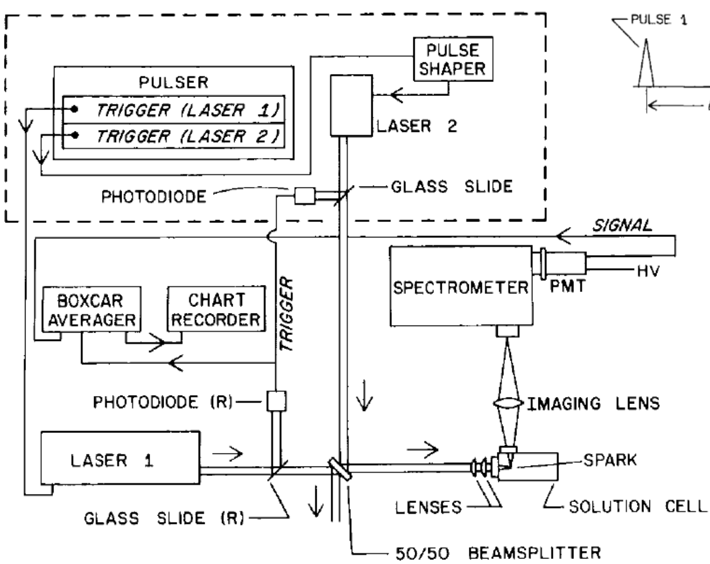
R. Nyga, W. Neu - Double-pulse technique for optical emission spectroscopy of ablation plasmas of samples in liquids, Opt. Lett., 18 (1993) 747

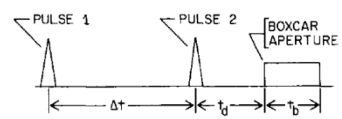
A.E. Pichahchy, D.A. Cremers, M.J. Ferris - Detection of metals underwater using laser-induced breakdown spectroscopy, Spectrochim. Acta Part B, 52 (1997) 25

A.E. Pichahchy, D.A. Cremers, M.J. Ferris
Detection of metals underwater using laser-induced breakdown spectroscopy, Spectrochim. Acta Part B, 52 (1997) 25

Table 1
Comparison of masses ablated from metal samples using the RSS and RSP

Sample	Conditions	Mass ablated per pulse/ng	Pulse energies (E_1/E_2)/mJ
1100 Aluminum	RSS under water	320 ± 80	216/0
1100 Aluminum	RSP under water	1200 ± 220	212/140
Brass	RSS under water	658 ± 82	216/0
Brass	RSP under water	1343 ± 131	212/140
Brass	RSS in air	36 ± 27	205/0
Brass	RSP in air	232 ± 83	201/133





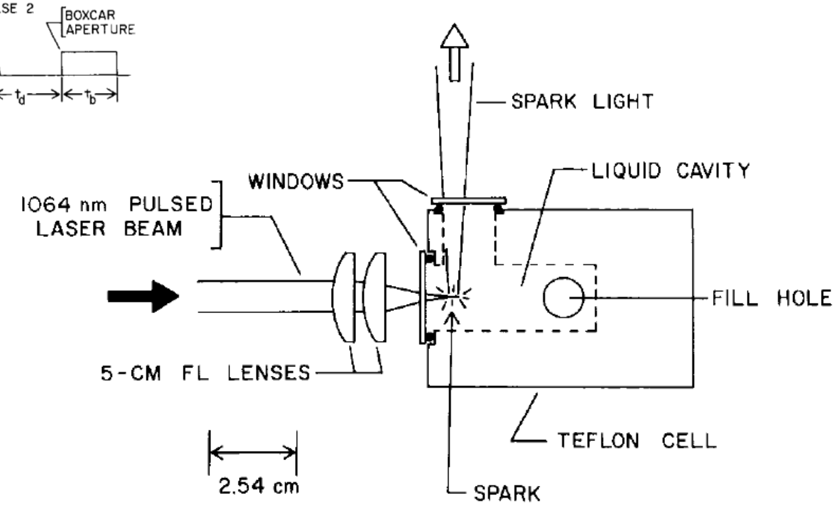


Table 2
Temperature (T) and electron density (n_e) of plasmas generated on Ti metal located under water and in air using the RSS and RSP.[a]

Type	Location	T/K	n_e/ × 10^{18} cm^{-3}	E_1/mJ	E_2/mJ
RSS (single pulse)	Under water	–[b]	–[b]	84	–
RSP (double pulse)	Under water	8,880	21	84	194
RSS (single pulse)	Air	7,180	1.3	277	–
RSP (double pulse)	Air	7,710	3.8	84	178

[a] Here t_d, t_b, and Δt were 0.99, 15, and 30 μs, respectively. The timing sequences shown in Fig. 2d and c were used for the RSS and RSP, respectively.
[b] T and n_e not measured because Ti emission lines were not observed.

Table 3
Detection limits for LIBS analysis of metals located under water using the RSP[a] (double pulse)

Analyte/ref. element	Wavelengths/nm	C_L^b/ppm	Corr. coeff.	RSD[c]%	Range[d]/ppm
Cu/Fe	324.75/330.60 + 330.63	520	0.95	7.3	510–6,600
Cr/Fe	425.44/432.58	367	0.98	4.0	1020–20,950
Mn/Fe	403.xx[e]/404.58	1200	0.99	6.0	2000–13,800
Si/Fe	288.16/281.33	1190	0.99	9.1	550–14,600

[a] Here t_d, t_b, and Δt were 0.99, 15, and 30 μs, respectively. For Mn and Cr: $E_1 = 199$ and $E_2 = 146$ mJ. For Si and Cu: $E_1 = 82$ and $E_2 = 159$ mJ. The timing sequence used is shown in Fig. 2c.
[b] $C_L = 3s/m$ where s is the standard deviation of six replicate measurements from the sample with the lowest analyte concentration, each measurement obtained by averaging 100 spectra, and m is the slope of the calibration curve. The samples were certified reference standards from the Bureau of Analysed Samples, Ltd.
[c] The RSD values listed here are the average of those obtained for measurements made at the analyte concentrations used to construct the calibration curves.
[d] The range of analyte concentrations in steel samples used to determine C_L and the RSD values.
[e] The four emission lines of Mn at 403.08/403.31/403.45/403.57 nm were not resolved.

Applied Spectroscopy, 2006

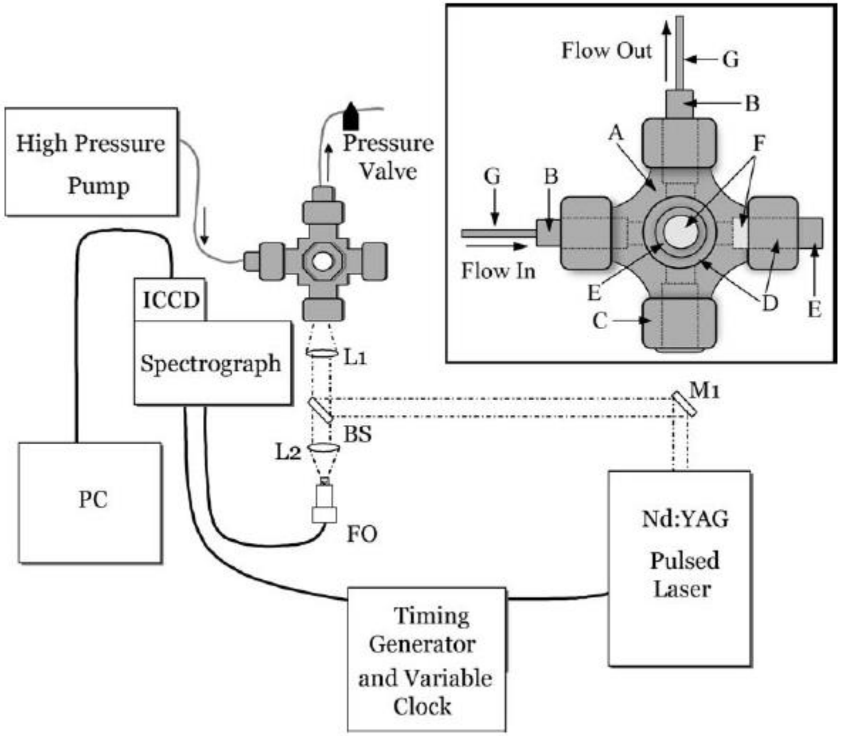
Laser-Induced Breakdown Spectroscopy of High-Pressure Bulk Aqueous Solutions

Applied Optics, 2007

Laser-induced breakdown spectroscopy of bulk aqueous solutions at oceanic pressures: evaluation of key measurement parameters

A. Michel, M. Angel, A. Chave et al.

- **Woods Hole Oceanographic Institution, Masssachusetts**
- **University of South Carolina**



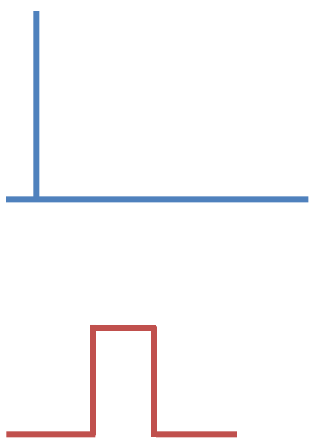
EXCITATION MODES IN LIBS

UNIVERSIDAD DE MÁLAGA

Clues for underwater LIBS of submersed solids

<u>Single pulse excitation</u>

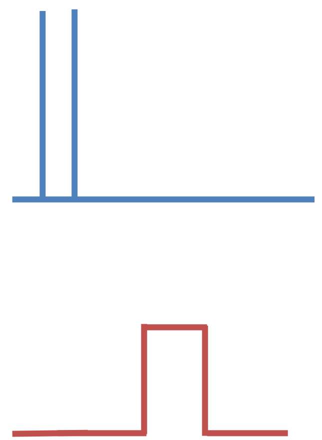
Short ns pulses



- **Simple design**
- **Efficient ablation**
- **Insufficient energy for plasma formation**

<u>Dual pulse excitation</u>

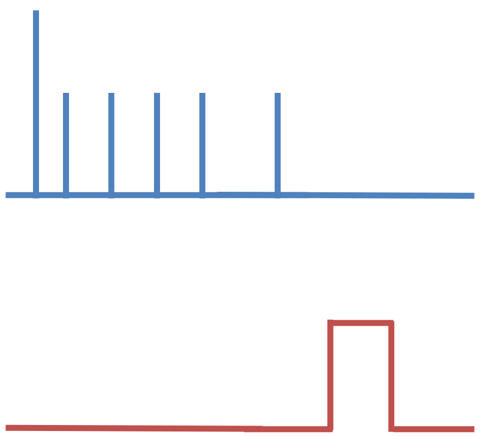
Short ns pulses



- **Difficult to maintain in extreme environment**
- **Efficient ablation**
- **Efficient plasma formation**

<u>Multi-pulse excitation</u>

Extended ns pulses

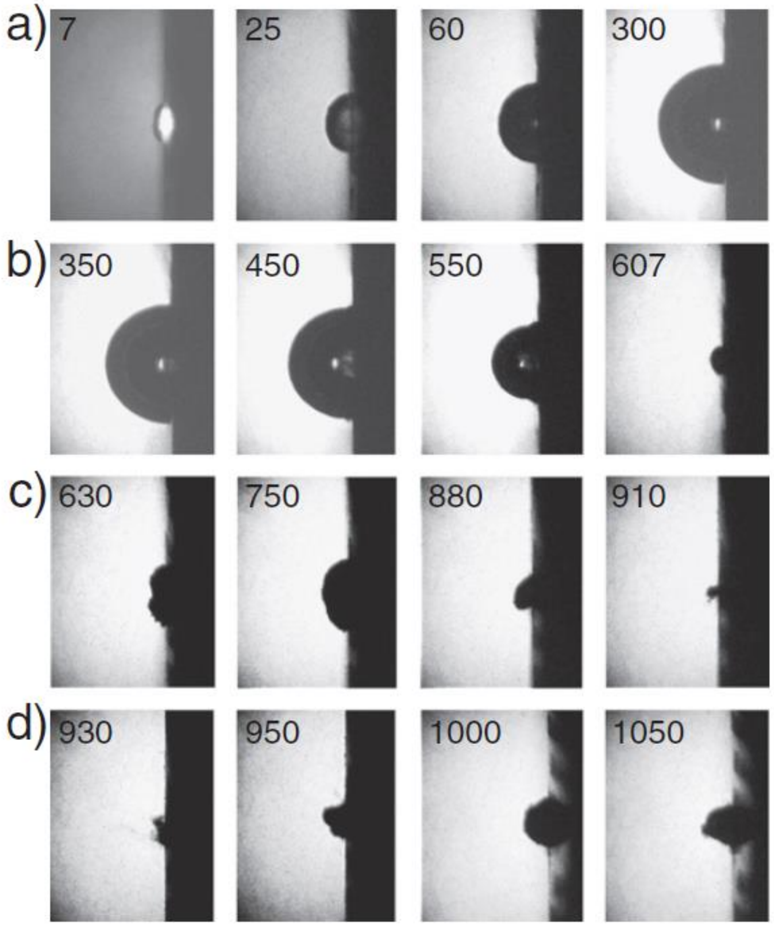


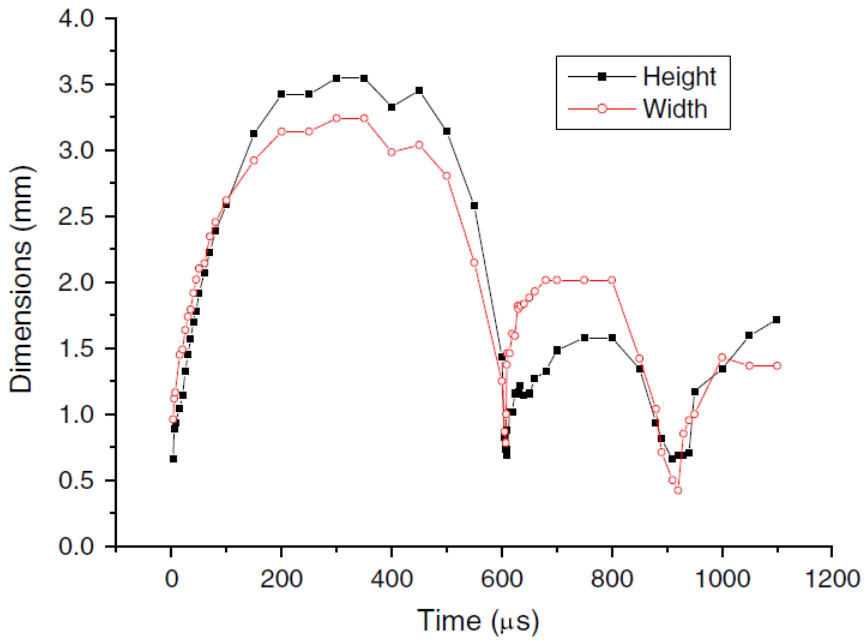
- **Simple design**
- **Large ablation rate**
- **Intense plasmas**

LIBS signal generation underwater using dual pulse excitation
V. Lazic, J.J. Laserna, S. Jovicevic
Spectrochim. Acta B 82 (2013) 42

UNIVERSIDAD DE MÁLAGA

Monopulse LIBS inside liquids





Double pulse LIBS inside liquids

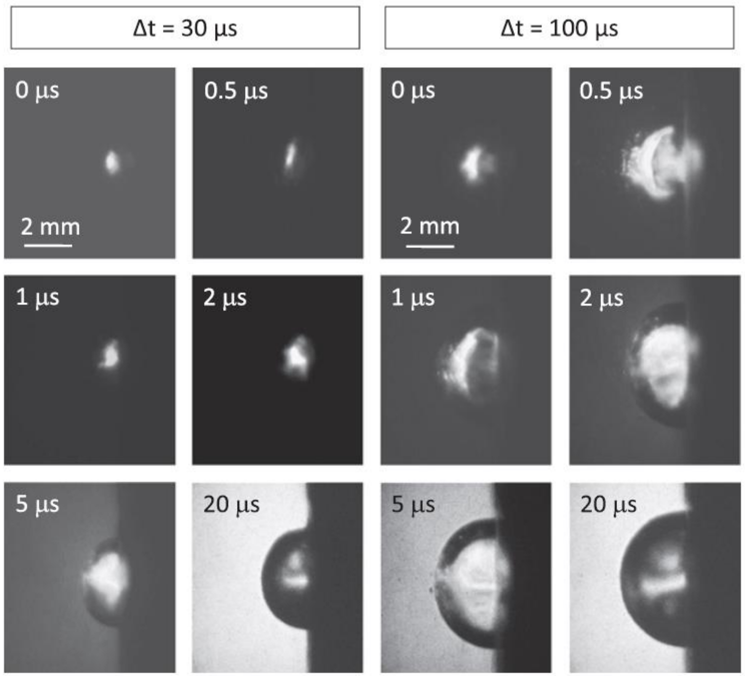


Fig. 6. Comparison between secondary plasma produced at two interpulse delays (30 μs and 100 μs) photographed at different acquisition delays from the second laser pulse. Integration time was 100 ns for delays up to 2 μs, otherwise it was 1 μs. The CCD intensification was varied from 0 (at delay 0) to the maximum.

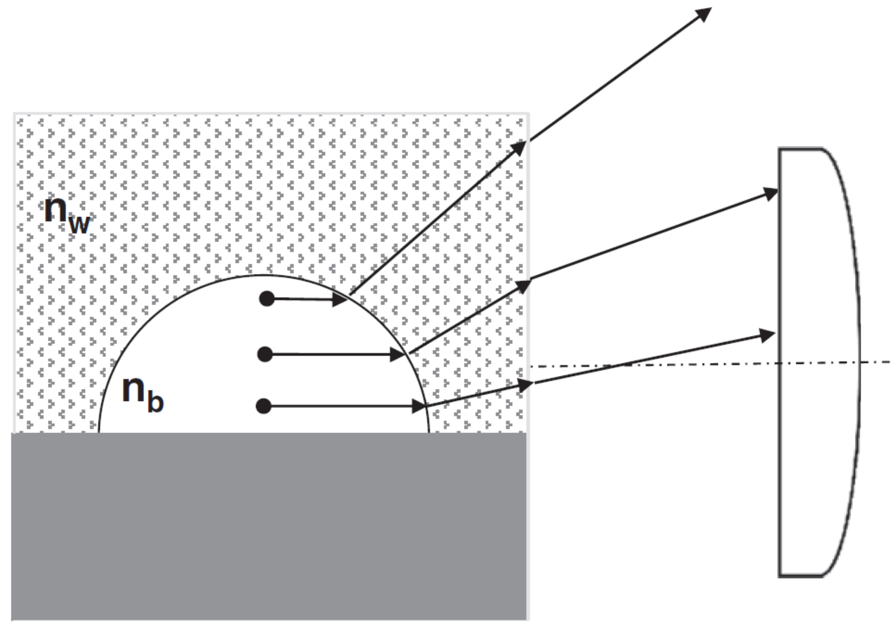


Fig. 8. Position dependent collection of the secondary plasma generated i expanded bubble – illustration.

Factors affecting the DP-LIBS signal

Factor	LIBS signal intensity	Comment
↑ Laser beam reflection from the bubble wall	↓	The contribution is very small, below 3.2% in UV-NIR range
↑ Defocusing of the laser and plasma radiation	↓	Refraction angle at the bubble wall increases
↓ Absorption of the vapor bubble	↔	Low contribution except in presence of a strong primary plasma
↑ Overall beam scattering at angles away from zero	↓	$\sim r^2$, where r is the bubble radius
↑ Snell's reflections at the bubble wall	↑	Allow the signal collection from large external plasma volume, otherwise fully deflected out of the detection system
↑ Vapor condensation inside the bubble	↓	Vapor clusters strongly scatter the second laser beam
↓ Plasma lifetime	↓	Cooling rate increases through heat exchange with the surrounding liquid
↓Reflected primary pressure wave (intensity decreases with time)	↑	Changes the refraction index of the focal volume; the peaks of the LIBS signal decrease gradually with the pressure wave attenuation

V. Lazic, J.J. Laserna, S. Jovicevic, Spectrochim. Acta B 82 (2013) 50

UNIVERSIDAD DE MÁLAGA

ELSEVIER

Spectrochimica Acta Part B 57 (2002) 1461–1471

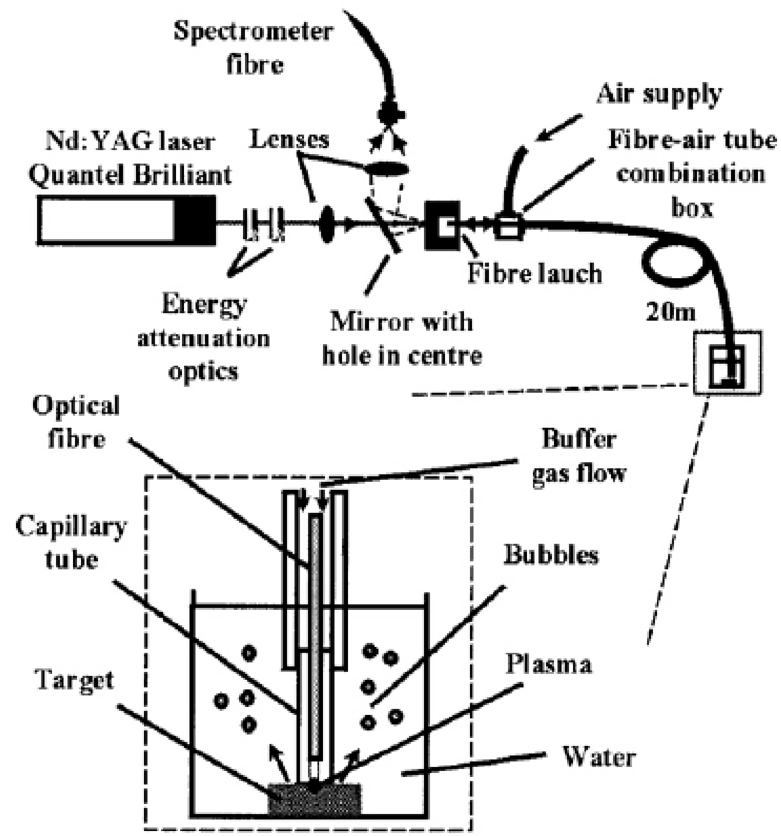
SPECTROCHIMICA ACTA PART B

www.elsevier.com/locate/sab

UNIVERSIDAD DE MÁLAGA

Single-pulse laser-induced breakdown spectroscopy of samples submerged in water using a single-fibre light delivery system

D. Beddowsa, O. Samek, M. Liska, H.Telle
University of Wales Swansea
Technical University of Brno



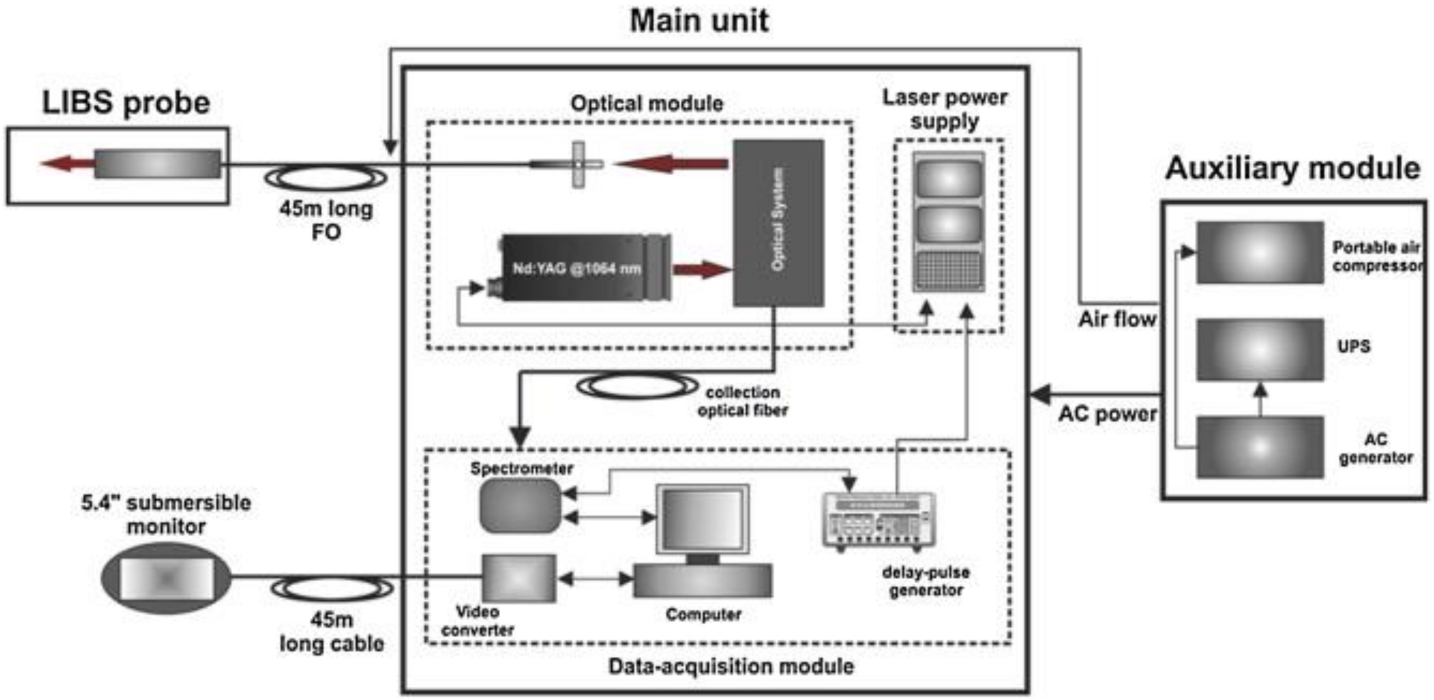


Fig. 1. Overview of the remote LIBS instrument used for the analysis of submerged archeological objects.

S. Guirado, F.J. Fortes, V. Lazic, J.J. Laserna

Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea

Spectrochimica Acta Part B: Atomic Spectroscopy, Volumes 74–75, 2012, 137–143

http://dx.doi.org/10.1016/j.sab.2012.06.032

Auxiliary module

Pressurized air supply

Power unit

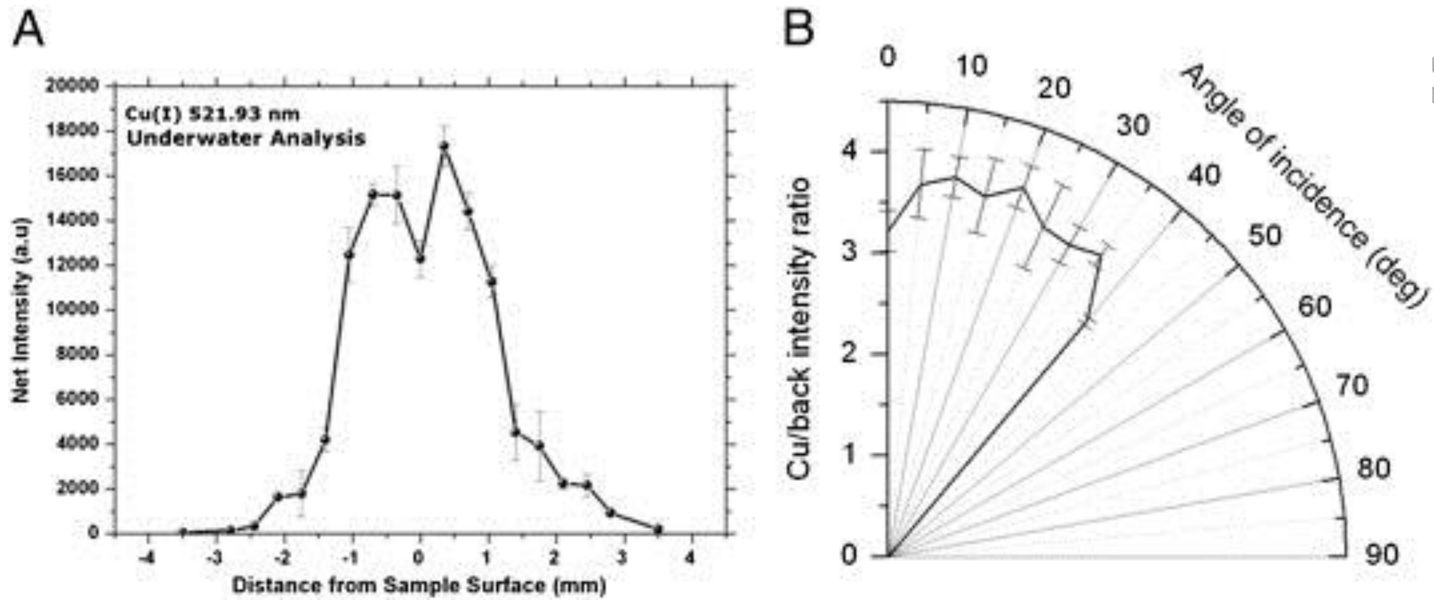


Fig. 2. Effect of operational parameters on underwater LIBS signal: A) net intensity of Cu (I) (521.93 nm) as a function of the lens-to-sample distance and B) Cu/background intensity LIBS ratio as a function of the angle of incidence between the laser radiation and the sample surface.

S. Guirado, F.J. Fortes, V. Lazic, J.J. Laserna

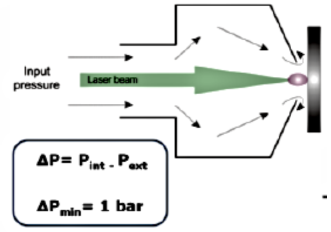
Chemical analysis of archeological materials in submarine environments using laser-induced breakdown spectroscopy. On-site trials in the Mediterranean Sea

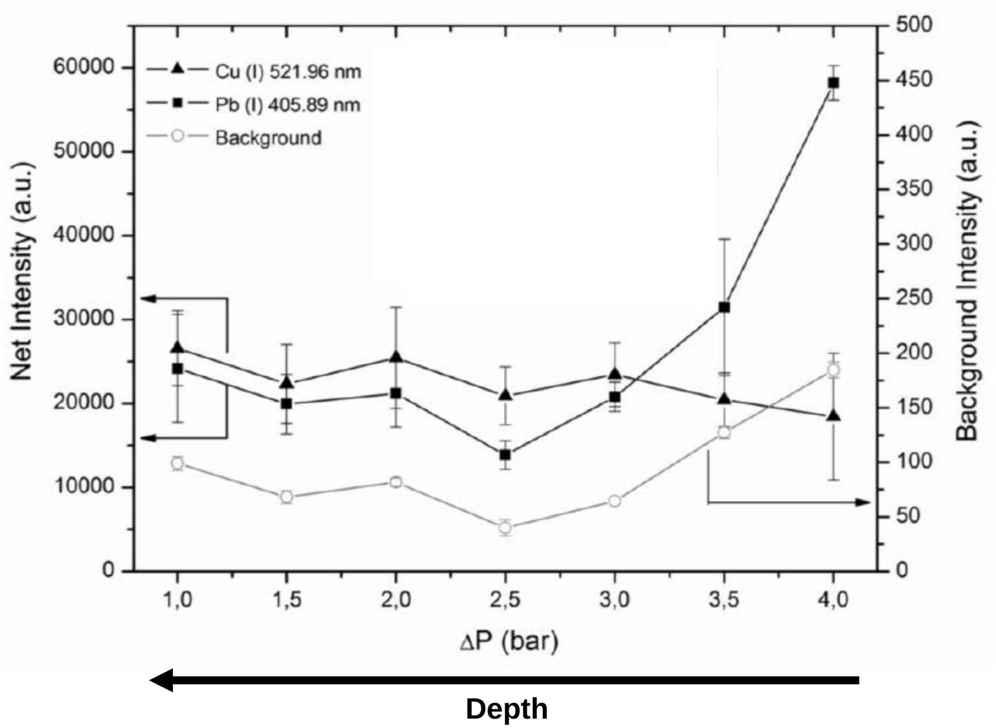
Spectrochimica Acta Part B: Atomic Spectroscopy, Volumes 74–75, 2012, 137–143

http://dx.doi.org/10.1016/j.sab.2012.06.032

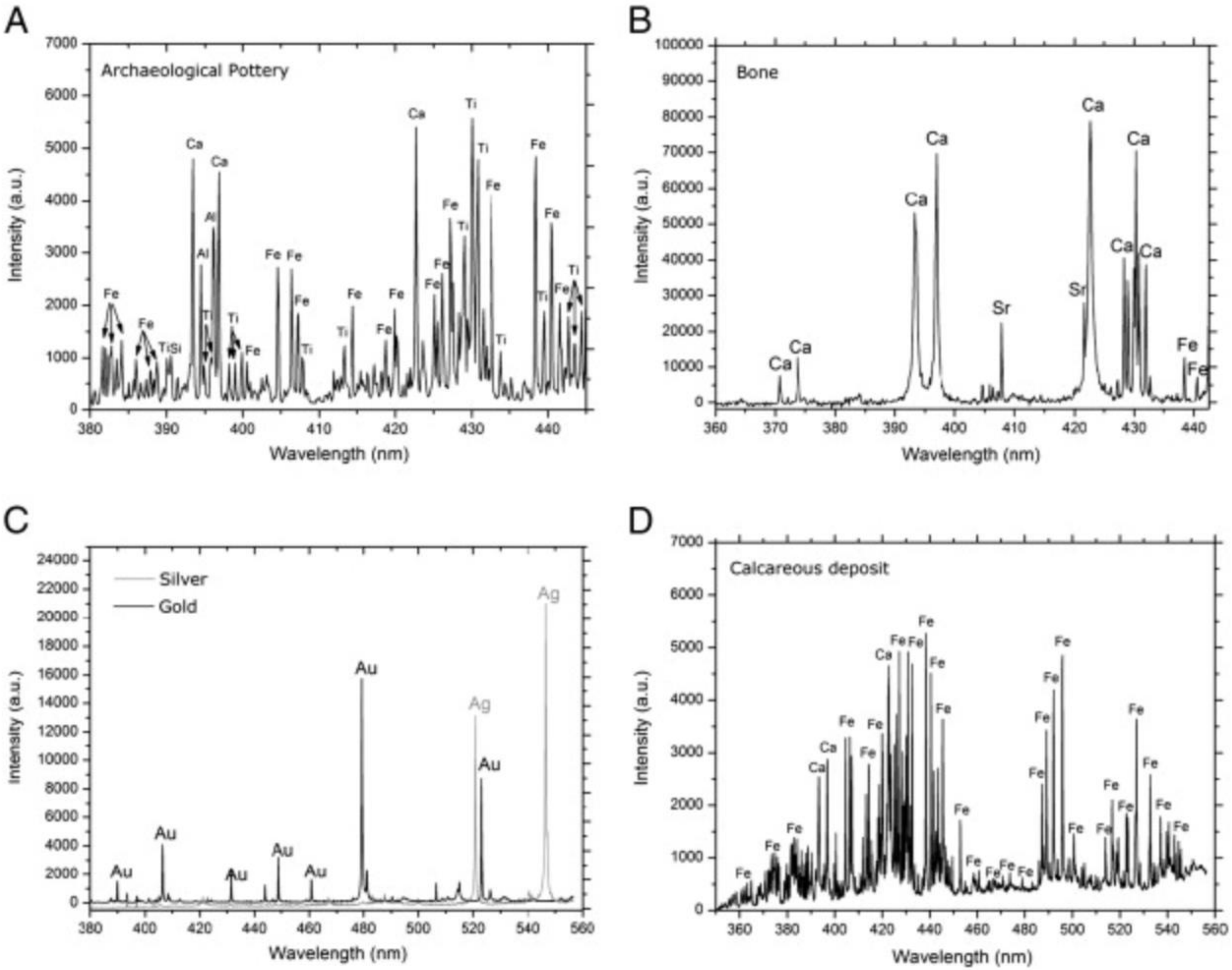
UNIVERSIDAD DE MÁLAGA

The effect of water pressure: matrix effect





UNIVERSIDAD DE MÁLAGA


A
Archaeological Pottery
Intensity (a.u.)
Wavelength (nm)
B
Bone
Intensity (a.u.)
Wavelength (nm)
C
Silver
Gold
Intensity (a.u.)
Wavelength (nm)
D
Calcareous deposit
Intensity (a.u.)
Wavelength (nm)

First Field Trials
Málaga Bay

UNIVERSIDAD
DE MÁLAGA

First Field Trials
Málaga Bay

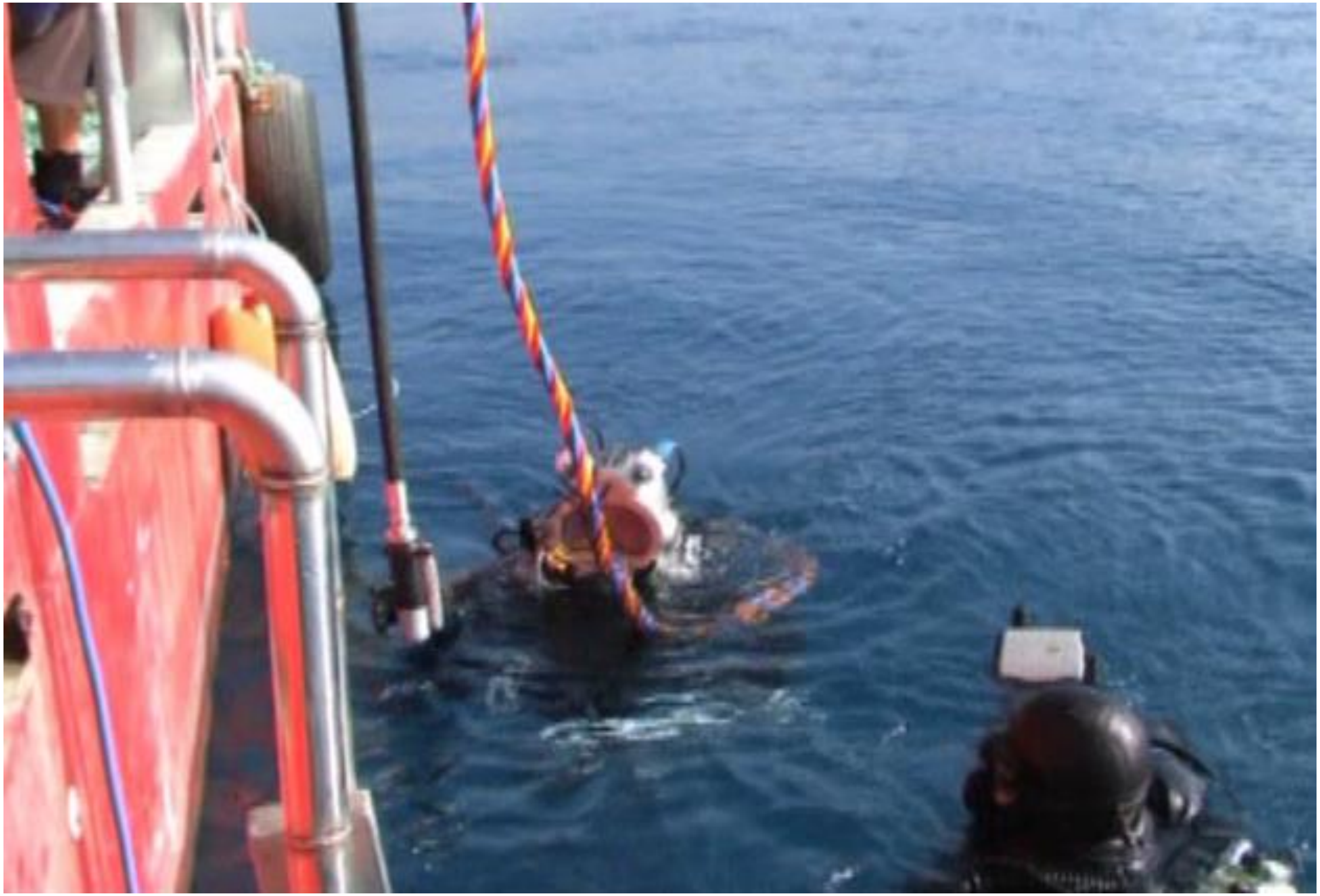
First Field Trials
Málaga Bay

UNIVERSIDAD
DE MÁLAGA

First Field Trials
Málaga Bay

UNIVERSIDAD
DE MÁLAGA

First Field Trials
Málaga Bay



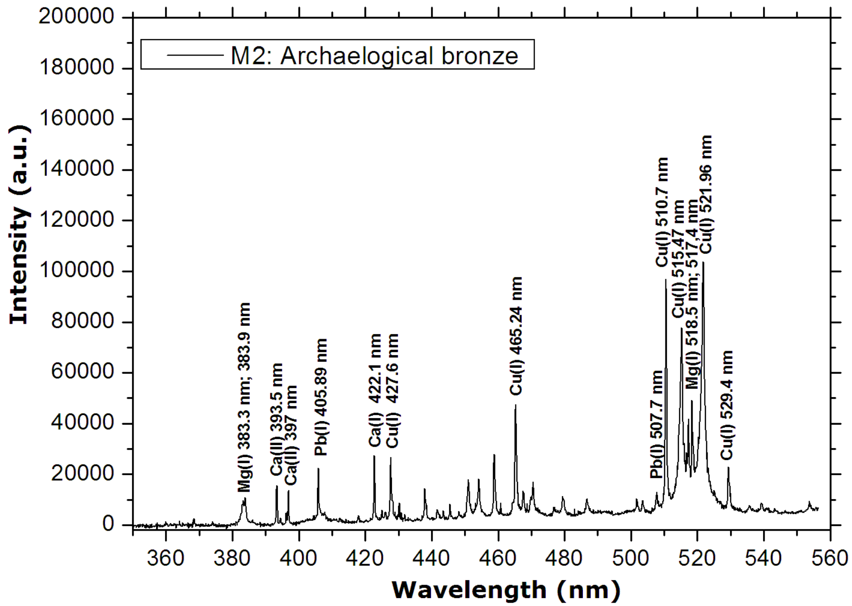
First Field Trials
Málaga Bay

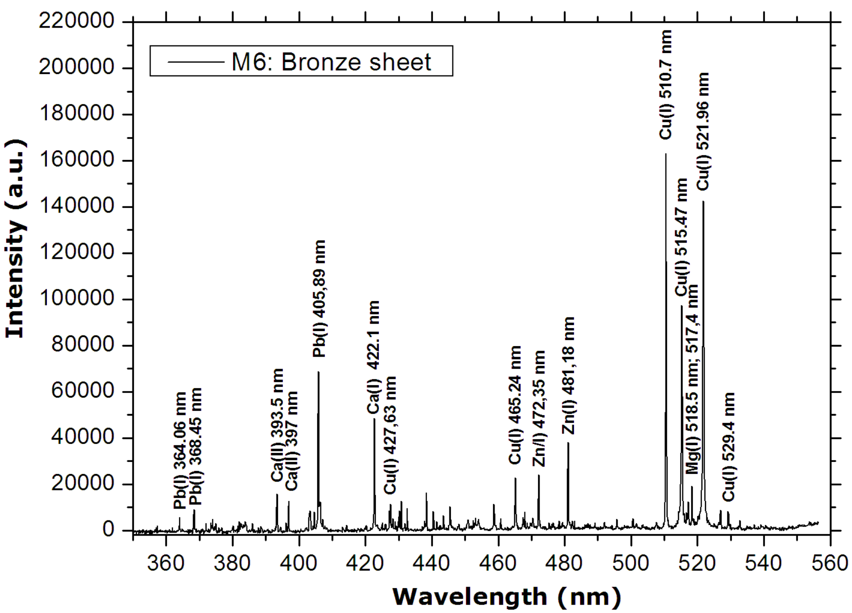
UNIVERSIDAD DE MÁLAGA

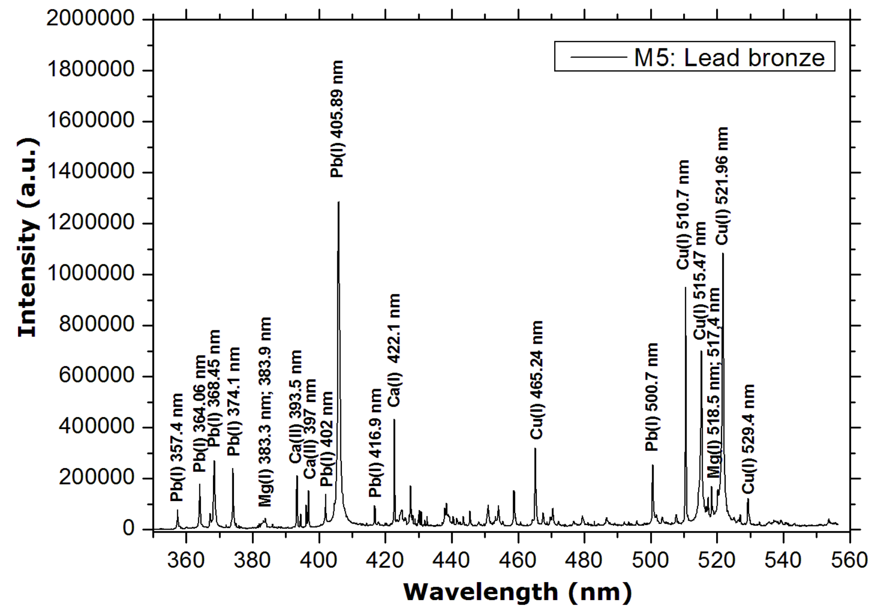
Materials recognition underwater using LIBS

UNIVERSIDAD DE MÁLAGA

Depth – 30 m







S. Guirado, F.J. Fortes, V. Lazic, J.J. Laserna
Spectrochimica Acta, Part B, **2012**, 74, 137

Next generation LIBS system for underwater solids analysis

UNIVERSIDAD DE MÁLAGA

Multipulse excitation through fiber optics

Talanta 137 (2015) 182–188

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

ELSEVIER

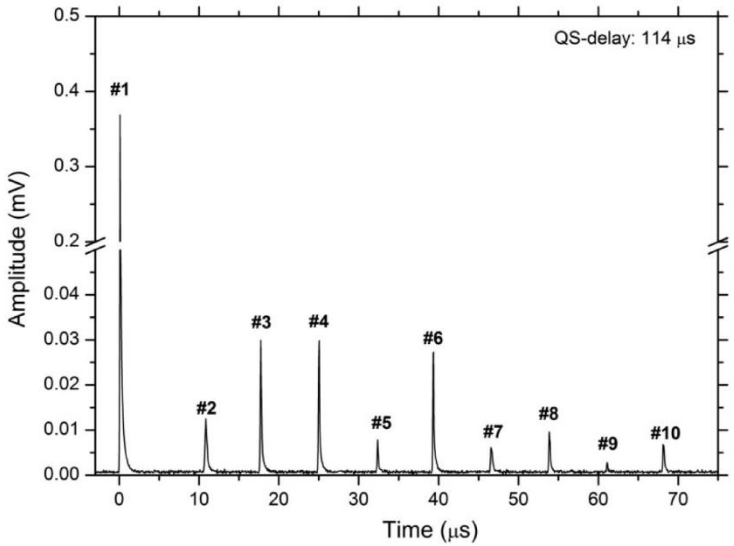
Elemental analysis of materials in an underwater archeological shipwreck using a novel remote laser-induced breakdown spectroscopy system

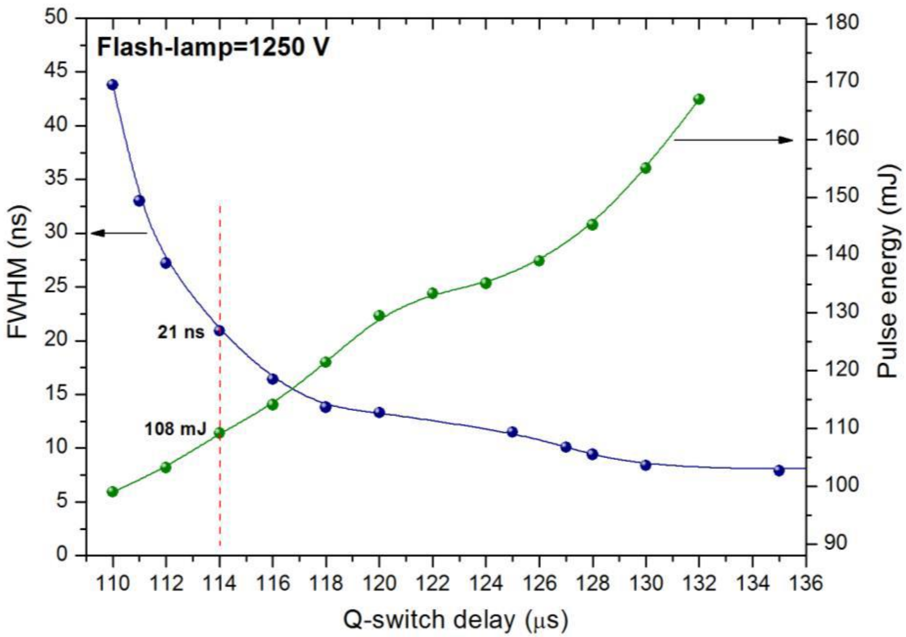
CrossMark

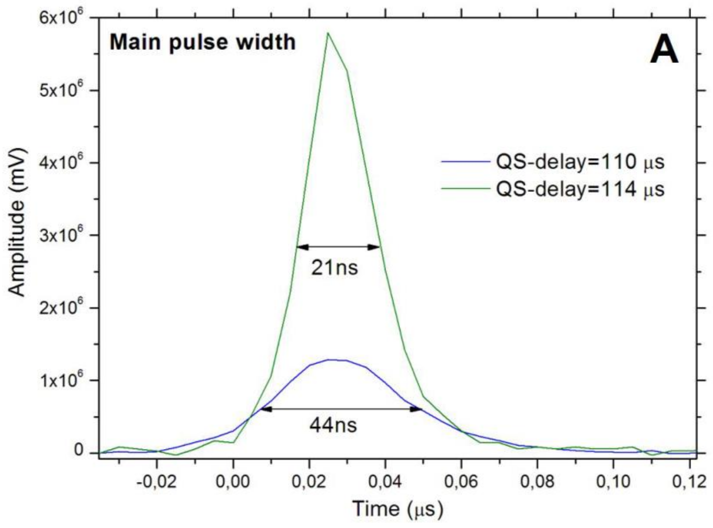
Salvador Guirado, Francisco J. Fortes, J. Javier Laserna*

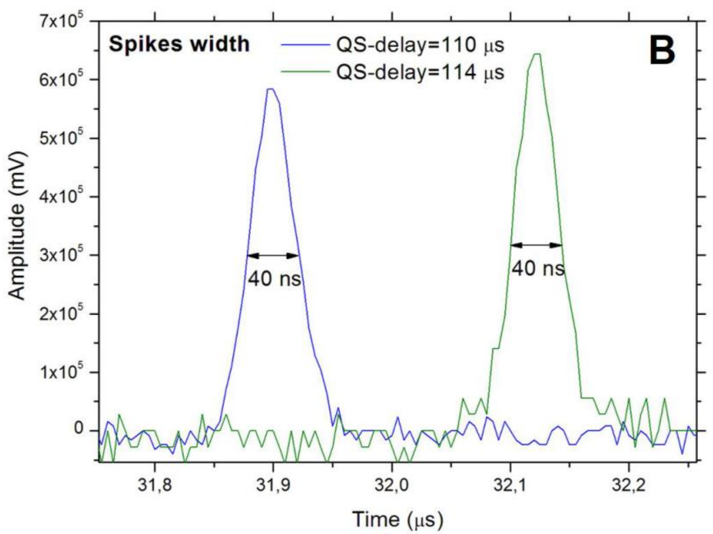
Universidad de Málaga, Facultad de Ciencias, Departamento de Química Analítica, Campus de Teatinos s/n, 29071 Málaga, Spain

Multipulse excitation in OF

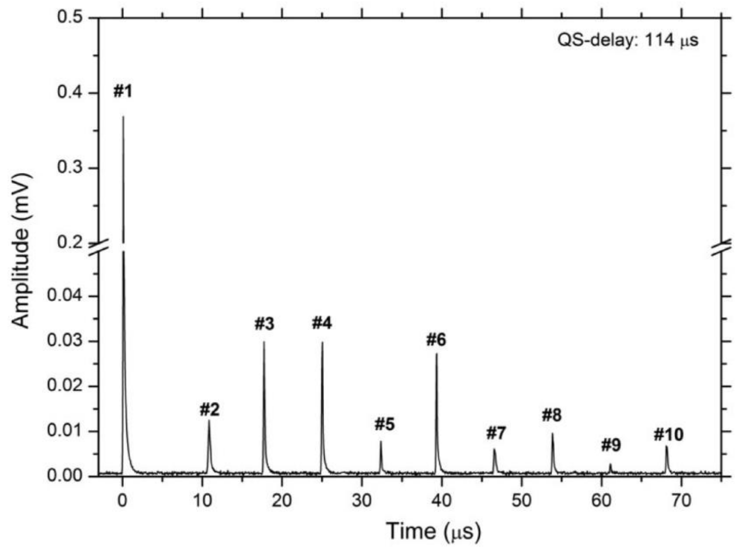








UNIVERSIDAD
DE MÁLAGA



Laser pulse and plasma plume parameters. Comparison between multi-pulse and single pulse configurations.

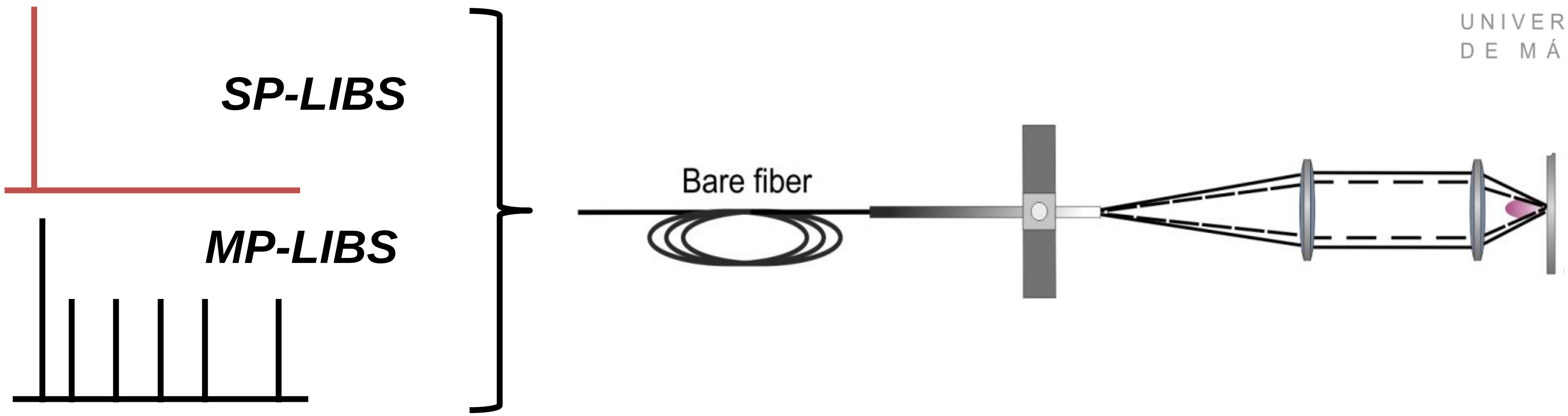
Iron sample

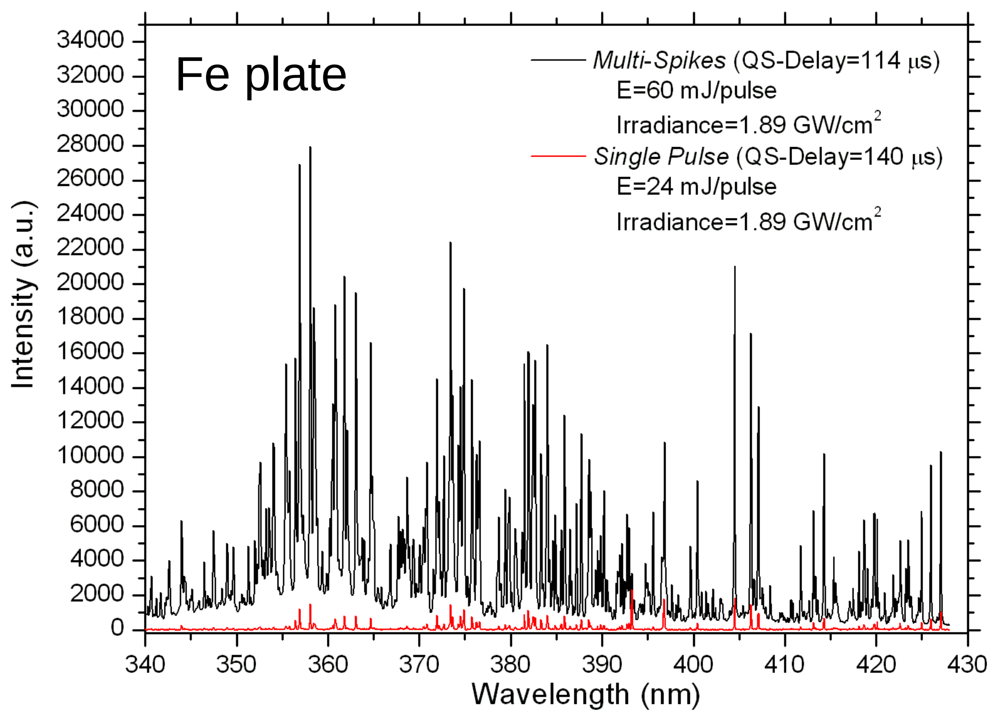
Parameters	MP-LIBS	SP-LIBS
Laser beam energy (mJ/pulse)	60	24
Crater diameter (μm)	450	450
Pulse duration (ns)	21	8
Irradiance (GW/cm^2)	1.89	1.89
Plasma temperature (K)	10,091	7635
Electron density ($\times 10^{16}$ cm^{-3})	1.92	0.77

$$\ln\left(\frac{\lambda_{mn} I_{mn}}{A_{mn} g_m}\right) = \ln(hcN) - \frac{E_m}{KT_e}$$

Single-pulse vs multi-pulse excitation

UNIVERSIDAD DE MÁLAGA





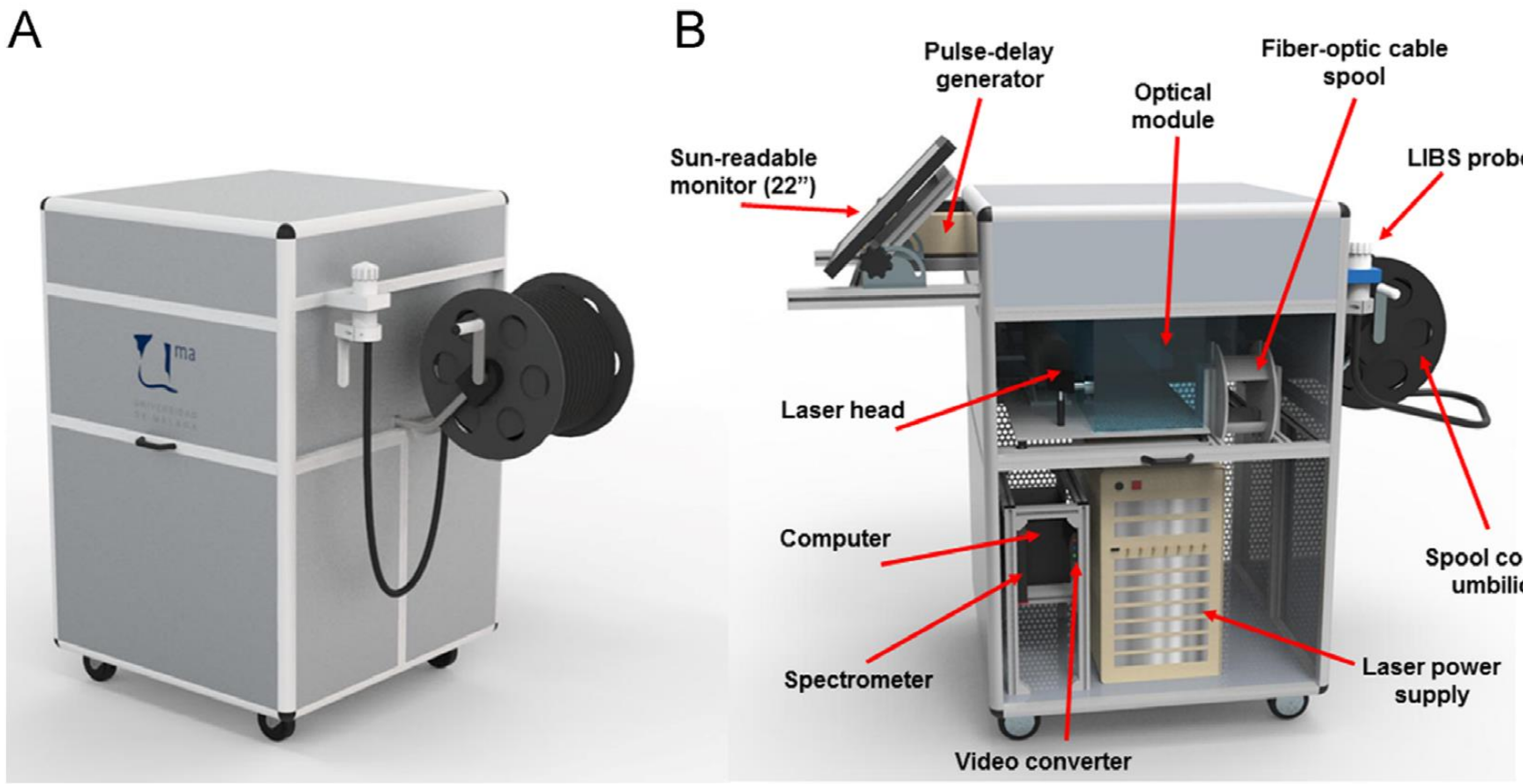
SP-LIBS

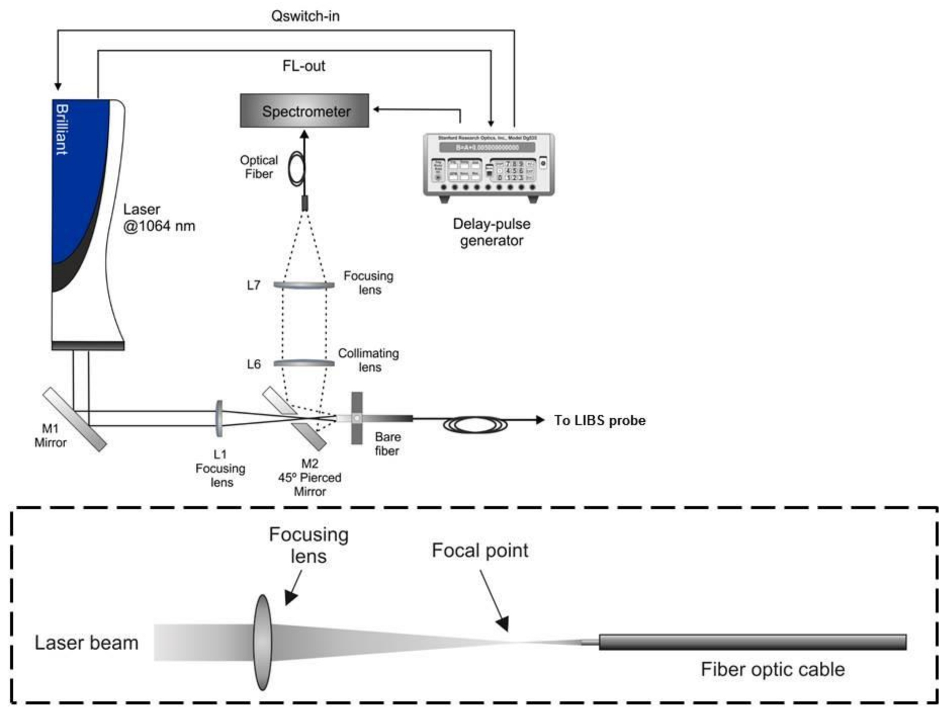
- Pulse duration: 8 ns
- **up to 30 mJ/pulse**

MP-LIBS

- Pulse duration: 21 ns
- **up to 95 mJ/pulse**

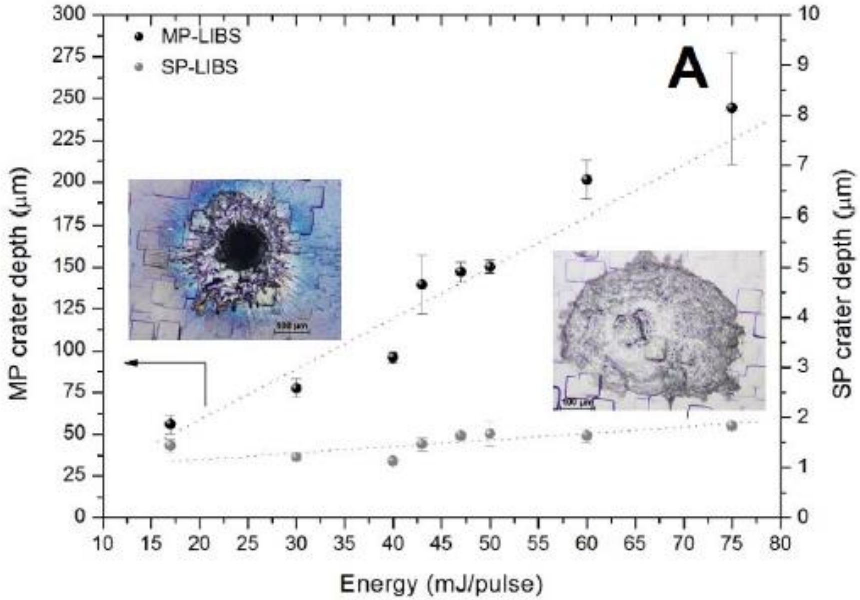
Implementation - multipulse excitation using an OF

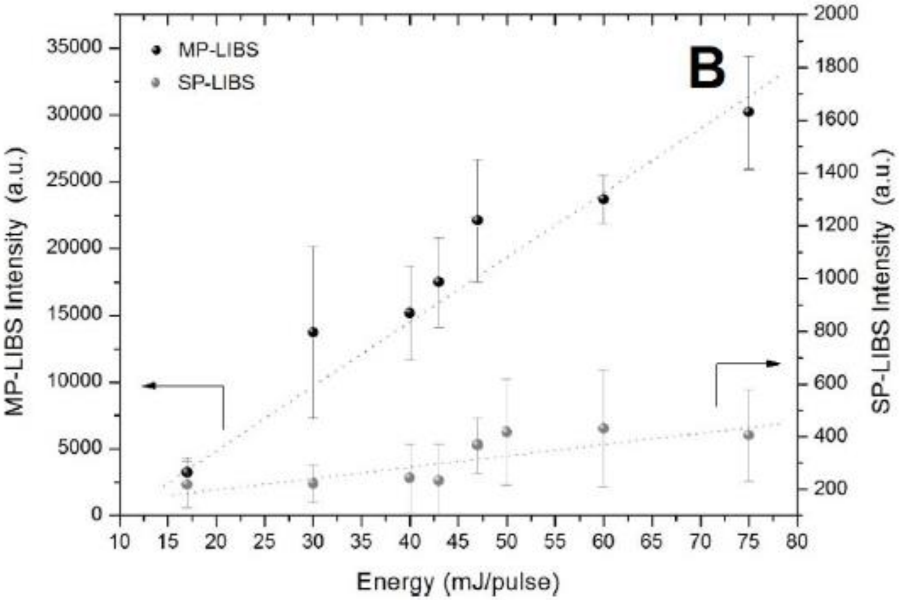



Qswitch-in
FL-out
Spectrometer
Brilliant
Optical Fiber
Laser @1064 nm
Delay-pulse generator
L7
Focusing lens
L6
Collimating lens
M1 Mirror
L1 Focusing lens
M2 45º Pierced Mirror
Bare fiber
To LIBS probe
Focusing lens
Focal point
Laser beam
Fiber optic cable

Single pulse vs multipulse excitation: experimental results

UNIVERSIDAD
DE MÁLAGA





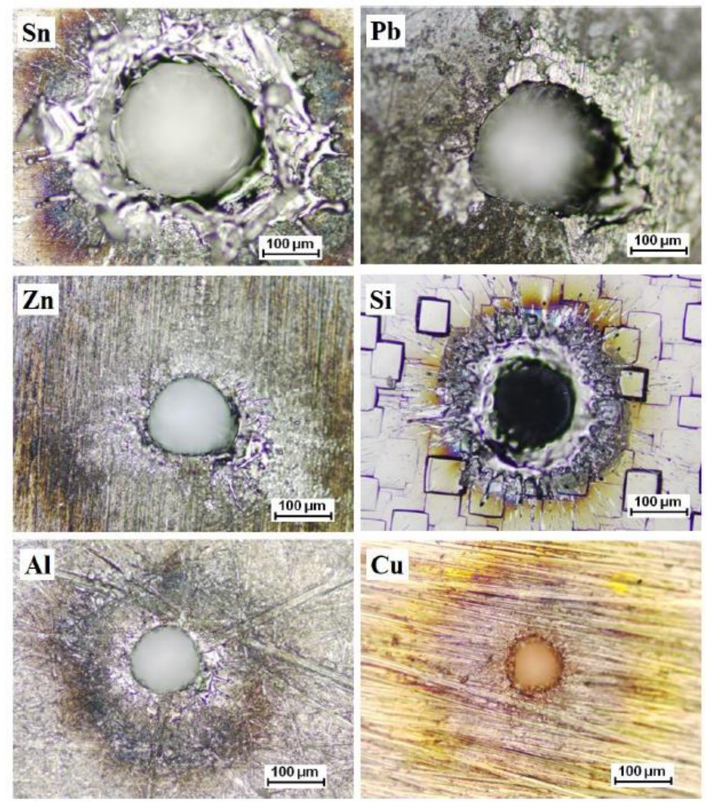


Figura 14. Cráteres producidos por un tren de multi-pulsos de idénticas características (75 mJ y FWHM = 14 ns) en distintos metales.

Single pulse vs multipulse excitation: experimental results

UNIVERSIDAD DE MÁLAGA

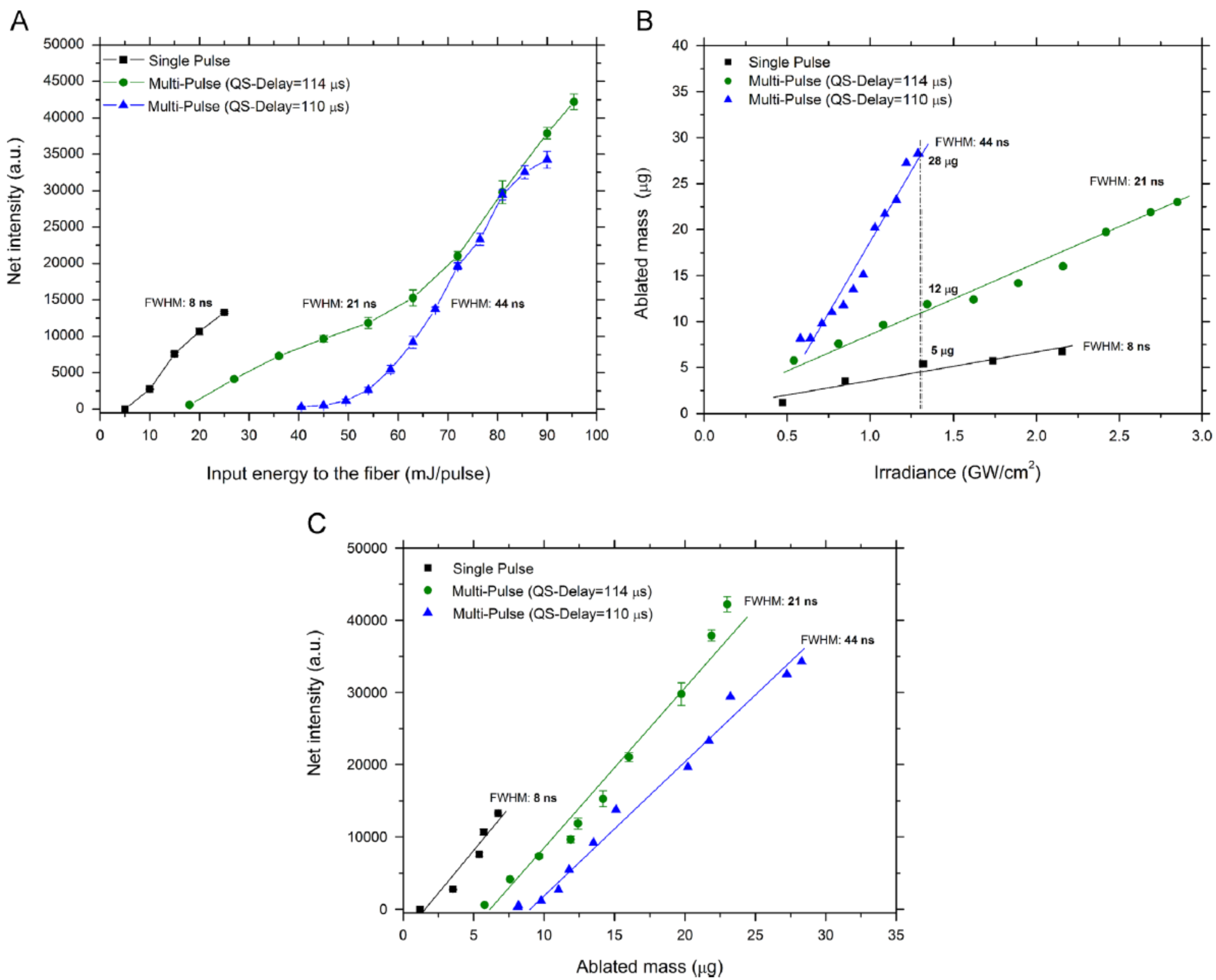


Fig. 2. (A) Net intensity of Zn I 468.14 nm as a function of laser input energy, (B) mass ablated as function of output irradiance and (C) net intensity of Zn I 468.14 nm as a function of mass ablated. In all cases, SP (QS-delay: 140 µs; 8 ns), MP (QS-delay: 114 µs; 21 ns) and MP (QS-delay: 110 µs; 44 ns) have been compared.

Ca in pottery

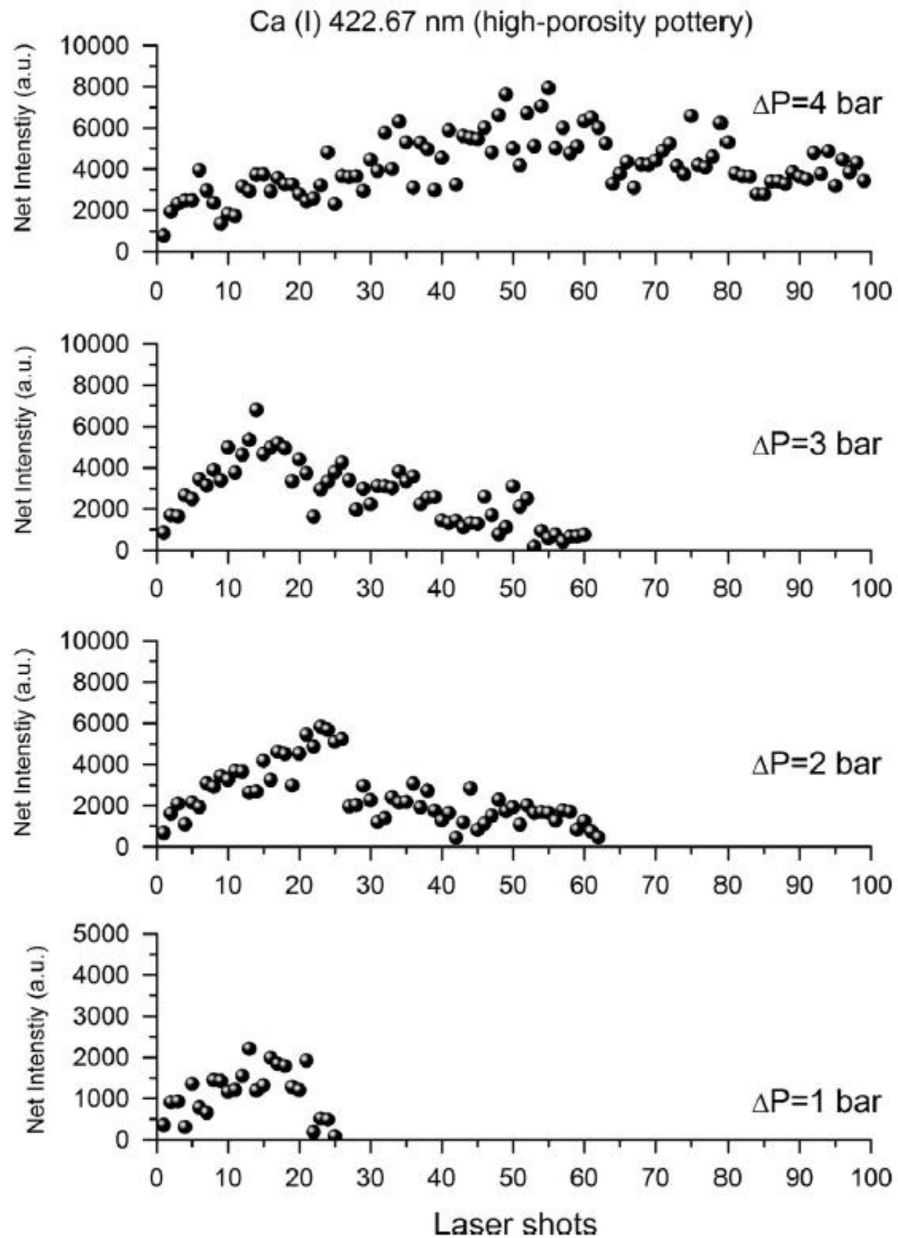
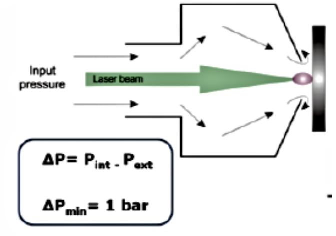
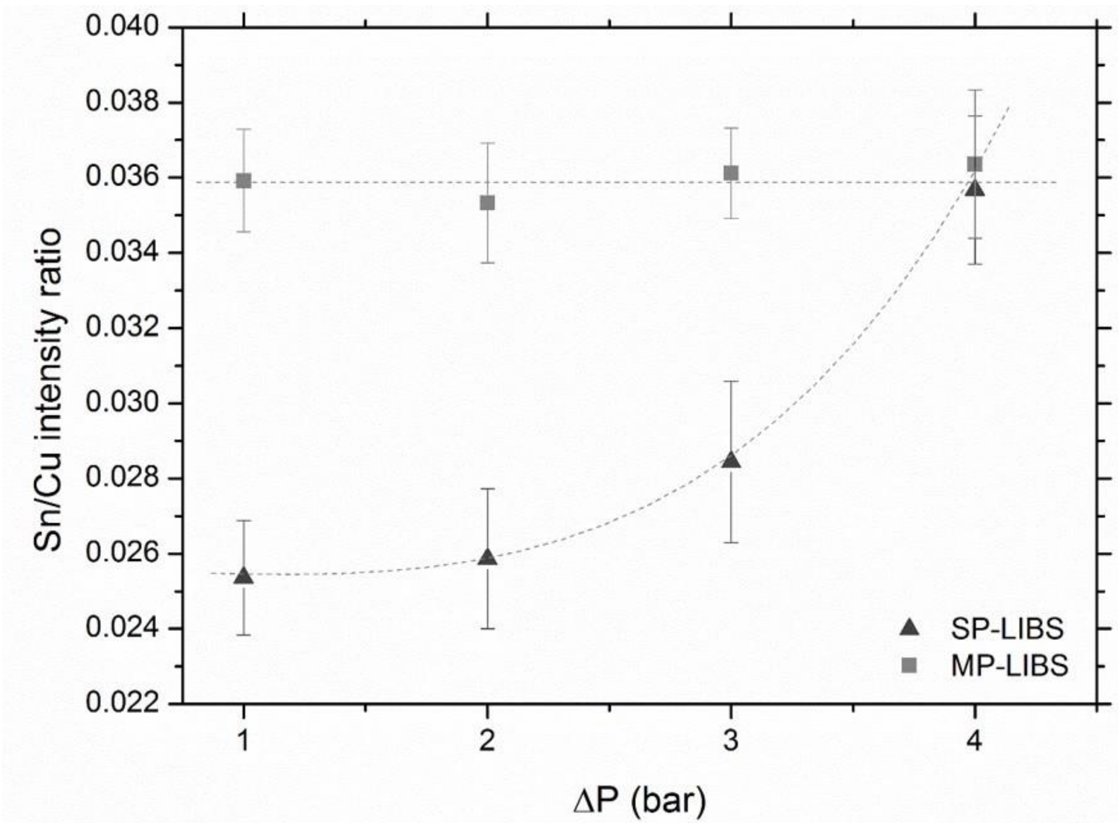


Fig. 5. Influence of air pressure on the signal intensity of Ca (I) at 422.67 nm in ceramic. ΔP is the pressure difference between the inside and outside of the probe.

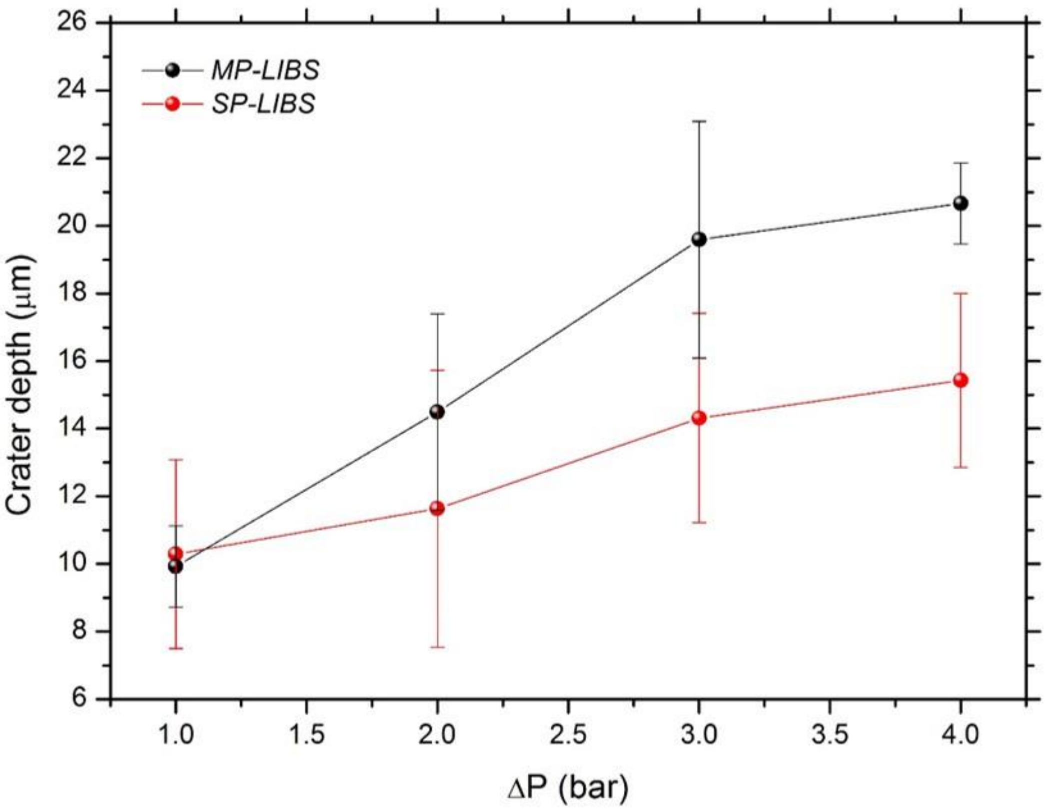
UNIVERSIDAD DE MÁLAGA

Fractionation in single pulse LIBS





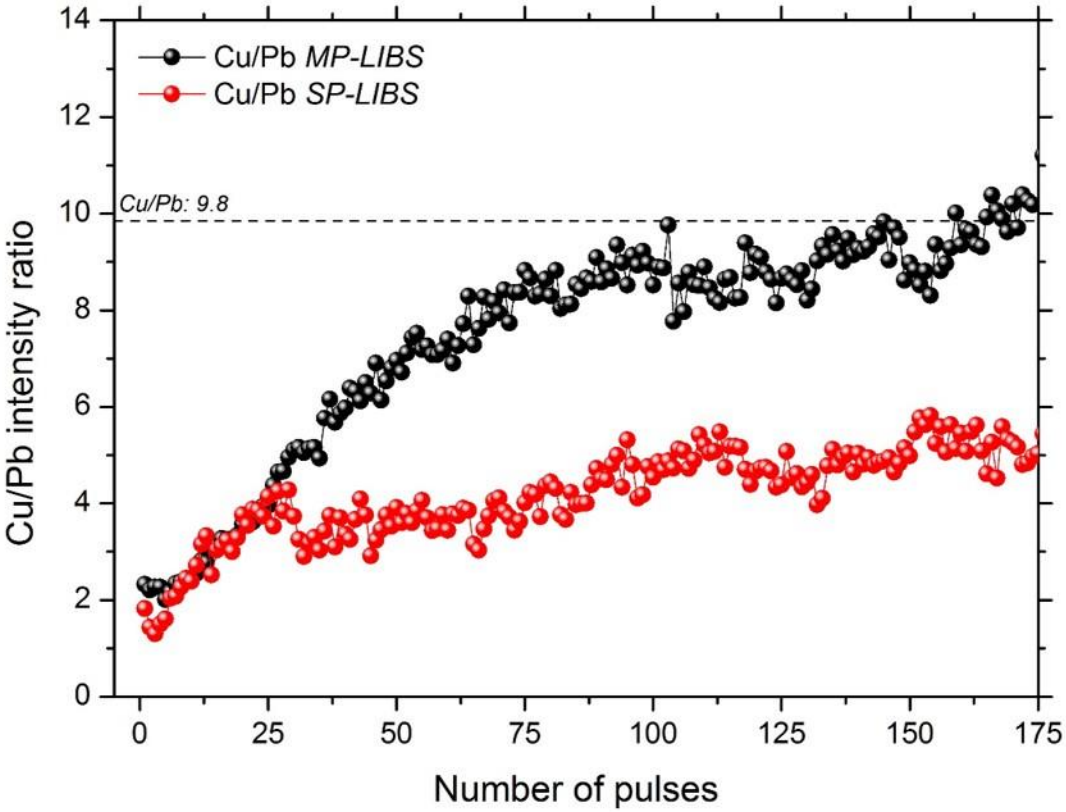
Depth



MP-LIBS
SP-LIBS
Crater depth (μm)
ΔP (bar)
26
24
22
20
18
16
14
12
10
8
6
1.0
1.5
2.0
2.5
3.0
3.5
4.0

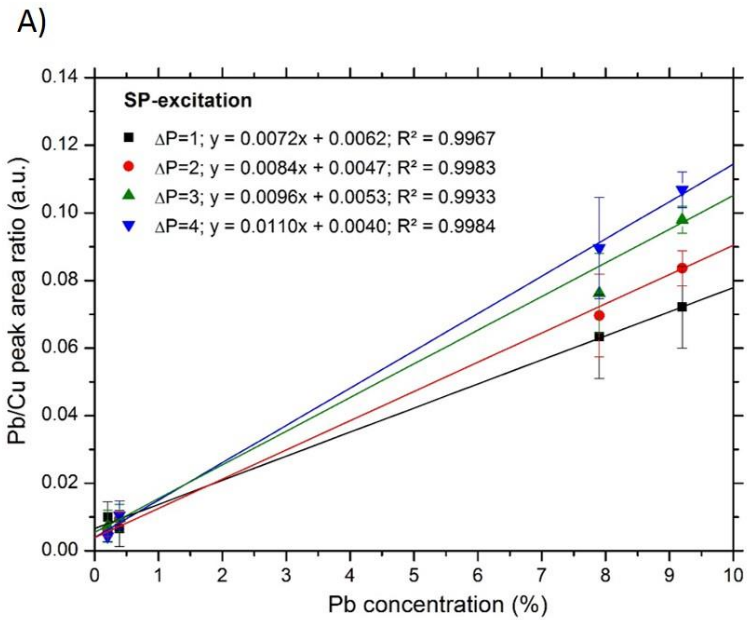
Figure 3

Single pulse vs multipulse excitation: experimental results



Calibration curves for bronces

Single pulse excitation vs multipulse excitation



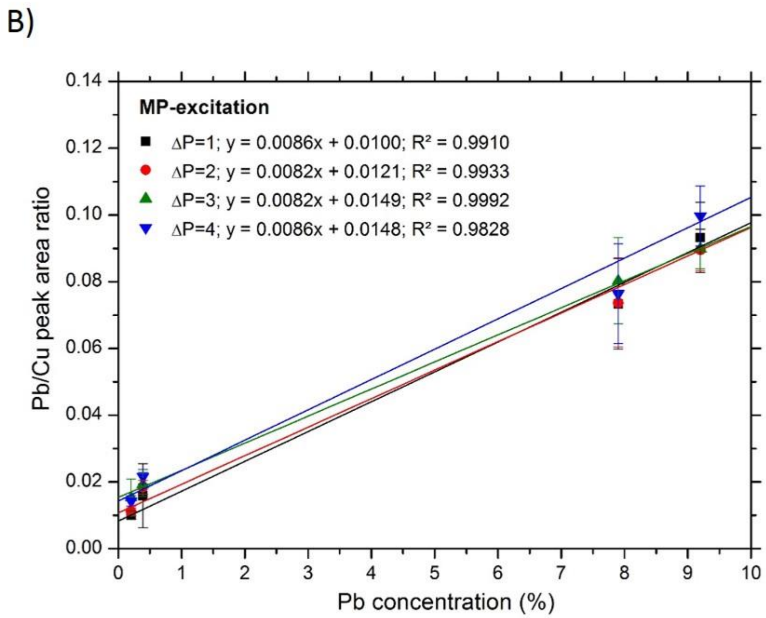
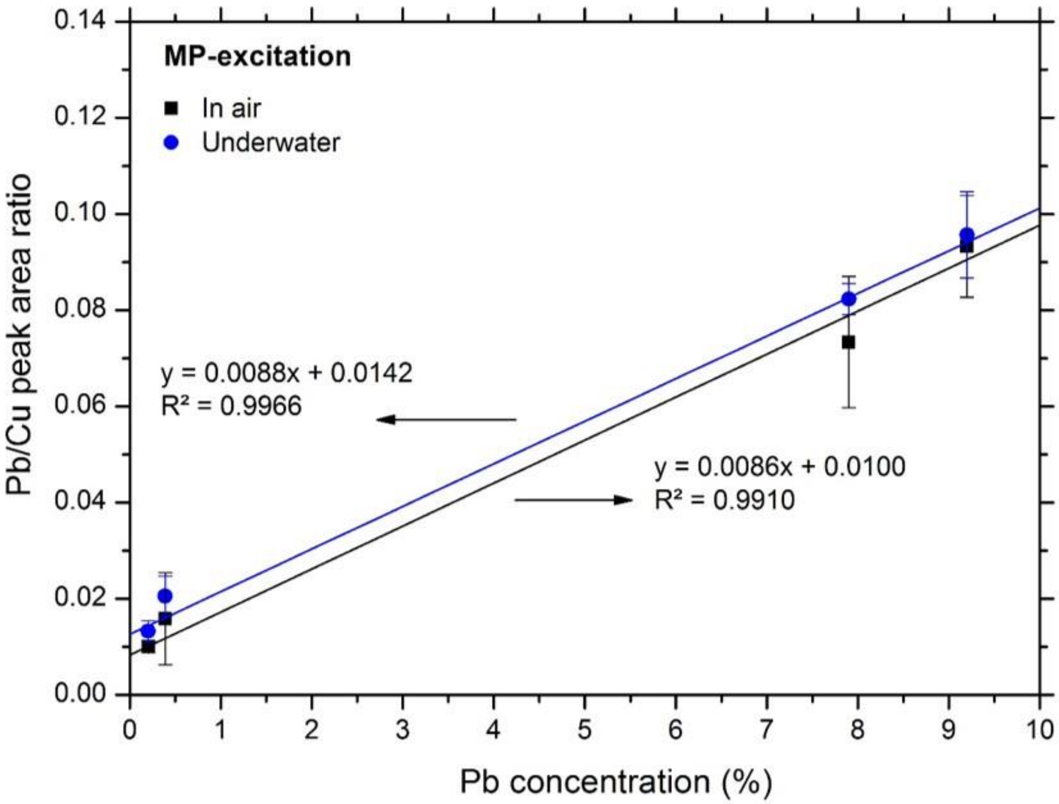


Figure 6

Calibration curves for bronces

UNIVERSIDAD DE MÁLAGA

In air vs underwater analysis



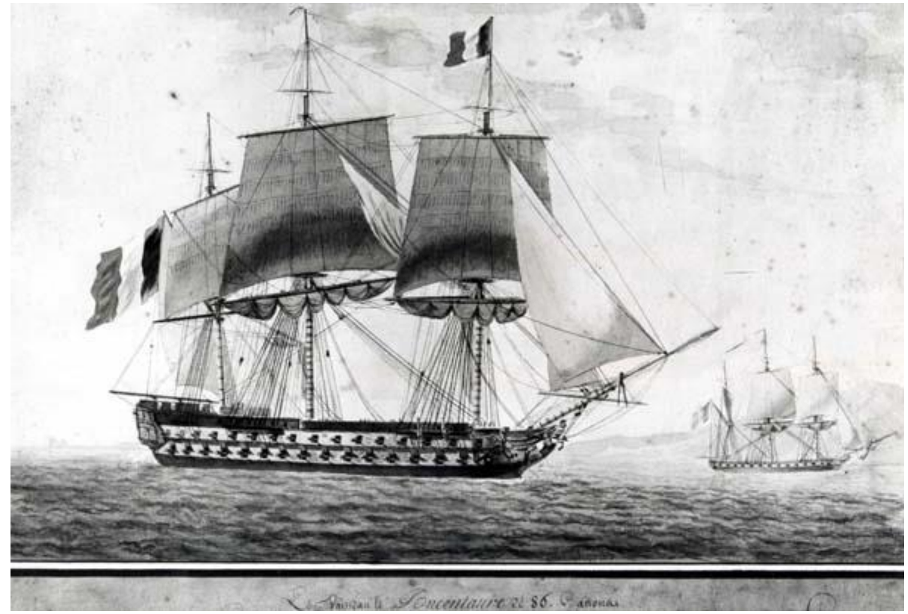
UNIVERSIDAD
DE MÁLAGA

Features

- Multipulse excitation
- Optical fiber length - 55 m
- Maximum depth - 50 m
- Power consumption - 2700 W
- Weight - 150 Kg
- Dimensions - 75 x 80 x 110 cm (0.66 m^3)

French ship *Bucentaure* (1803)

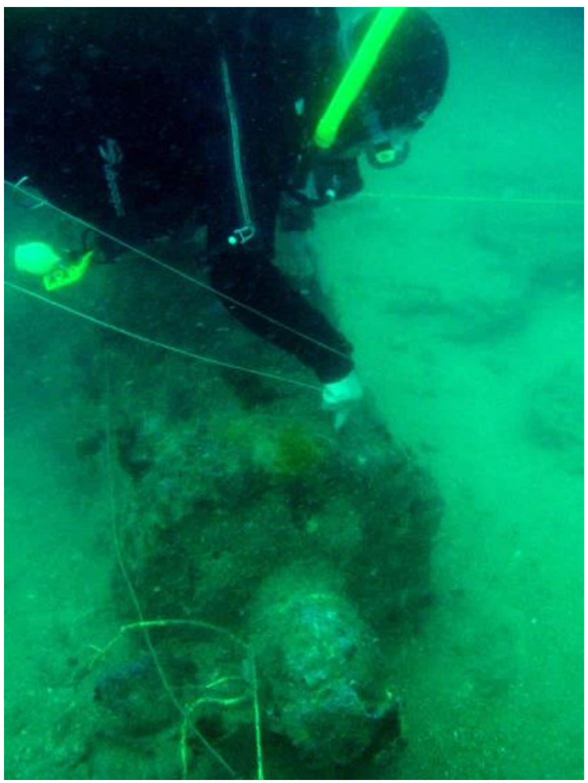
Builder:	Arsenal de Toulon
Laid down:	1802
Launched:	1803
Commissioned:	1804
In service:	1804-1805
Out of service:	1805 (wrecked on 23 October 1805)
Struck:	23 October 1805
Captured:	21 October 1805 (Battle of Trafalgar) - later re-captured from the British prize crew
Fate:	Wrecked on 23 October 1805 - CADIZ
General characteristics	
Class and type:	*Bucentaure* class ship of the line
Displacement:	1 630 tonnes
Length:	• 51 m (167 ft) (gundeck) • 59,26 m (overall)
Beam:	14 m (46 ft)
Draught:	6 m (20 ft)
Complement:	840
Armament:	• 80 guns • 30 × 36-pounders • 32 × 24-pounders • 18 × 12-pounders • 6 × 36-pounder howitzers

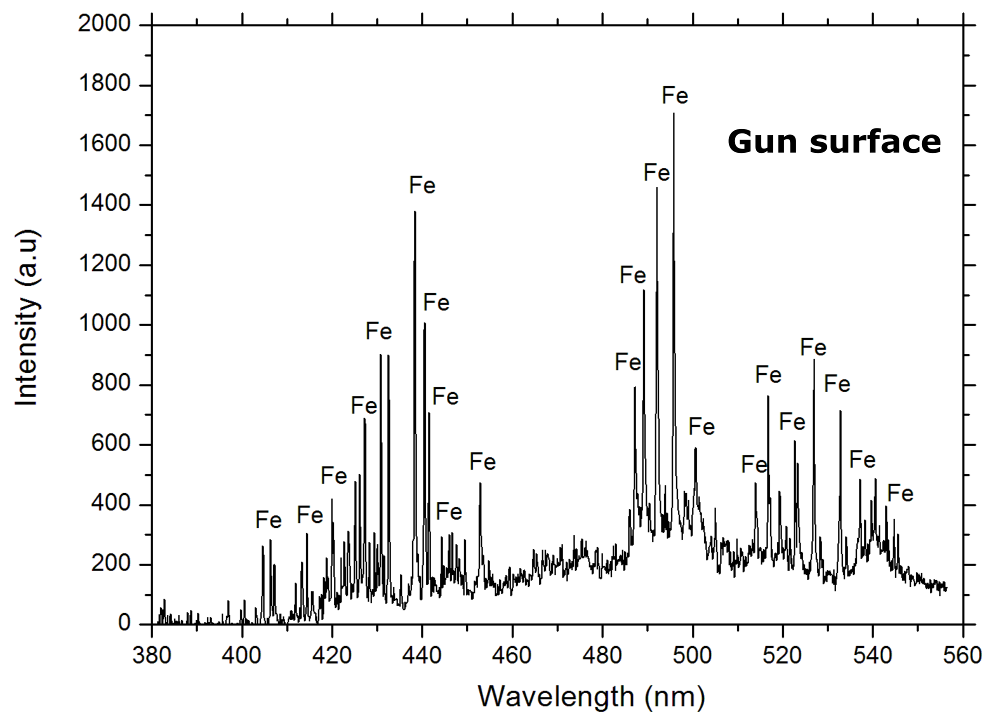


Source: Wikipedia

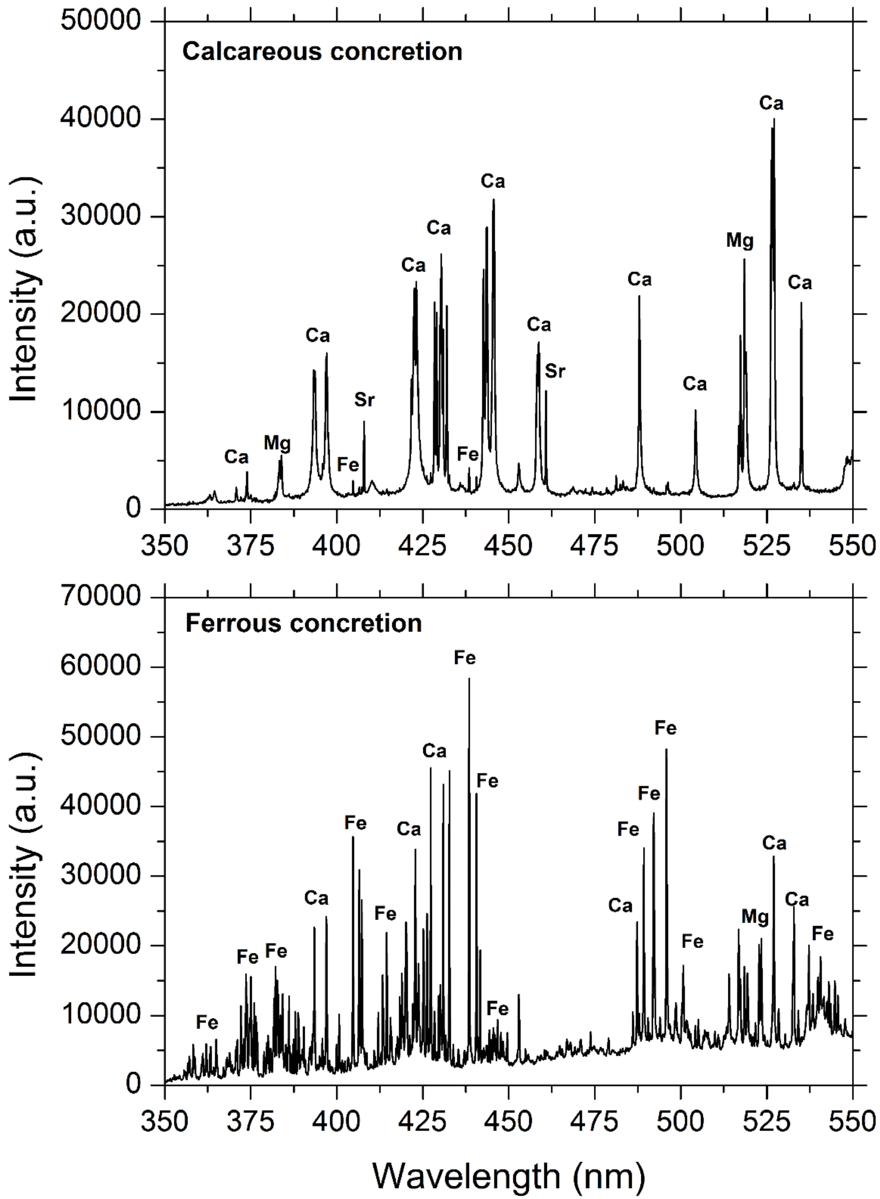
Inspection of
Shipwreck of the Bucentaure

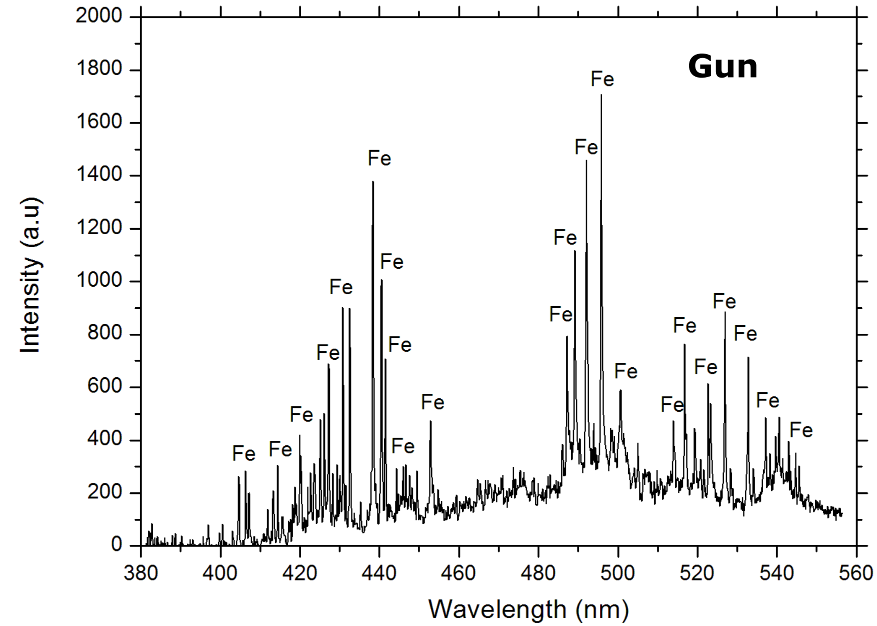
UNIVERSIDAD
DE MÁLAGA





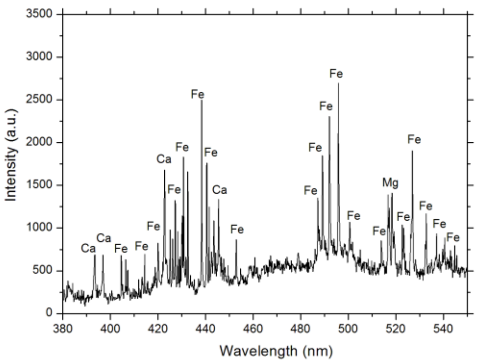
UNIVERSIDAD DE MÁLAGA



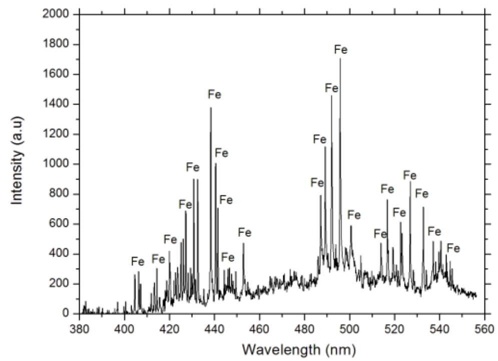


Inspection of Shipwreck of the Bucentaure

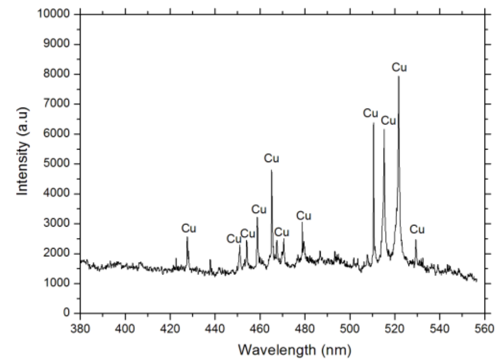
Other objects analyzed underwater (depth - 17 m)



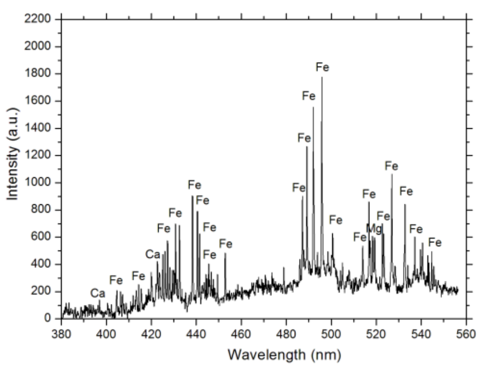
PIECE OF BALLAST



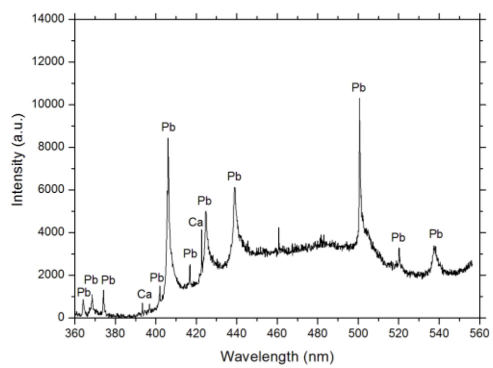
GUN



PIECE OF COPPER



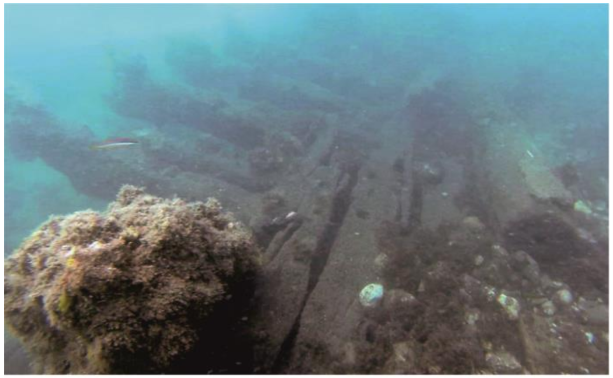
UNIDENTIFIED PIECE

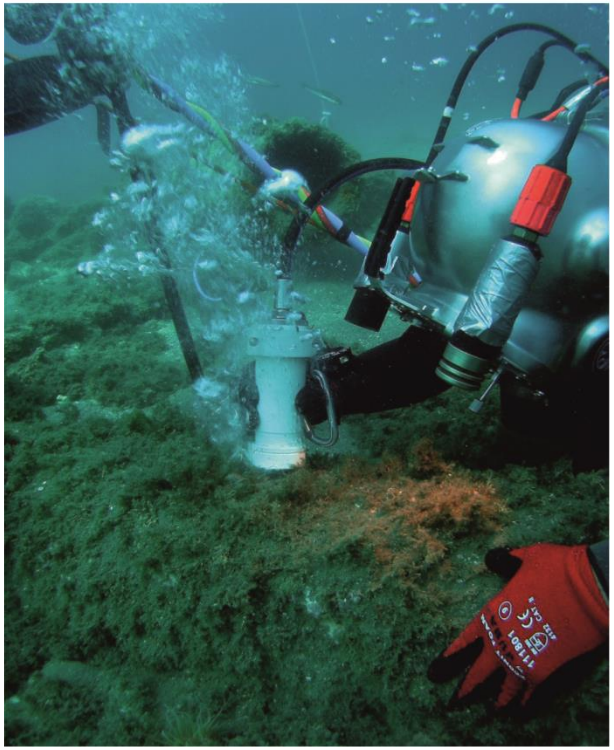


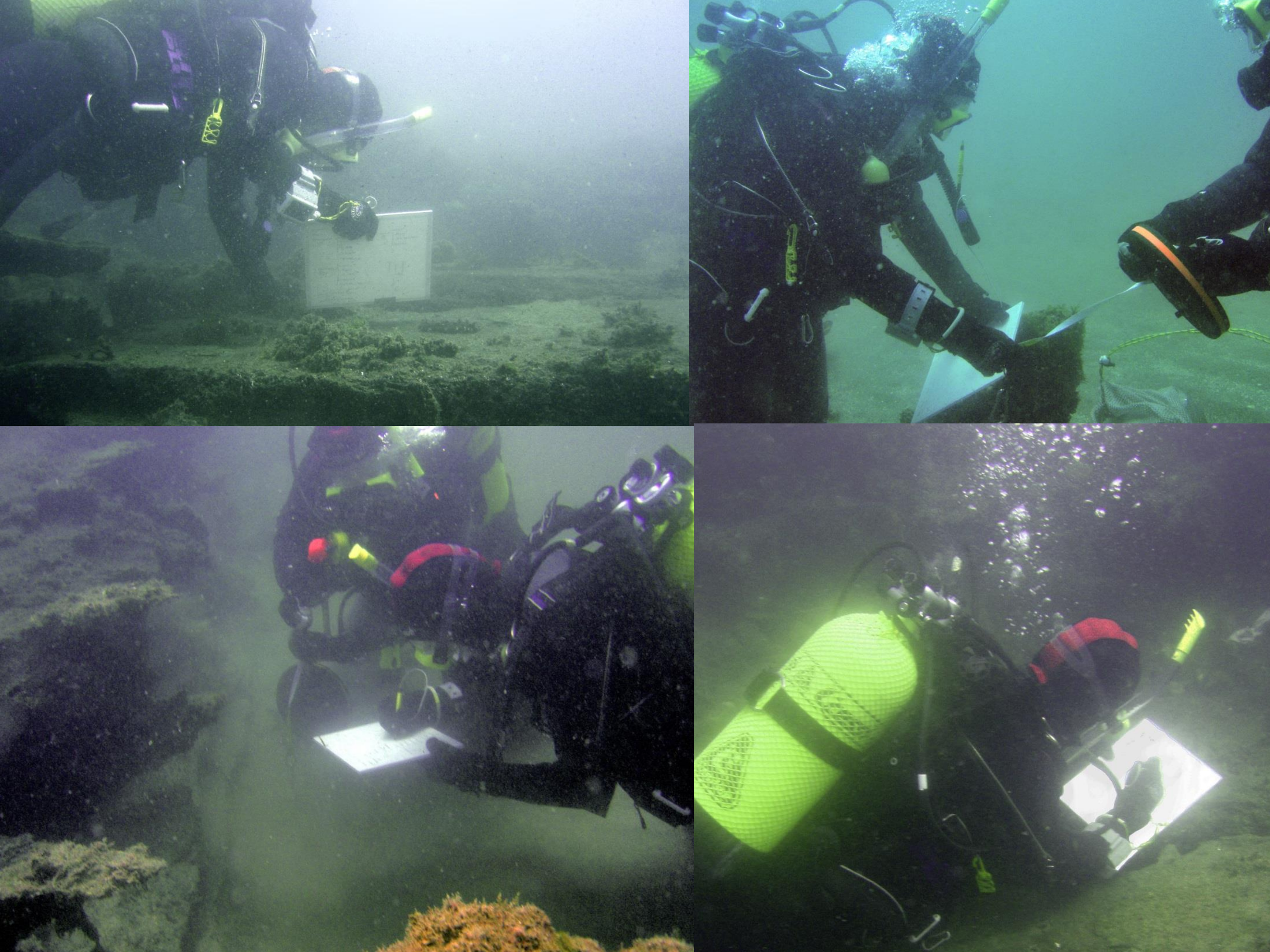
PIECE OF LEAD

Inspection of the San Pedro de Alcántara - July 2015 shipwreck - unknown date and origin – possibly XVIII century, spanish

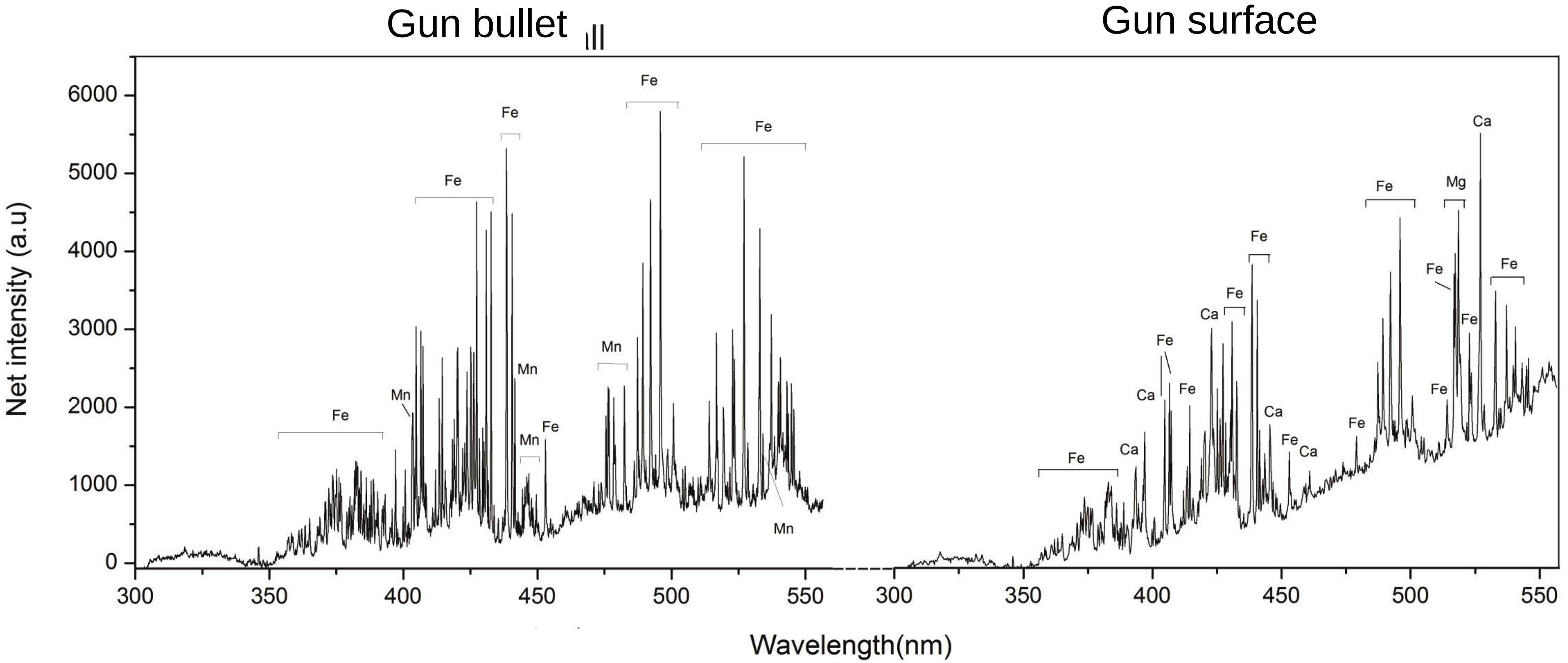
UNIVERSIDAD DE MÁLAGA





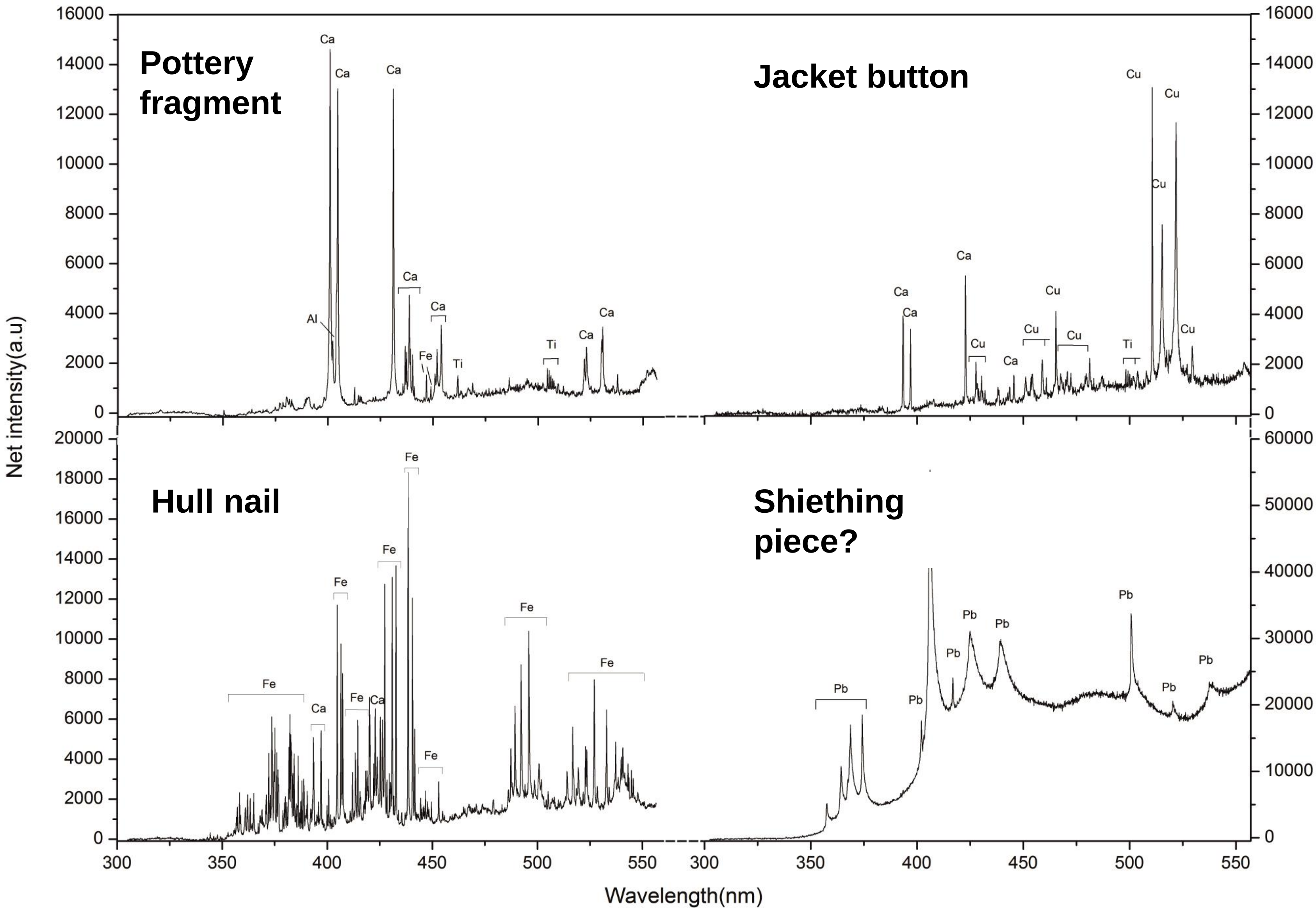


Inspection of the San Pedro de Alcántara - July 2015 shipwreck - unknown date and origin – possibly XVIII century, spanish

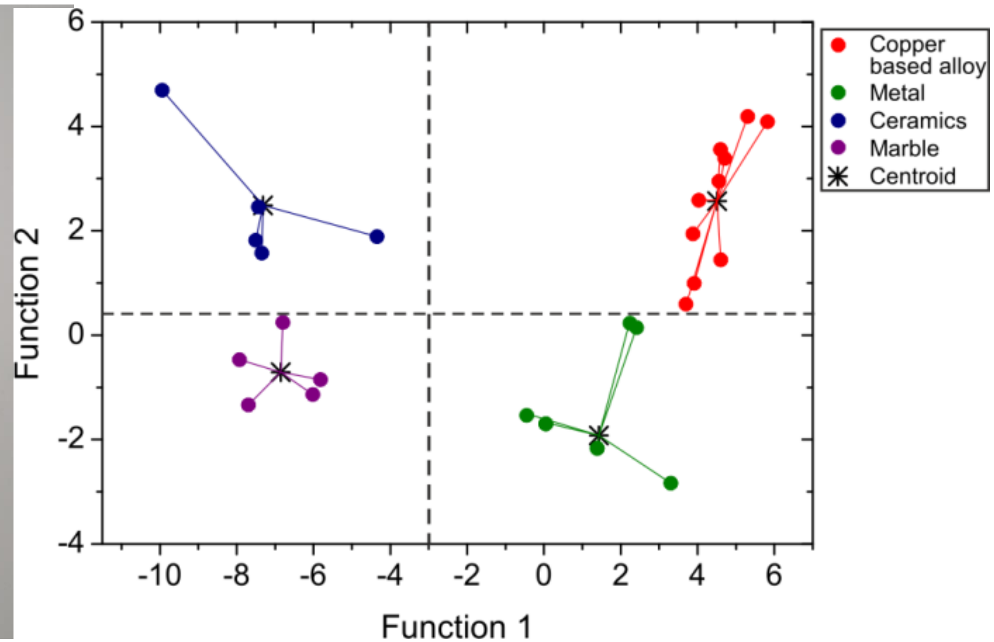


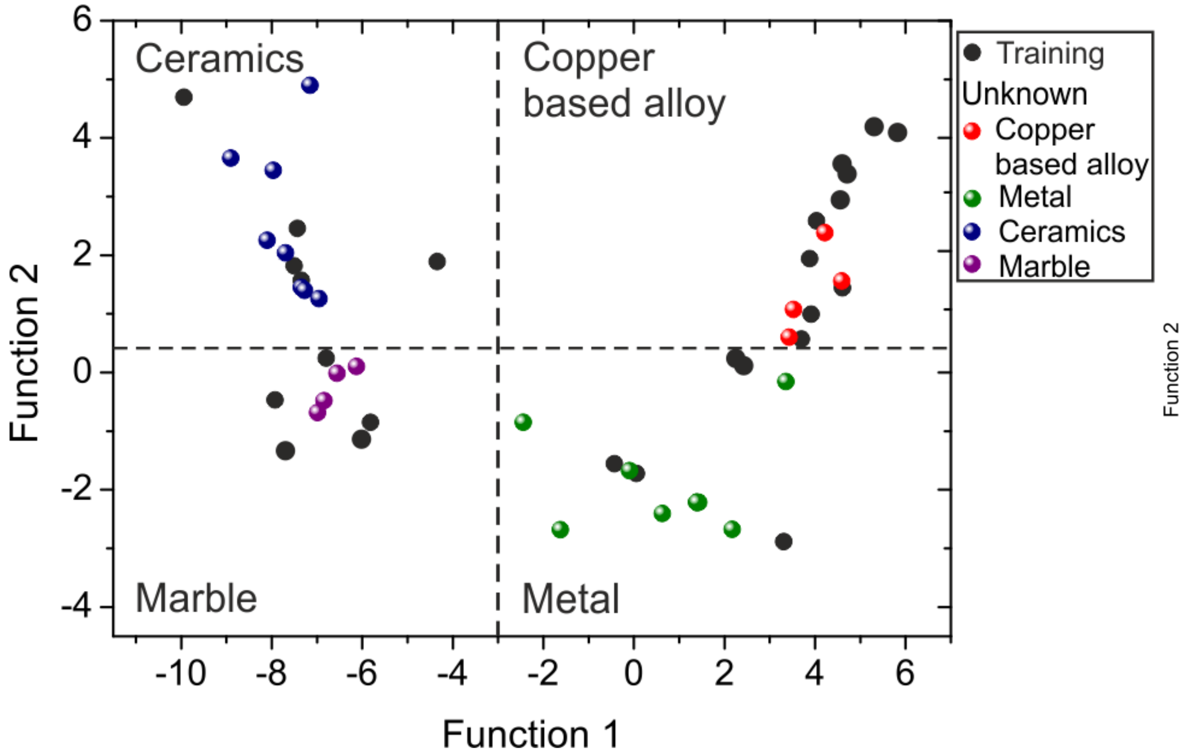
Inspection of the San Pedro de Alcántara shipwreck - unknown date and origin – possibly XVIII century, spanish - July 2015

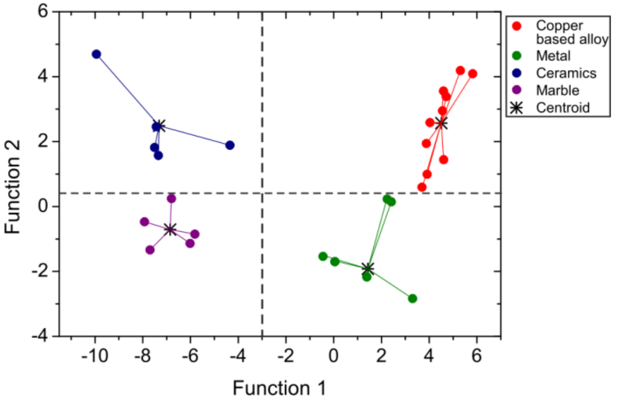
UNIVERSIDAD DE MÁLAGA



Inspection of the shipwreck of San Pedro de Alcántara – July 2015
Sorting model based on discriminant function analysis







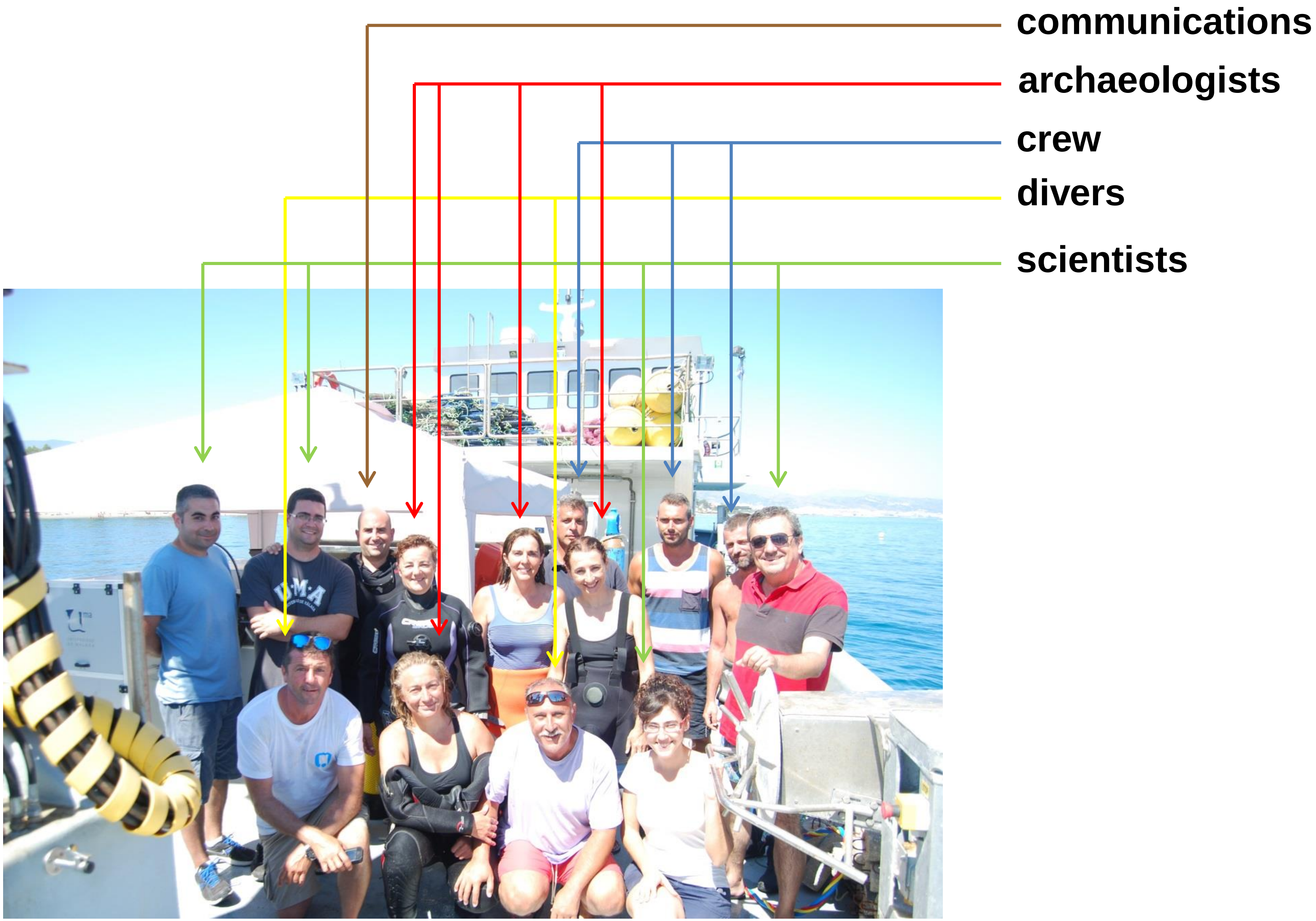
UNIVERSIDAD
DE MÁLAGA

UNIVERSIDAD DE MÁLAGA

Subsea measurement campaigns

The 2015 team

UNIVERSIDAD DE MÁLAGA



UNIVERSIDAD
DE MÁLAGA

LOGISTICS

Boat, crew, facilities

Professional divers

Submarine LIBS

Surface LIBS team

UNIVERSIDAD DE MÁLAGA

LOGISTICS

Good weather!

Boat, crew, facilities

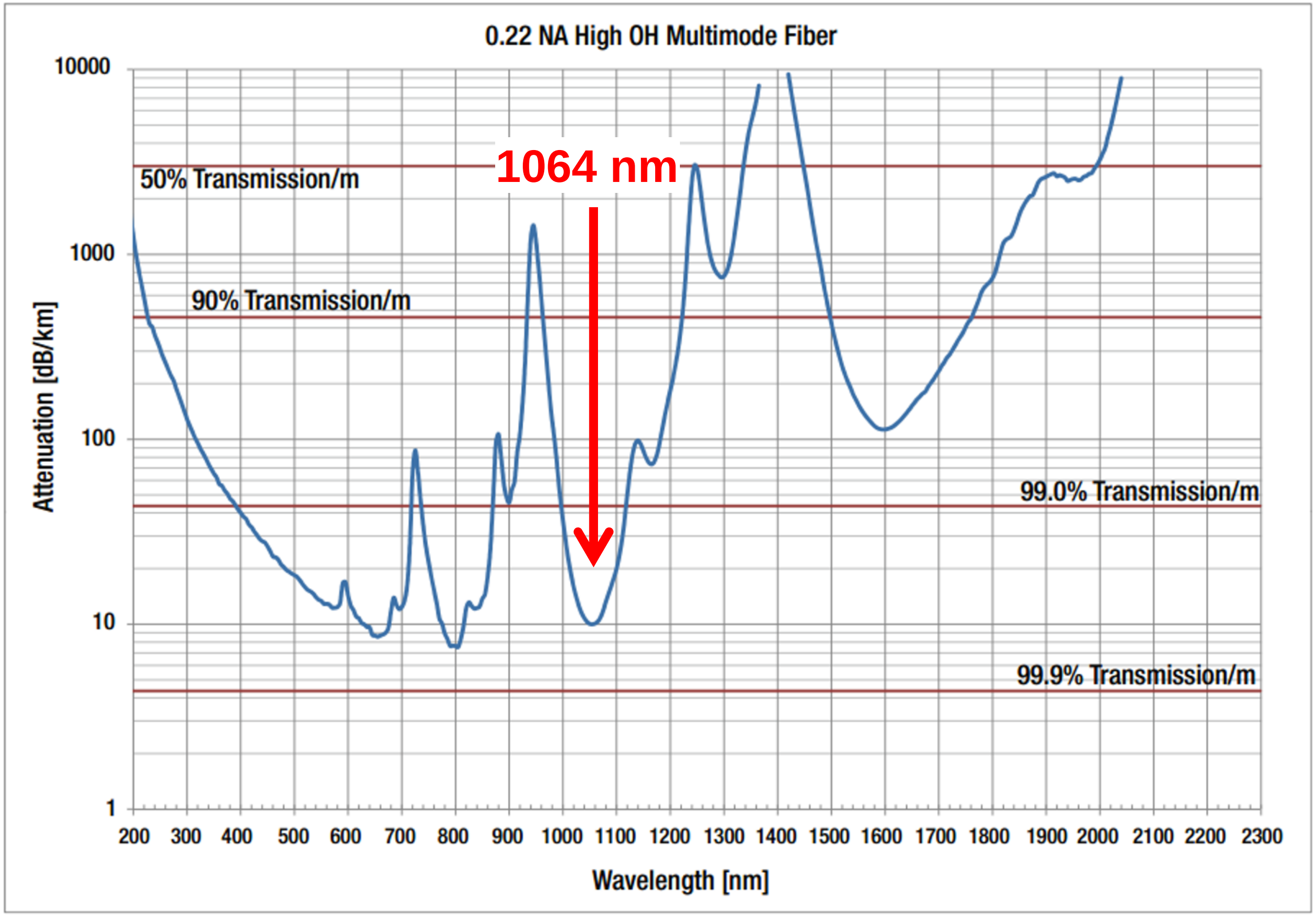
Professional divers

Submarine LIBS

Surface LIBS team

Maximun depth with a submersible-probe fiber optics LIBS?

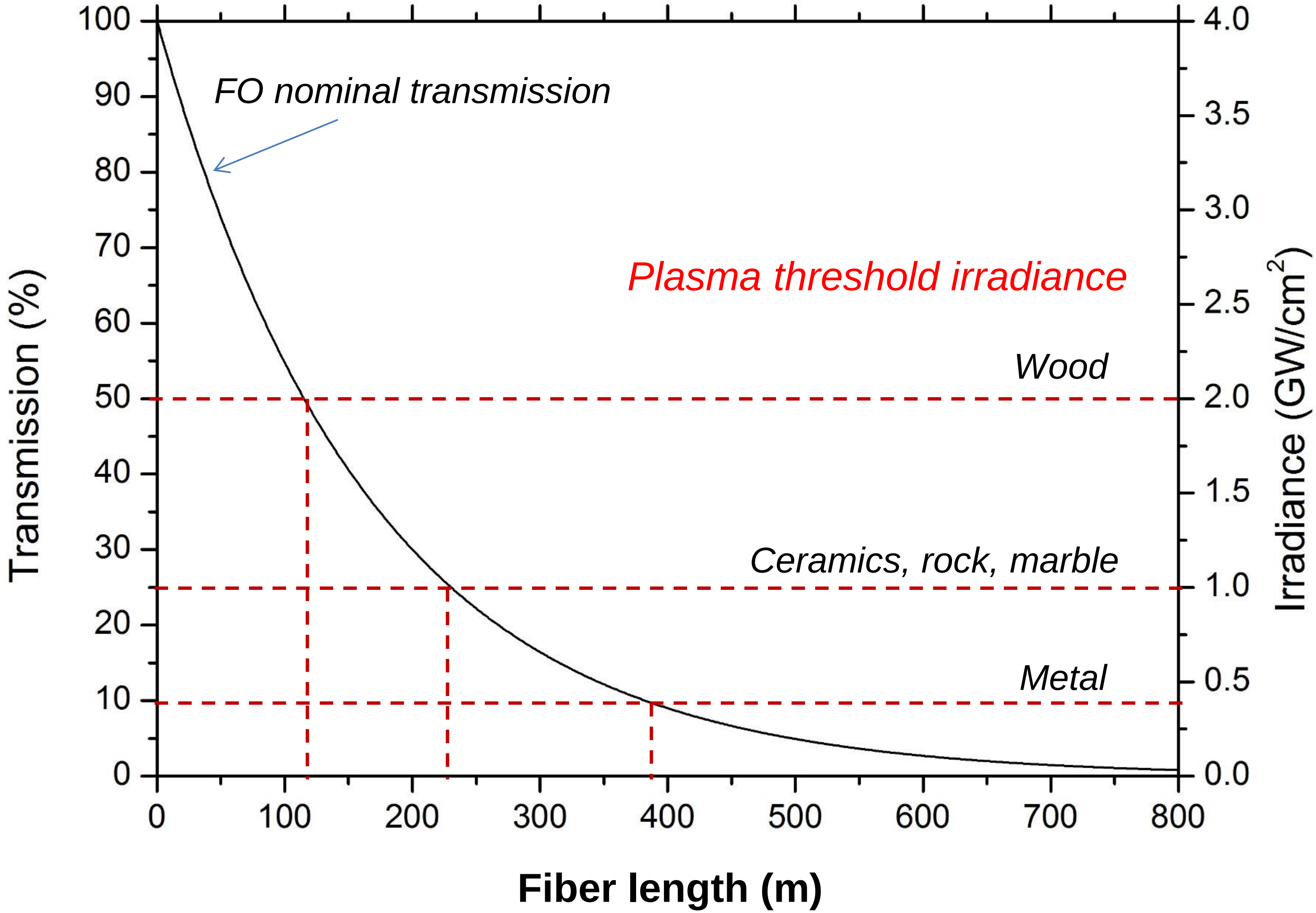
UNIVERSIDAD DE MÁLAGA



Maximum depth with a submersible-probe fiber optics LIBS analyzer?

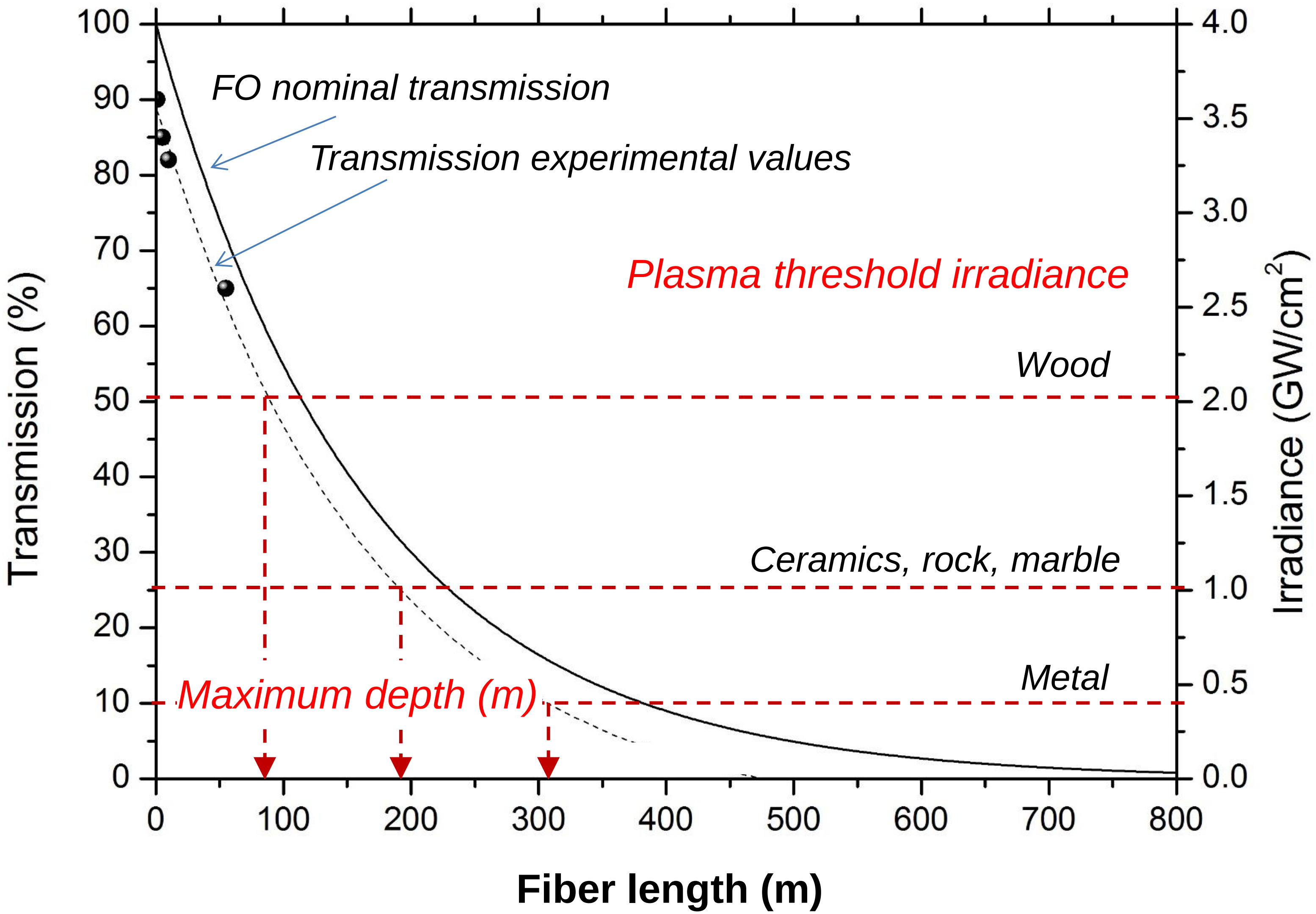
UNIVERSIDAD DE MÁLAGA

600 microns fiber **Input irradiance – 4 GW cm^{-2}**
just below the damage threshold of the fiber



Maximun depth with fiber optics LIBS

600 microns fiber **Input irradiance – 4 GW cm^{-2}**
just below the damage threshold of the fiber



Underwater standoff LIBS

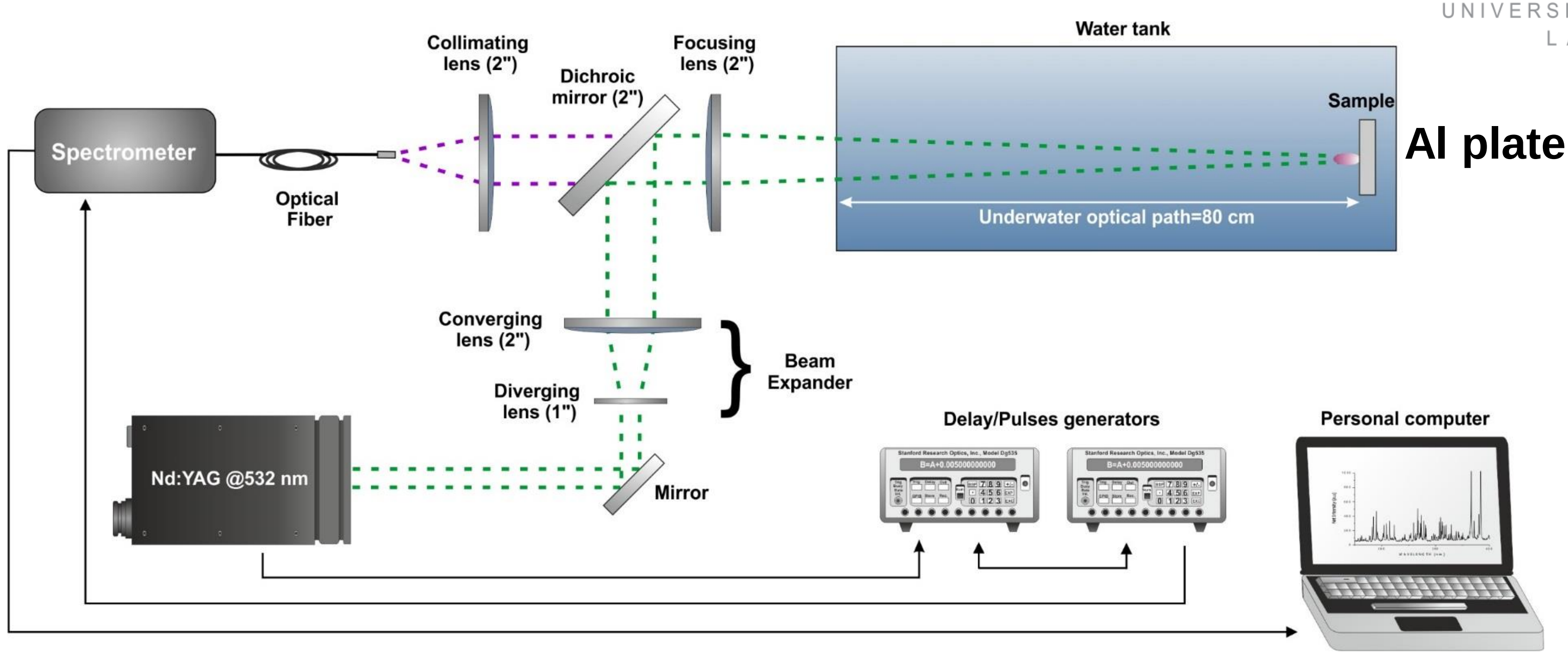
UNIVERSIDAD
DE MÁLAGA

A study of underwater stand-off laser-induced breakdown spectroscopy for chemical analysis of objects in the deep ocean, F.J. Fortes, S. Guirado, A. Metzinger, J.J. Laserna
Journal of Analytical Atomic Spectrometry, 30 (2015) 1050

Motivation

- **Reach deeper waters**
- **Increase the laser energy at sample**
- **Provide sampling flexibility**

Laboratory proof of concept: dual-pulse excitation



Working parameters

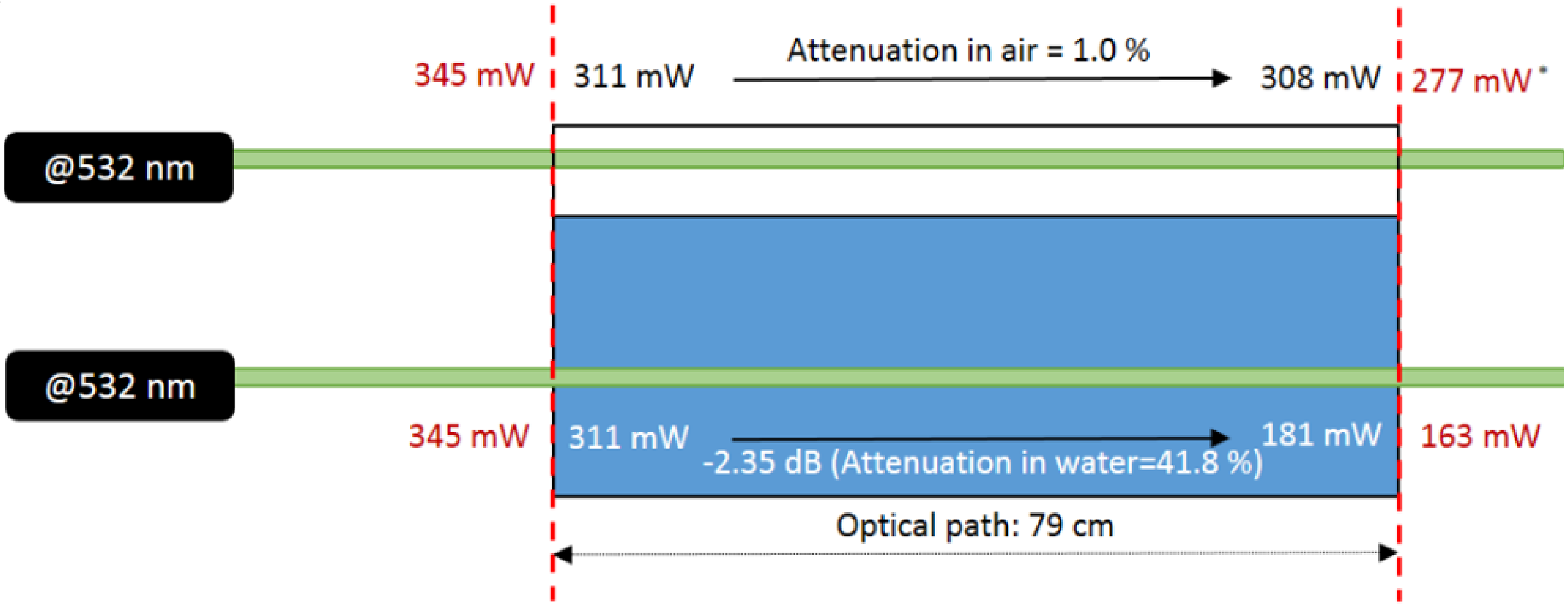
Dual-pulse excitation 200 mJ + 200 mJ

Laser wavelength - 532 nm

Solid-water interface

Underwater optical path up to 80 cm

Attenuation of laser beam @ 532 nm



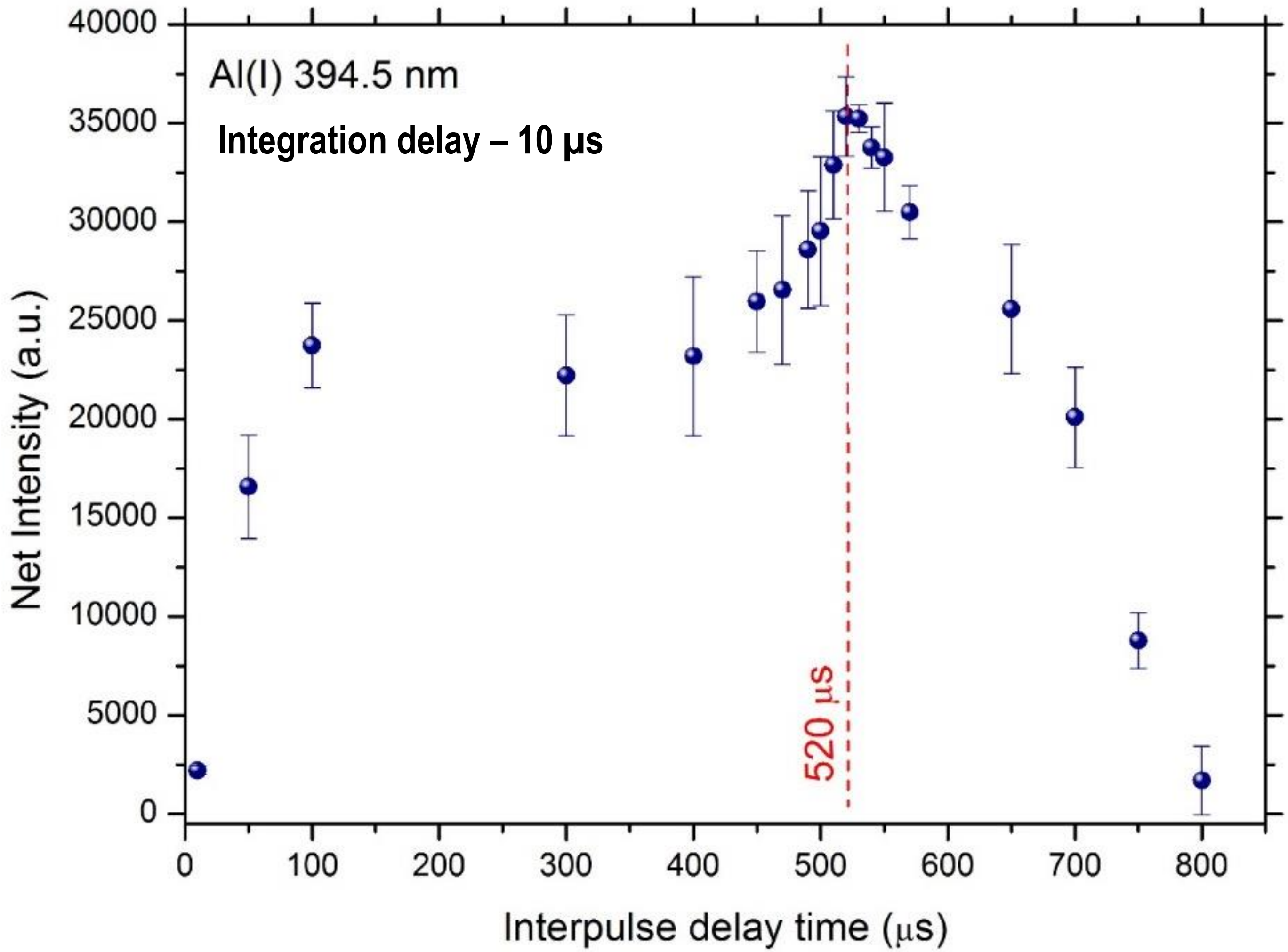
Intensity is reduced by 0.53 % in a 1 cm underwater path

Dual-pulse excitation (200 mJ + 200 mJ)

Interpulse delay

Underwater optical path - 80 cm

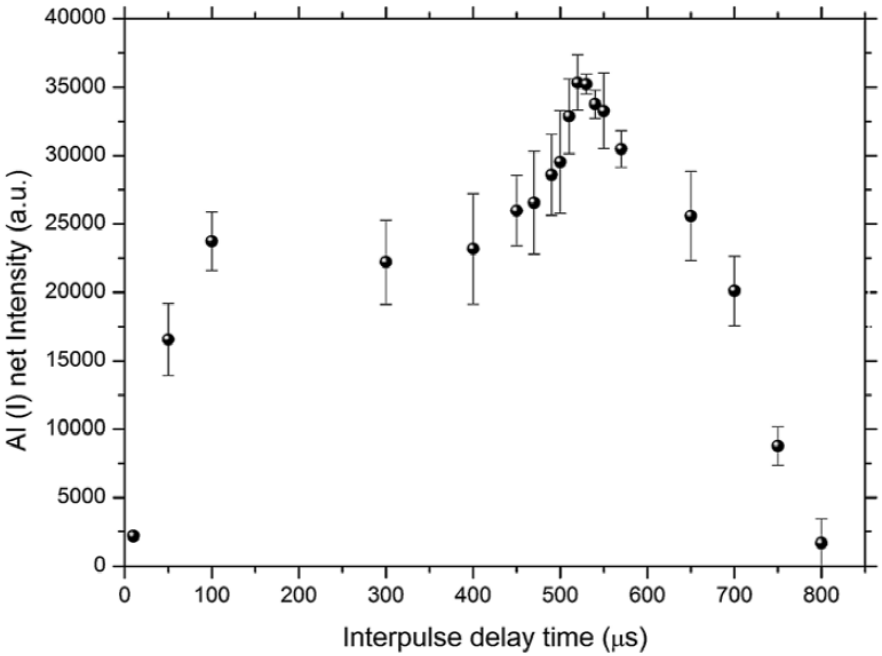
Aluminum plate



UNIVERSIDAD DE MÁLAGA

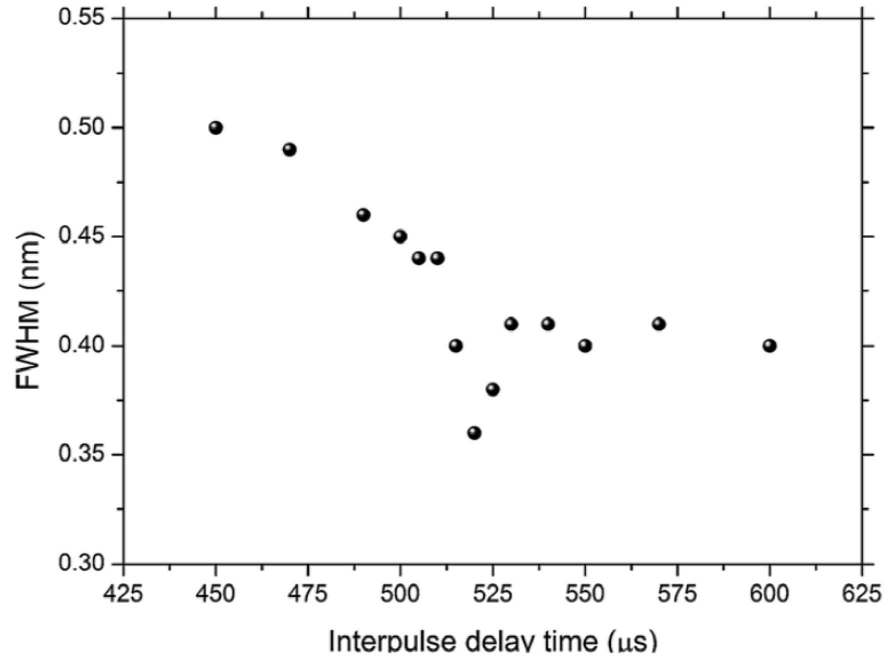
Intensity vs interpulse delay

A)



Peak width vs interpulse delay

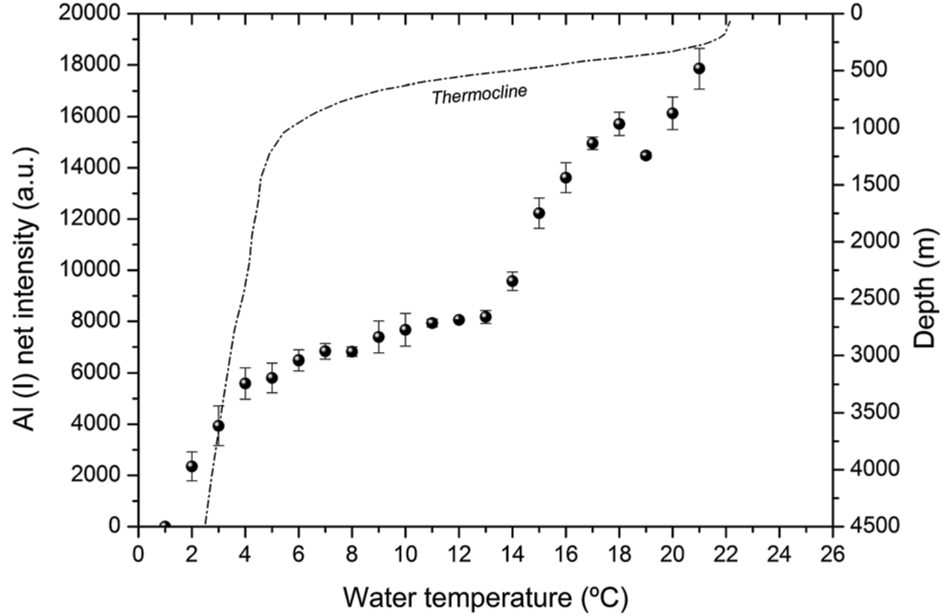
B)



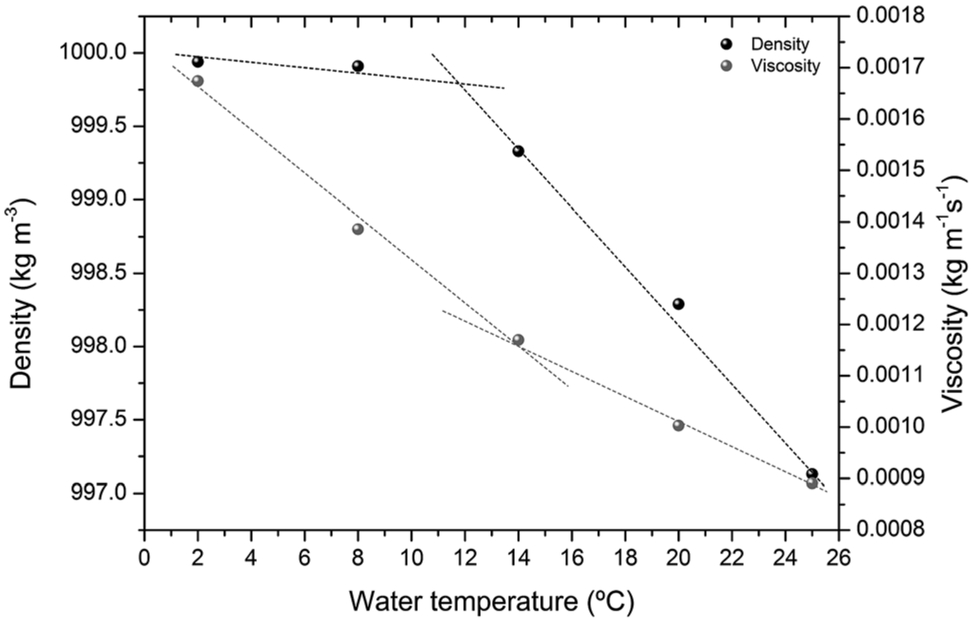
UNIVERSIDAD DE MÁLAGA

Effect of water temperature on LIBS intensity

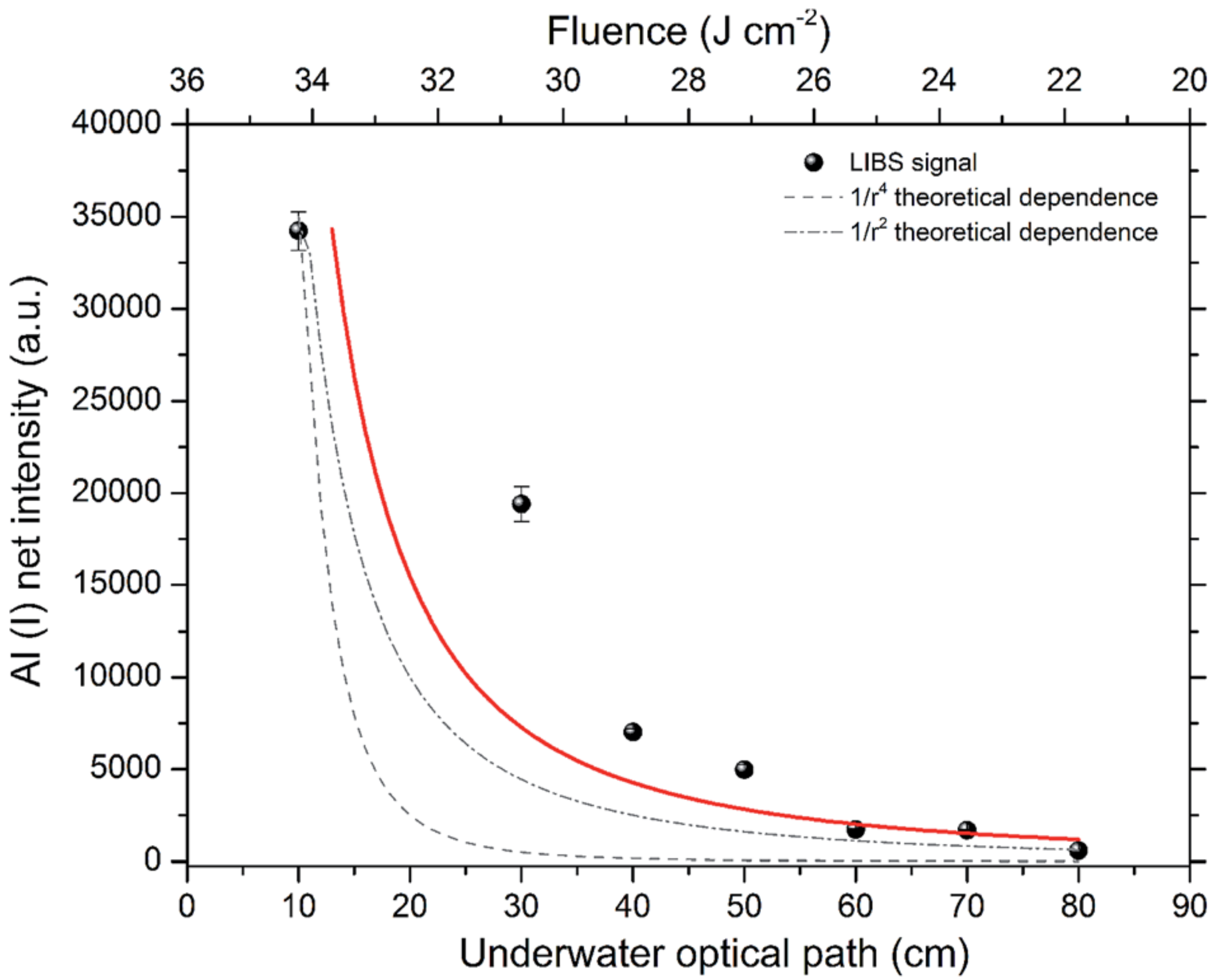
A)



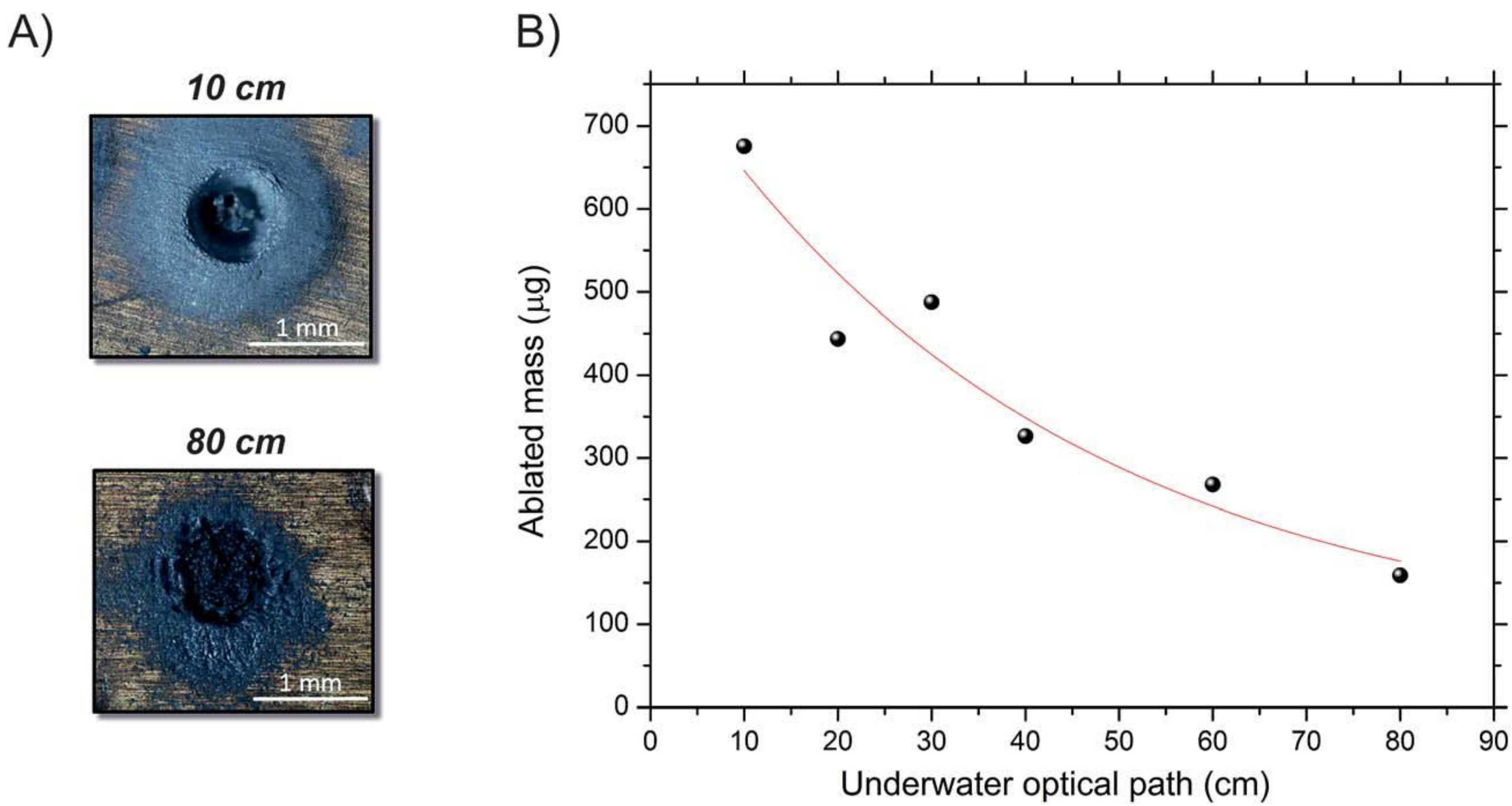
B)



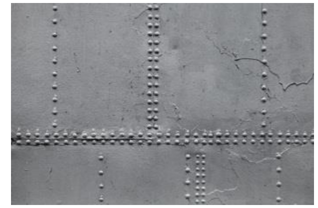
Infuence of path length on the LIBS signal



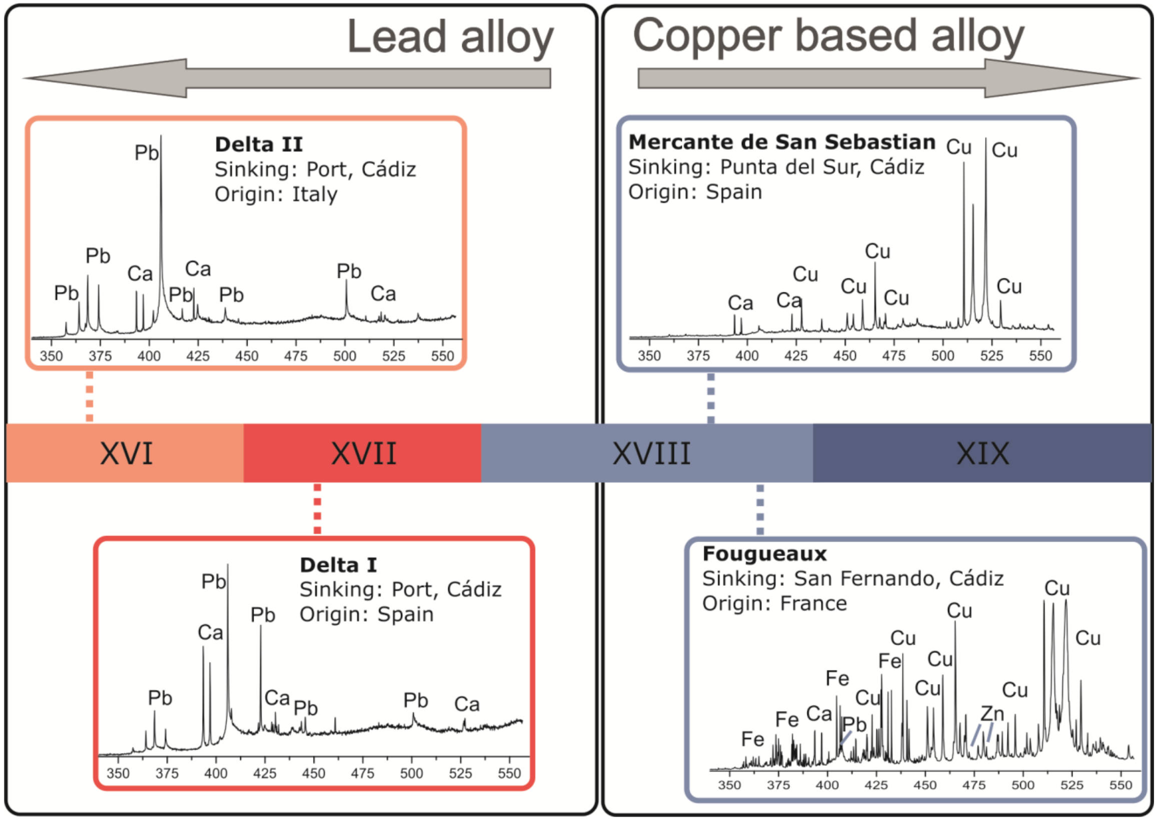
UNIVERSIDAD
DE MÁLAGA



Analysis of ship hull sheathings

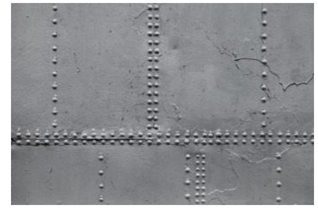


UNIVERSIDAD DE MÁLAGA

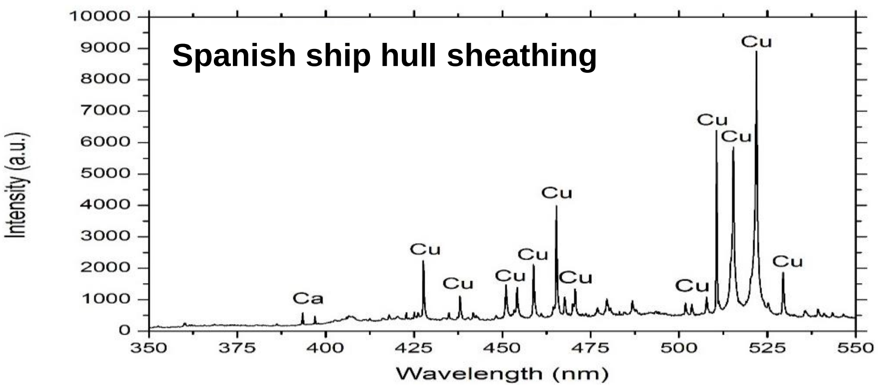


Analysis of ship hull sheathings

Underwater optical path - 80 cm

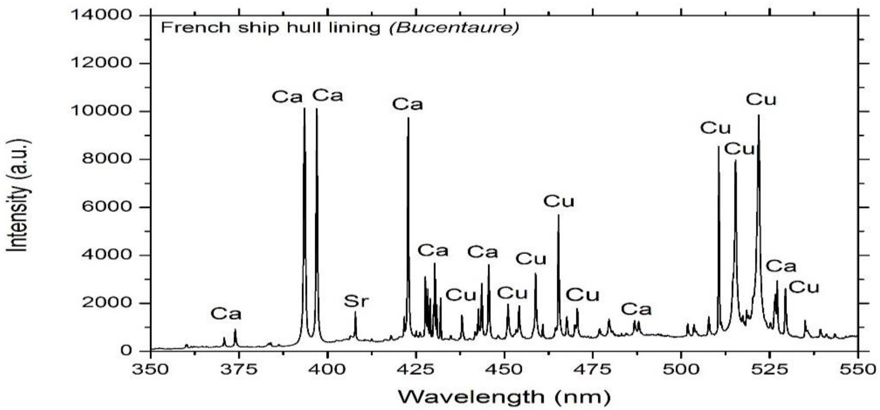


UNIVERSIDAD DE MÁLAGA

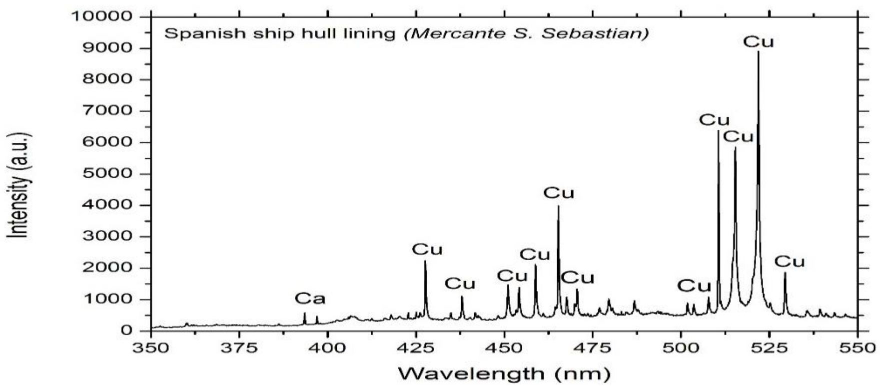


Underwater optical path - 80 cm

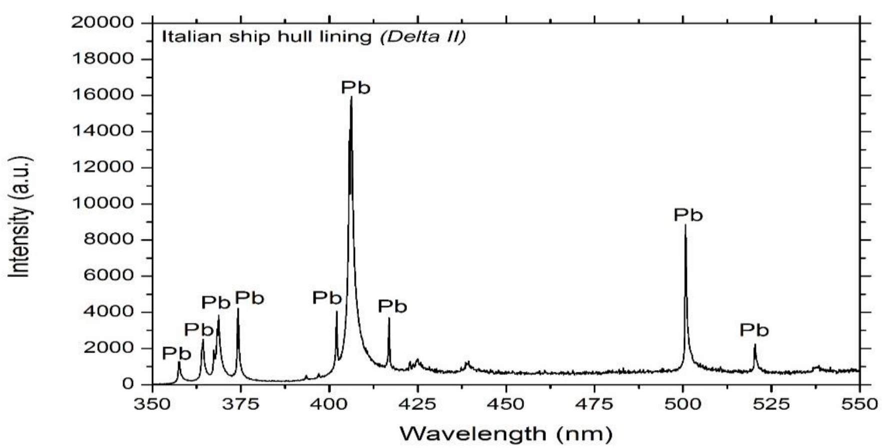
UNIVERSIDAD DE MÁLAGA



French ship
Early 19th Century



Spanish ship
Late 19th Century



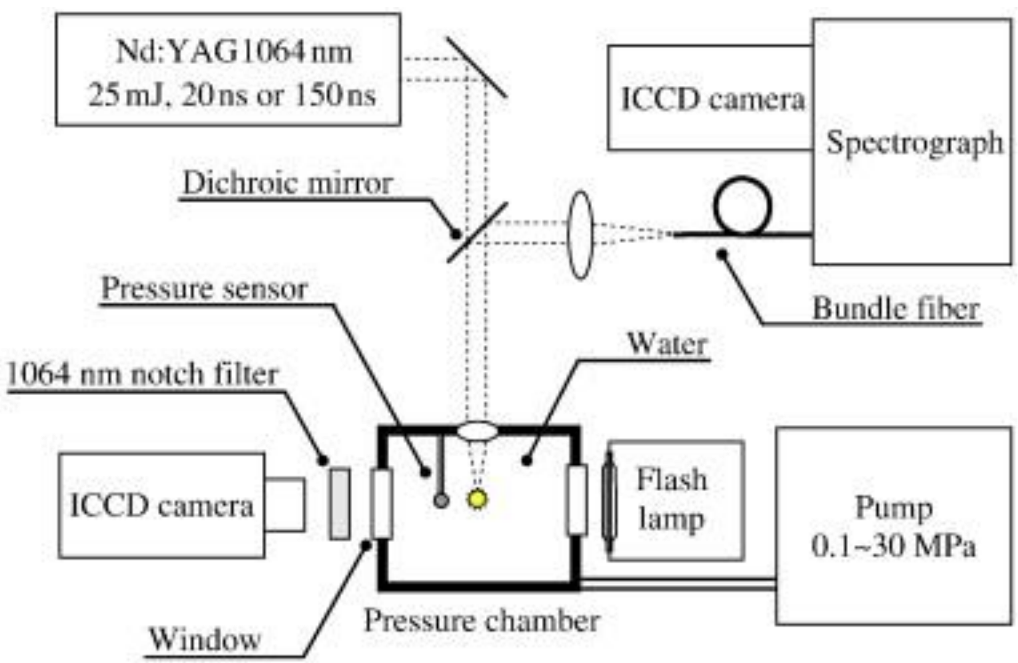
Italian (?) ship
Unknown date

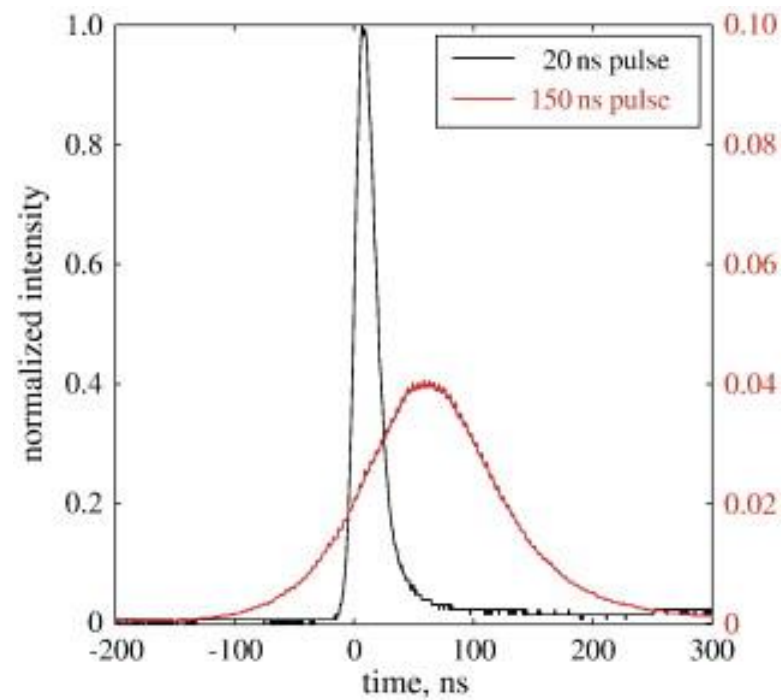
Spectrochimica Acta Part B: Atomic Spectroscopy
Volume 97, 1 July 2014, Pages 7–12

UNIVERSIDAD DE MÁLAGA

Long-duration nano-second single pulse lasers for observation of spectra from bulk liquids at high hydrostatic pressures

Blair Thornton[a], Tetsuo Sakka[b], Tatsuya Masamura[a], Ayaka Tamura[b], Tomoko Takahashi[a], Ayumu Matsumoto[b]

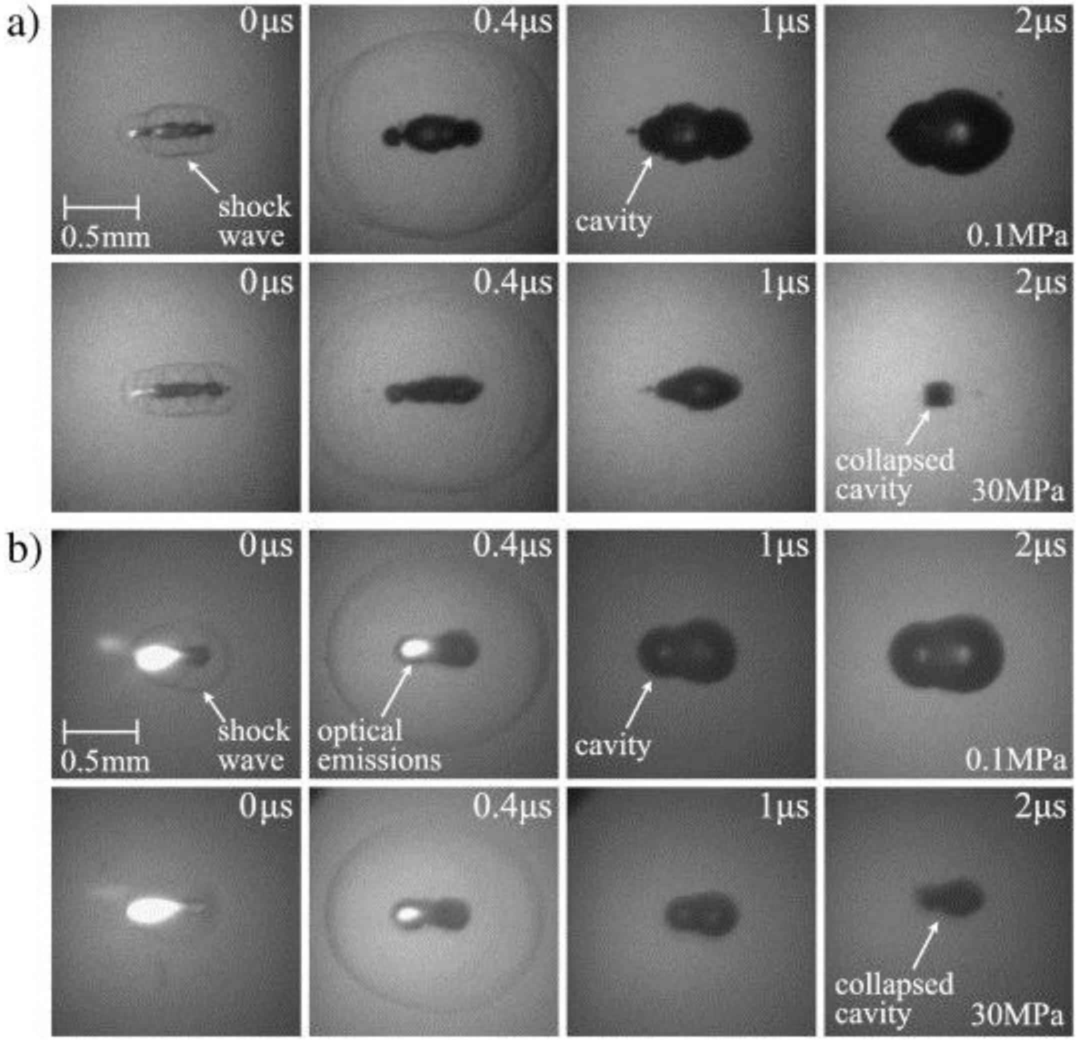




Shadowgraphy images from bulk water

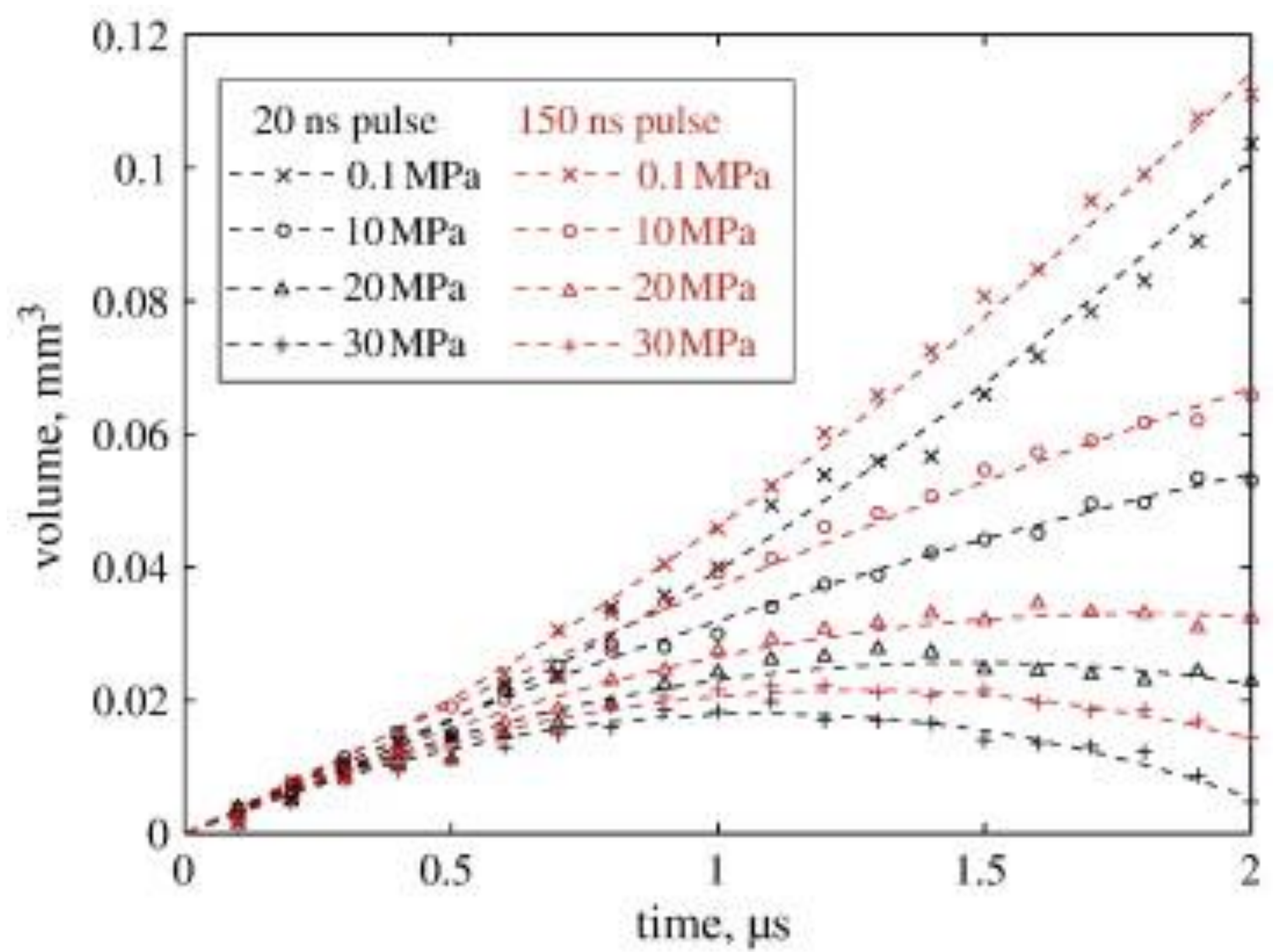
20 ns pulse

150 ns pulse



UNIVERSIDAD DE MÁLAGA

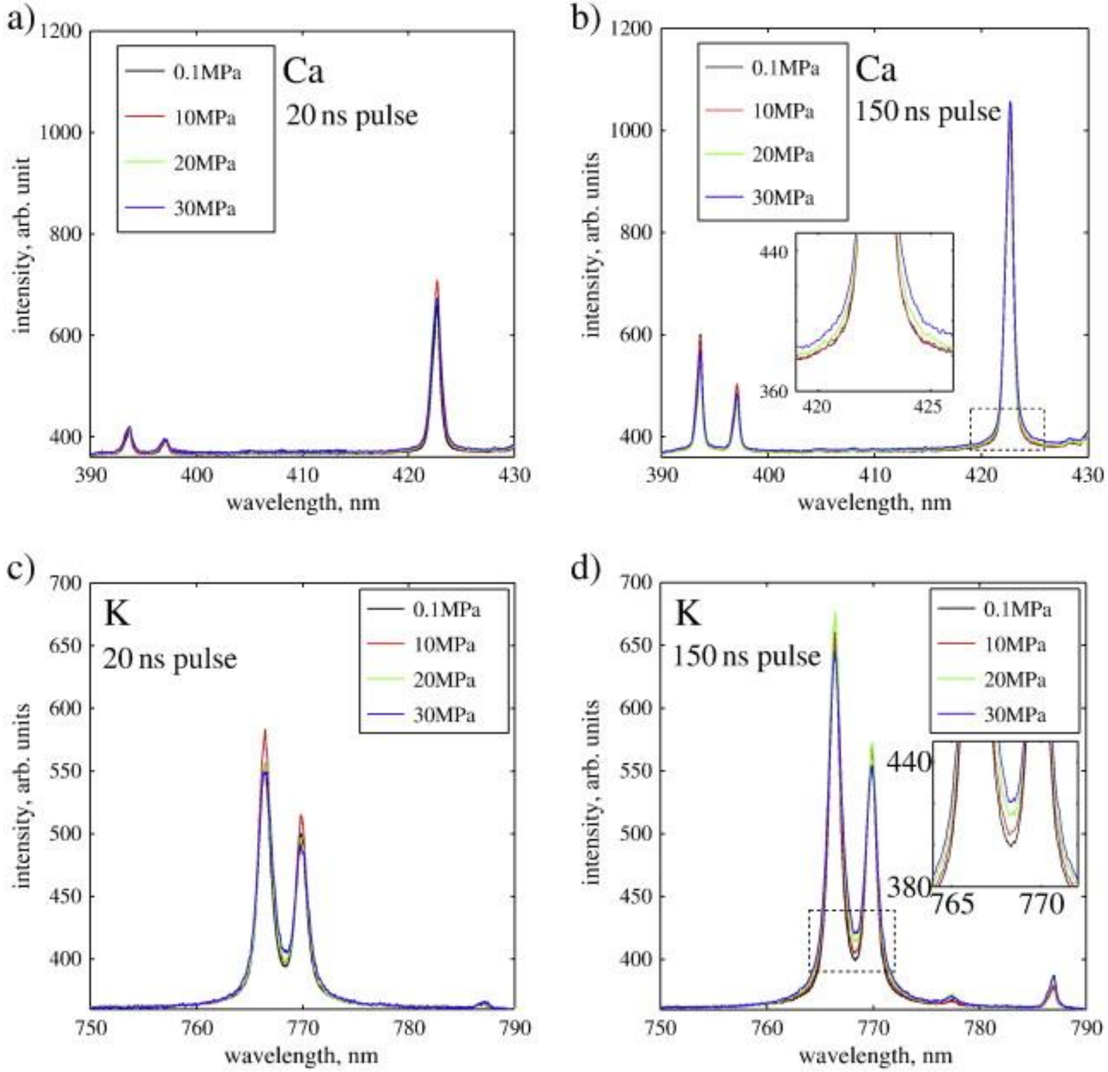
Volume of cavity generated after irradiation of a 20 and a 150 ns single pulse in a bulk liquid at 0.1, 10, 20 and 30 MPa.



Spectroscopic measurements of ionic solutions

containing 410 ppm Ca
(a) a 20 ns pulse, and (b) a 150 ns pulse, and 370 ppm K using (c) a 20 ns pulse, and (d) a 150 ns pulse, at pressures of 0.1, 10, 20, and 30 MPa respectively. A gate de...

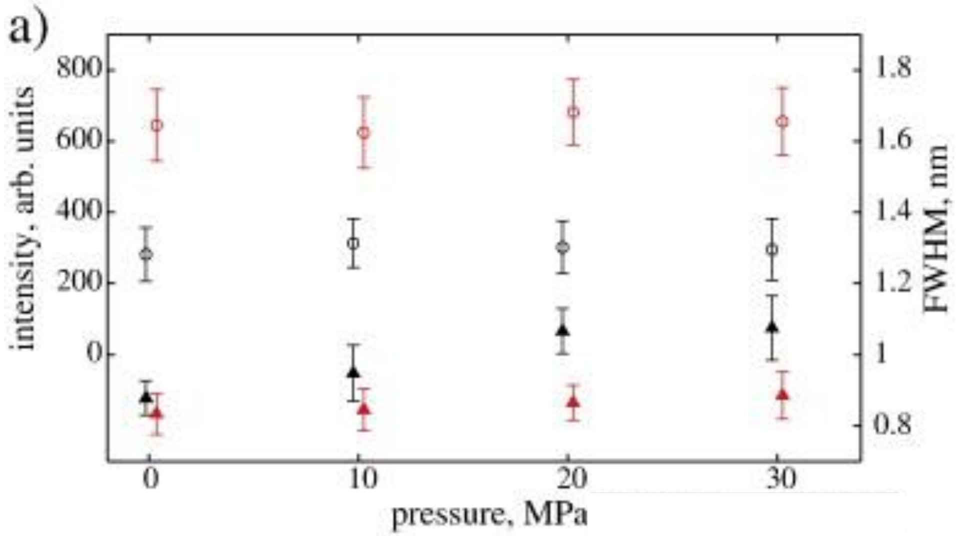
UNIVERSIDAD DE MÁLAGA

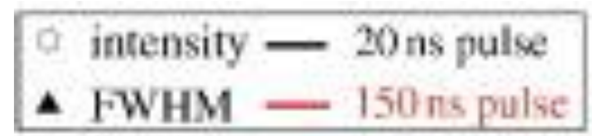


UNIVERSIDAD DE MÁLAGA

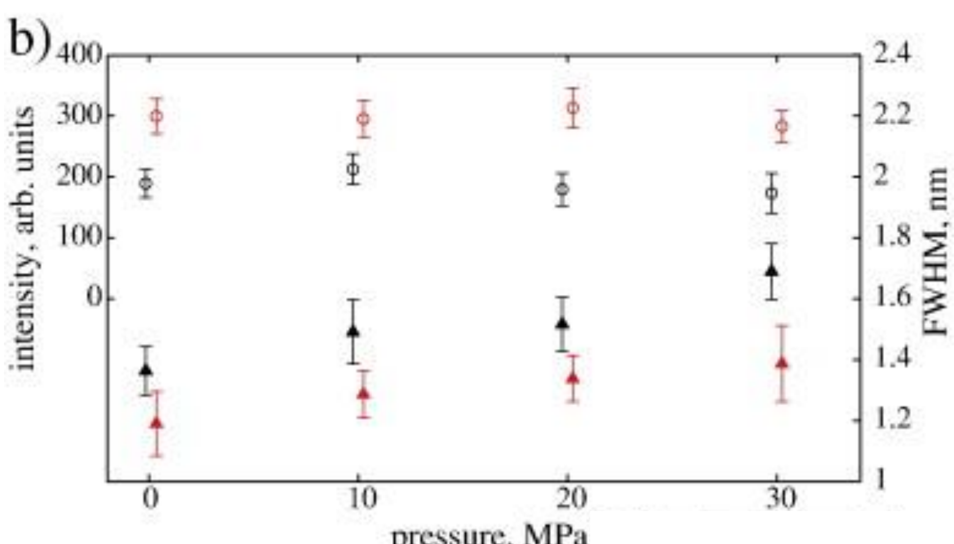
Peak width and intensity vs pressure

Ca





K



Deep-Sea Research I 95 (2015) 20–36

Contents lists available at ScienceDirect

Deep-Sea Research I

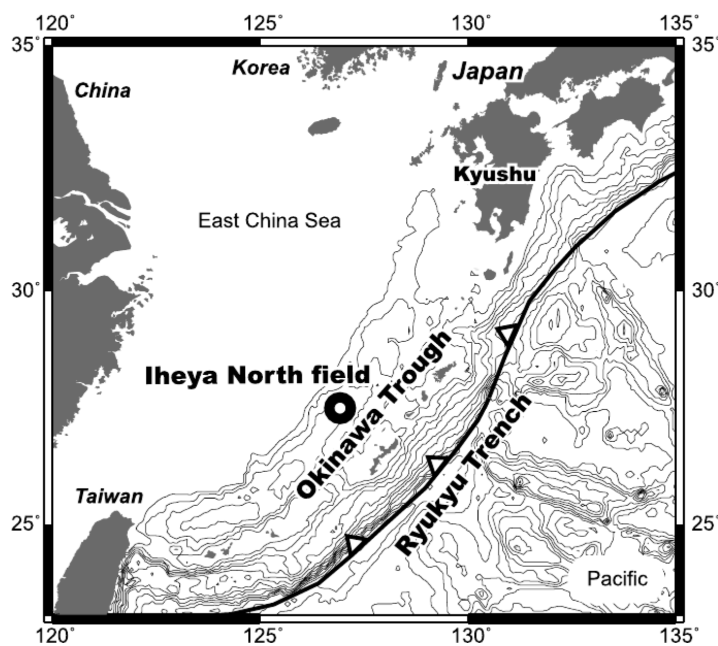
journal homepage: www.elsevier.com/locate/dsri

Instruments and Methods

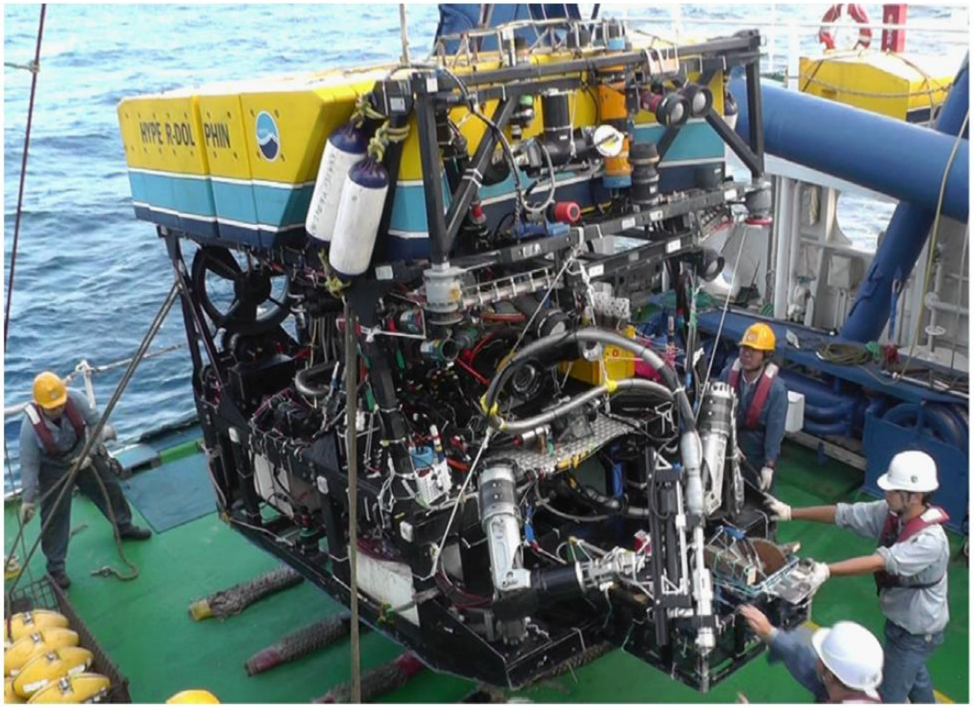
Development of a deep-sea laser-induced breakdown spectrometer for in situ multi-element chemical analysis

Blair Thornton [a,*], Tomoko Takahashi [a], Takumi Sato [a], Tetsuo Sakka [b], Ayaka Tamura [b], Ayumu Matsumoto [b], Tatsuo Nozaki [c], Toshihiko Ohki [a,d], Koichi Ohki [d]

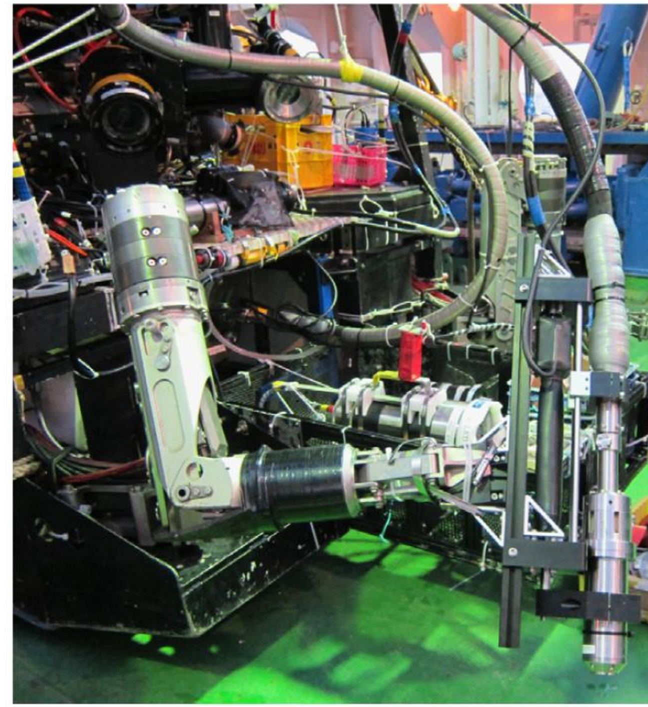
[a] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505, Japan
[b] Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan
[c] Research and Development Center for Submarine Resources, Japan Agency for Marine-Earth Science and Technology, Yokosuka, Kanagawa 237-0061, Japan
[d] OK Lab. Co. Ltd., 8-7-3 Shimorenjyaku, Mitaka, Tokyo 181-0013, Japan

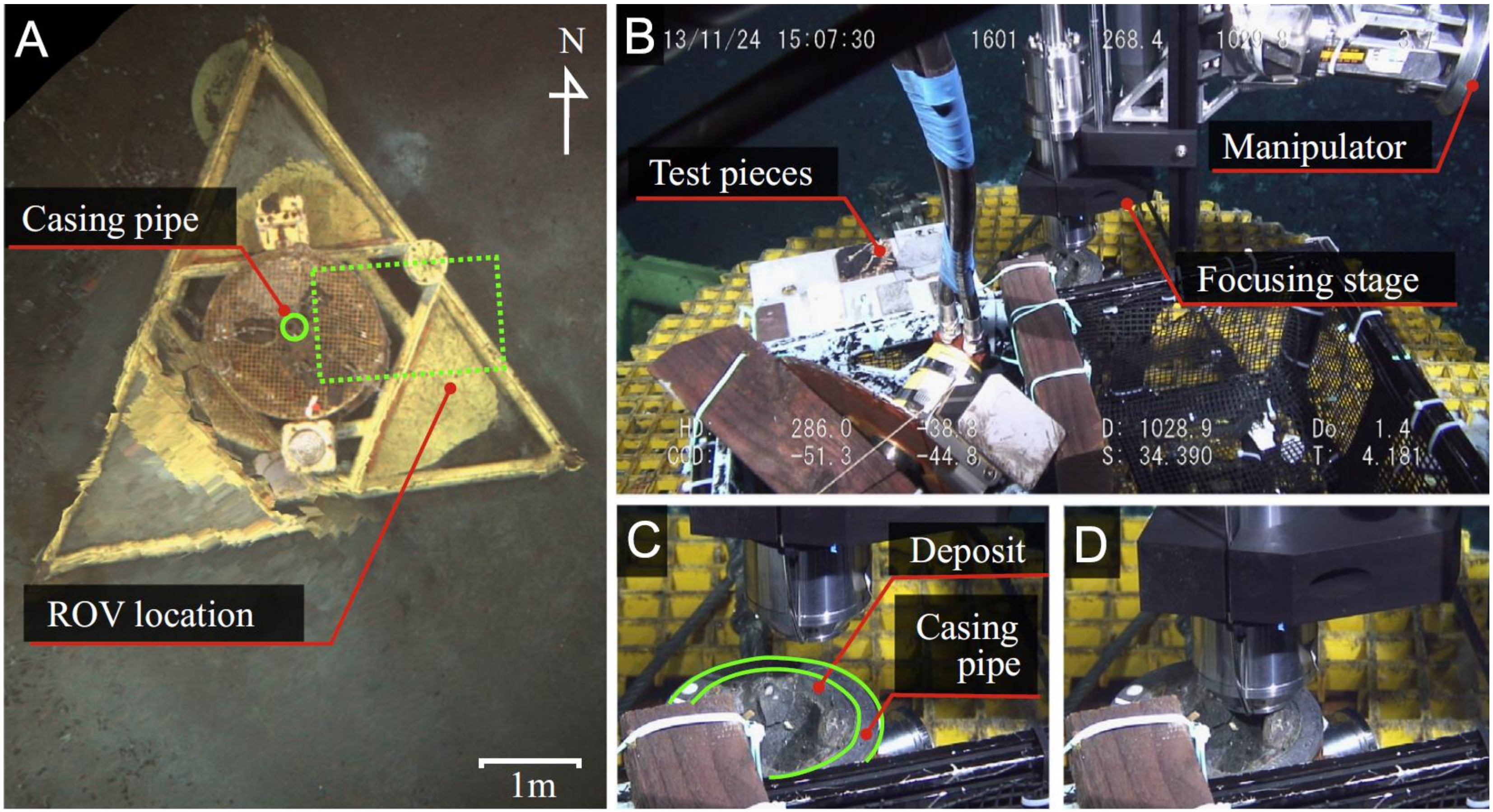


A



B

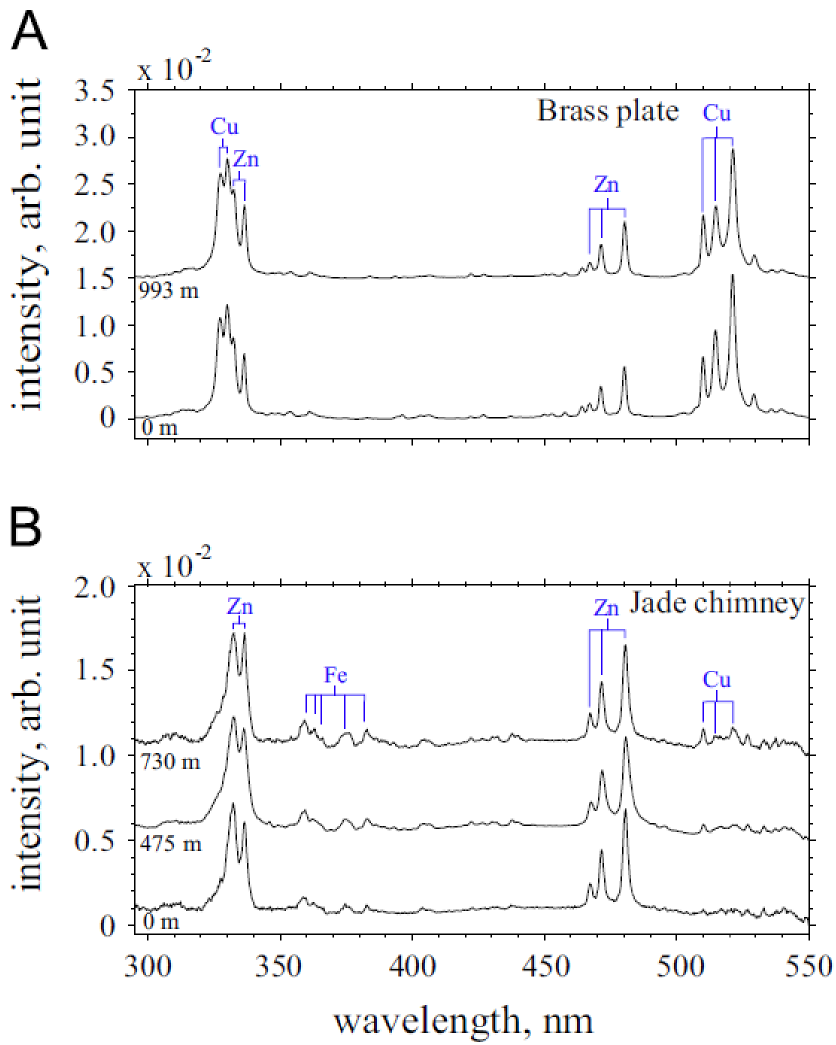



A
N
Casing pipe
ROV location
1m
B
13/11/24 15:07:30
1601
268.4
Test pieces
Manipulator
Focusing stage
286.0
-51.3
-44.8
D: 1028.9
S: 34.390
T: 4.181
C
Deposit
Casing pipe
D

Spectra at variable depth

Brass plate

Chimney deposit



Single shot spectra

20 mJ pulse
Duration 250 ns
Gate delay of 800 ns
Gate width of 500 ns

Spectra at depth of 1032 m

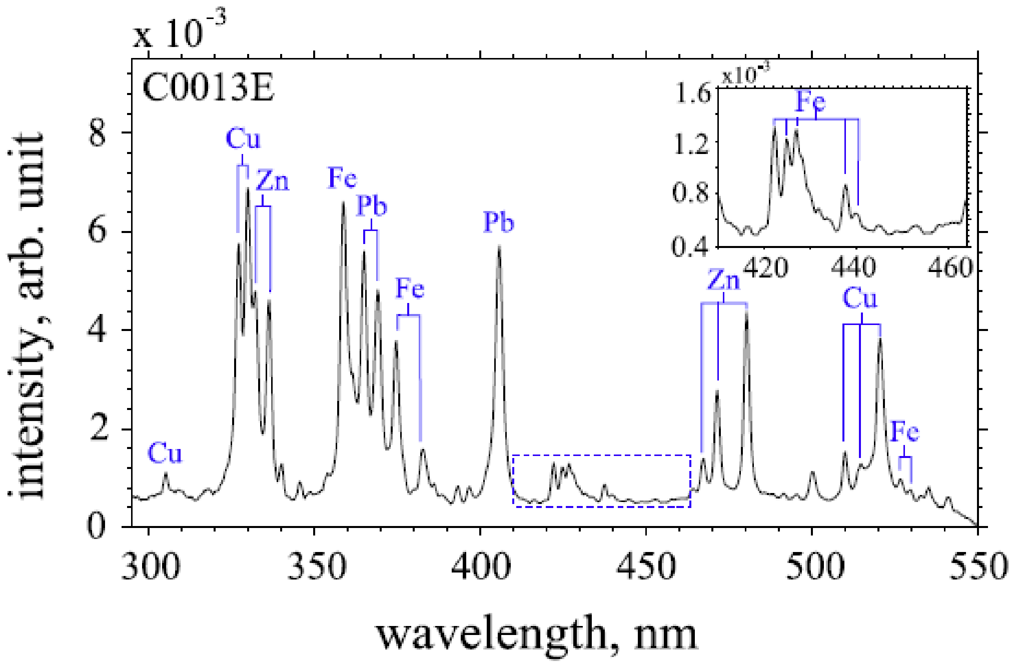


Fig. 19. Single shot measurement of the hydrothermal deposits in the C0013E casing pipe. The deposits, visible in Fig. 15C and D were measured in situ at a depth of 1032 m. Well-resolved lines of Zn, Pb, Cu, and Fe can be seen in the spectrum.

Conclusions

- LIBS is available for chemical analysis of subsea objects
- Qualitative and quantitative spectral information is used in the same way than in regular lab applications
- A single laser working either in monopulse or multipulse excitation constitutes a practical solution to these measurements
- Laser beam delivery through an optical fiber imposses a limit to the energy available for sample excitation
- Long pulses of 100+ ns produce quality LIBS spectra compatible with deep sea applications

UNIVERSIDAD
DE MÁLAGA

LIBS for deep sea applications

Javier Laserna

Departamento de Química Analítica
Universidad de Málaga

http://laser.uma.es

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