Fundamental of Laser Induced Plasmas: Instrumentations

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KFUPM, Dhahran, 26 April 2010
National Research Council of Canada (NRC)

- Federal government agency
- 4,150 full-time employees
- 1,200 guest workers
- 25 institutes
- 700 millions $/year

![Map of NRC Research Facilities and IRAP Office locations across Canada](image)
Industrial Materials Institute (IMI)
Boucherville

200 employees, 15 millions $
Fundamental of Laser-Induced Plasmas: Instrumentations

- Overview on the LIBS technique development
- Plasma characterization by atomic emission spectroscopy
  - Temperature and electron density
  - Spectrochemistry
- LIBS components: Laser, Detector, Spectrometer
  - Laser
    - Influence of the laser parameters on the LIBS analytical performance
    - Selection of a laser for LIBS application
  - Desirable requirements for atomic emission spectroscopy
  - Spectrometer
    - Conventional spectrometer
    - Paschen-Runge spectrometer
    - Echelle spectrometer
  - Detector
    - Solid-state detectors (ICCD, Interline CCD, IPDA, etc.)
    - Photomultiplier
    - Comparison of detection systems
- LIBS tools
  - Enhancement of LIBS sensitivity
  - Enhancement of LIBS reproducibility
  - Diagnostics of failure of the LIBS system
- Comparison with conventional techniques
- Conclusions
Ablation Mechanisms

 ⇨ Nanoseconde regime

1. Laser/absorption

2. Heating

3. Vapor

4. Plasma

5. Emission

6. Crater

LIBS

λ
Characteristic typical time scales for the different processes


• Free e\textsuperscript{-} heating and thermalization : \textasciitilde 100 fs

• Hot e\textsuperscript{-} gas cooling and energy transfer to the lattice: few ps

• Thermal diffusion into the bulk: 10 ps

• Onset of thermal melting and ablation: >0.1 ns
Emission Spectroscopy
Laser ablation

- Emission
- Or
- Ablated mass

⇒ Chemical composition by optical emission
⇒ Chemical composition by ablated mass coupled to another source of excitation
Laser ablation coupled to inductively coupled plasma (ICP) or Mass spectrometer

Fig. 1. Schematic of a laser ablation system.
Laser Induced Breakdown Spectroscopy: Acronyms

- LIPS: Laser Induced Plasma Spectroscopy
- LIBS: Laser Induced Breakdown 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 papers evolution

Over 2000 papers published in the last 5 years
2943 papers

Scopus

2009 (339)
2008 (303)
2007 (252)
2006 (225)
2005 (227)
2004 (188)
2003 (168)
2002 (145)
2001 (160)
2000 (127)
1999 (107)
1998 (98)
1997 (104)
1996 (91)
1995 (57)
1994 (60)
1993 (35)
1992 (27)
1991 (28)
1990 (23)
1989 (21)
1988 (16)
1987 (26)
1986 (20)
1985 (20)
1984 (20)
1983 (14)
1982 (5)

Consiglio Nazionale delle Ricerche (100)
University of Florida (89)
Nagoya University (51)
Los Alamos National Laboratory (50)
ENEA Centro Ricerche Frascati (42)
U.S. Army Research Laboratory (42)
Mississippi State University (41)
Universidad de Malaga (40)
Università degli Studi di Bari (39)
Technische Universität München (38)
CEA Saclay (34)
Oak Ridge National Laboratory (33)
Conseil national de recherches Canada (32)
University of South Carolina (32)
University of Fukui (31)
Fraunhofer-Institut für Lasertechnik (29)
Huazhong University of Science and Technology (29)
Lunds Universitet (26)
Forschungszentrum Karlsruhe (25)
CNRS (24)
Cairo University (23)
Lawrence Livermore National Laboratory (23)
Foundation for Research and Technology-Hellas (23)
Lawrence Berkeley National Laboratory (22)
Universität Duisburg-Essen (22)
Université Claude Bernard Lyon 1 (21)
University of Tokyo (21)
Kyoto University (20)
Queen's University Belfast (20)
### Distribution of LIBS papers in the literature

2688 papers published in the period 1965-2007

<table>
<thead>
<tr>
<th>Name of the periodical journal</th>
<th>Number of papers</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrochimica Acta B</td>
<td>299</td>
<td>11.1%</td>
</tr>
<tr>
<td>SPIE Proceeding</td>
<td>254</td>
<td>9.4%</td>
</tr>
<tr>
<td>Applied Spectroscopy</td>
<td>174</td>
<td>6.5%</td>
</tr>
<tr>
<td>Journal of Applied Physics</td>
<td>165</td>
<td>6.1%</td>
</tr>
<tr>
<td>J. Analytical Atomic Spectrometry</td>
<td>107</td>
<td>3.9%</td>
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<tr>
<td>Applied Surface Science</td>
<td>97</td>
<td>3.6%</td>
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<tr>
<td>Applied Optics</td>
<td>68</td>
<td>2.5%</td>
</tr>
<tr>
<td>Analytical Chemistry</td>
<td>35</td>
<td>1.3%</td>
</tr>
<tr>
<td>Analytical Bioanalytical Chemistry</td>
<td>30</td>
<td>1.1%</td>
</tr>
<tr>
<td>Applied Physics A</td>
<td>29</td>
<td>1.0%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1258</strong></td>
<td><strong>46.8%</strong></td>
</tr>
</tbody>
</table>
Development of the LIBS technique

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 date: Applications emerge
- Industrial lasers, intensified detectors and echelle spectrometers enter commercial market
- Growth in research activity
LIBS components

**Components and Functions:**

- **Target:** Surrounding atmosphere, pressure, nature
- **Laser:** Pulse energy, duration, spot size, wavelength
- **Spectrometer:** Échelle spectrometer, Czerny-Turner, Rowland circle
- **Detector:** IPDA, ICCD, Interline CCD, gated CCD, PMs
- **Controller:** Lenses, Plasma
- **PC:** Reflectivity, heat capacity, melting and boiling point, thermal conductivity etc.

**Key Terms:**
- **LIBS:** Laser Induced Breakdown Spectroscopy
- **IPDA:** Intense Pulse Diode Array
- **ICCD:** Intensified Charge-Coupled Device
- **Interline CCD:** A type of CCD sensor
- **Gated CCD:** A type of image sensor
- **PMs:** PhotoMultiplier Tubes
- **Échelle spectrometer:** A type of spectrometer
- **Czerny-Turner:** A type of optical layout
- **Rowland circle:** A concept used in optics
- **IPDA, ICCD, Interline CCD, gated CCD, PMs:** Imaging sensors used in LIBS
- **Reflectivity, heat capacity, melting and boiling point, thermal conductivity etc.:** Properties measured in LIBS
Overview on the LIBS technique development

Plasma characterization by atomic emission spectroscopy
- Temperature and electron density
- Spectrochemistry

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LIBS tools
- Enhancement of LIBS sensitivity
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Conclusions
Influence of the surrounding atmosphere

Helium

Argon

air

10 torr

100 torr

760 torr
Time-resolved LIBS spectra on copper alloy sample: Spectroscopic aspects
Determination of Plasma Temperature

Influence of laser pulse energy on the plasma temperature

![Graph showing the influence of laser pulse energy on the plasma temperature. The graph plots temperature (K) against time (µs) for different laser pulse energies: 170 mJ (circles), 100 mJ (squares), and 60 mJ (triangles). The temperature decreases over time for all energy levels, with 170 mJ showing the highest peak temperature.](image-url)
Influence of laser pulse duration on the plasma temperature

B. Le Drogoff, J. Margot, F. Vidal, S. Laville, M. Chaker, M. Sabsabi, T. W. Johnston, and O. Barthélemy, 
Influence of laser pulse duration on the electron density

\[
\Delta \lambda_{\text{Stark width}} = 2 \times 10^{-22} w n_e \left[ 1 + 5.53 \times 10^{-6} n_e^{1/4} \alpha \left( 1 - 6.8 \times 10^{-2} n_e^{1/6} T^{-1/2} \right) \right]
\]

\[
\Delta \lambda_{\text{Stark shift}} = 10^{-22} w n_e \left[ \frac{d}{w} + 6.32 \times 10^{-6} n_e^{1/4} \alpha \left( 1 - 6.8 \times 10^{-2} n_e^{1/6} T^{-1/2} \right) \right]
\]

\[
\Delta \lambda \approx 2\omega \left( \frac{N_e}{10^{16}} \right)
\]

LIBS technique

- Line intensity
- Ratio of two lines

\[ I_{mn} = \frac{A_{mn} N_{g_m}}{U(T)} \cdot \frac{hc}{\lambda_{mn}} \exp \left( -\frac{E_m}{kT} \right) \]

\[ \frac{\varepsilon_t}{\varepsilon_m} = \alpha \cdot \frac{N_t}{N_m} \cdot f(T) \]

with

\[ f(T) = \exp \left( -\frac{\Delta E}{kT} \right) \]

\[ \alpha = \frac{g_1 A_1 U_2 \lambda_2}{g_2 A_2 U_1 \lambda_1} \]
Fundamentals of LIBS

Laser → Grating → SPECTROMETER → Transient signal

Temporal resolution

Plasma

hv

Intensity

Delay

Gate

Laser shot

without temporal resolution

I(t) \propto N^* \cdot h \cdot \nu

N^* = N_0 \cdot \exp(-E/kT(t))

Calibration

Intensity (I)

Concentration
• The combination of spectrometer and detector is an important factor to consider in optical emission spectroscopy for any plasma characterization or analytical spectrochemistry.
• The experimentalist must choose the type of measurements to be made, the concentration range to be monitored.
• Spectroscopist’s need:
  – Reproducibility
  – Sensitivity
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LIBS components

Source of energy
Laser

Plasma

Detection system
Spectrometer/Detector

Target
1917 Einstein First theorized about stimulated emission, the process which makes lasers possible

1958 Shawlow, Tawns Theorized about a visible laser

1960 Maiman Built first ruby laser with optical pumping

1962 Brech, Cross Birth of LIBS: detection of spectrum from ruby laser induced plasma

1964 Runger et al. First direct spectrochemical analysis by LIBS

1985 Mourou Chirped Pulse Amplification (CPA)
Selecting a Laser for LIBS applications

- Pulse energy
  Focusing conditions, spot size, fluence, stability.
- Wavelength
  Absorption, reflectivity, thermal conduction, laser-induced plasma shielding, ablated mass.
- Pulse duration
  Ablation regime, ablated mass, plasma spectrochemistry, thermal conduction, laser-induced plasma shielding etc.
- Repetition rate and beam quality
  Reproducibility, rapidity of analysis
- Divergence
  Focusing conditions, spot size
LIBS LEXICON:
CHARACTERIZATION OF LASER RADIATION

• ENERGY
• INTENSITY
• POWER
• IRRADIANCE
• POWER DENSITY
• ENERGY DENSITY
• FLUENCE
USE

- FLUENCE or RADIANT EXPOSURE (Energy/Area) e.g., J cm\(^{-2}\)
- IRRADIANCE (Power/Area) e.g., W cm\(^{-2}\)
- (INTENSITY) same as Irradiance
- If given per unit frequency (wavelength), then add “spectral”
- Photon Flux (photons/time), e.g., s\(^{-1}\)
- Photon Irradiance (photons/time-area) e.g., s\(^{-1}\) cm\(^{-2}\)

AVOID

- Energy density when units are given in (J cm\(^{-2}\))
- Power density when units are given in (W cm\(^{-2}\))
- Using Fluence and Irradiance interchangeably
**Beam focusing:**
A laser beam can be focused into a small spot using a positive lens, thus increasing the power/energy density in the lens’ focal plane.

Assuming a laser beam with diameter $D$, the minimum (diffraction limited) spot diameter $d_0$ is given by:

$$d_0 \approx \frac{1.27 f \lambda}{D}$$

where $f$ is the lens’ focal length.
Actual laser beams are never perfectly Gaussian. To address the issue of non-Gaussian beams, a beam quality factor, $M^2$, has come into general use.

For a theoretical Gaussian beam, the value of the radius-divergence product is:

$$w_0 \theta = \frac{\lambda}{\pi}$$

For a real laser beam, we have:

$$w_{0M} \theta_M = M^2 \frac{\lambda}{\pi} > 1$$

where $w_{0M}$ and $\theta_M$ are the $1/e^2$ intensity waist radius and the far-field half-divergence angle of the real laser beam, respectively. The beam quality factor $M^2$ can therefore be defined by:

$$M^2 = \frac{w_{0M} \theta_M \pi}{\lambda}$$

Typical values of $M^2$ for laser systems:

- HeNe: $1.0 < M^2 < 1.1$
- Ion lasers: $1.1 < M^2 < 1.3$
- Collimated TEM$_{00}$ diode lasers: $1.1 < M^2 < 1.7$
- High energy multimode lasers: $M^2$ up to $3 - 4$
LIBS components:
Laser

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

Cost: 3-250k$
Lasers used for LIBS

Q-switched Nd-YAG
- Flashlamp
- Laser rod
- Laser power supply
- Crystals for harmonics generation
- Q-switch cell

Excimer laser
- TEA CO2 laser
- Ground
- High voltage pulse
- Gas
Literature on LIBS with ultra-short laser pulses

- In the last 5 years we counted more than 1800 papers on LIBS. Most of them are dealing with ns laser pulses.
- Only 50 papers were devoted to LIBS with ultra-short laser pulses.
General conclusions from literature comparing fs to ns

- For femtosecond regime in the $10^{13}-10^{14}$ W/cm$^2$, the pulse duration is shorter than the plasma expansion, the heat conduction time and the electron to ion energy transfer time.
- No thermal effect (without collateral damage to the rest of the target)
- No plasma shielding
- No thermal stress
- Cutting and drilling holes with high precision
- Improved spatial resolution
- Fs laser is 10 times higher in price than ns laser
Why doing LIBS analysis by ultra-short pulses?

- **nanosecond interaction** $10^{-9}$s

- **femtosecond interaction** $10^{-15}$s

Influence of laser pulse duration on the crater diameter

B. Le Drogoff, M. Chaker, T. W. Johnston, S. Laville, F. Vidal, O. Barthélemy, J. Margot and M. Sabsabi, 
Spectrochemistry

Analytical figure of merit: sensitivity

Si(I) 288.16 nm

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The requirements for the ideal spectrometer and detector to provide for simultaneous determination of any combination of elements in the spectrum include:

- **A high resolution** of 0.01-0.003nm to resolve the lines of interest and avoid interferences.
- **Wide wavelength coverage** is needed, typically from 165 nm to 800-950 nm to be able to detect simultaneously several elements.
- **A large dynamic range** is necessary to provide the optimum signal-to-noise ratio (SNR) for a large range of elemental intensities; the detector has to have a wide dynamic range, typically 6 to 7 orders of magnitude.
- **The spectrometer/detector combination should have a high sensitivity and a linear response to radiation.**
- **The detector has to have high quantum efficiency** particularly in the near infrared and UV and low noise characteristics.
- **For rapid analysis the read out and data acquisition time should be shorter at least less than the time lap between the laser pulses.**
Paschen-Runge and Czerny-Turner spectrometer systems
Spectrometer set-up

- Czerny Turner Spectrometer
- Échelle Spectrometer
Comparison of spectrometers

\[ \sin \alpha \pm \sin \beta = kn\lambda \]

Where \( \alpha \) and \( \beta \) are respectively the incidence and diffracted angle, \( n \) is the grating density (number of grooves/mm), \( \lambda \) is the wavelength and \( k \) is diffraction order. For example, if we take \( \sin \alpha + \sin \beta = 1 \) and \( \lambda = 333 \text{ nm} \), the product \( kn \) will be 3000: for \( k = 1 \), \( n = 3000 \) grooves/mm, while for \( k = 50 \), \( n = 60 \) grooves/mm.

Comparison of a conventional grating and an echelle grating in terms of spectral features

<table>
<thead>
<tr>
<th>Feature</th>
<th>Conventional grating</th>
<th>Echelle grating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Focal length (m)</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Grating density (grooves/mm)</td>
<td>1200</td>
<td>79</td>
</tr>
<tr>
<td>Diffraction angle</td>
<td>10°22’</td>
<td>63° 26’</td>
</tr>
<tr>
<td>Width (mm)</td>
<td>52</td>
<td>128</td>
</tr>
<tr>
<td>Spectral order at 300nm</td>
<td>1</td>
<td>75</td>
</tr>
</tbody>
</table>
Detectors

- Intensified CCD or Intensified PDA

Poor quantum efficiency (below 20%), limited wavelength coverage, high gain, 16 bits dynamic range, simultaneous measurements, high cost.

Cost: 25-50 k$
Basics of ICCD

1-Photocathode: converts photons to electrons
2-Microchannel Plate (MCP): amplifies the photoelectrons
3-Phosphor: converts electron to photons
CCD development

- 1970 CCD invented by Smith and Boyle, Bell NJ
- 1973 introduced by Fairfield
- 1979 Scientific applications by RCA.
- 1983 Use in spectroscopy
- 1990 Integrated in ICP instrumentations by several companies.
- Intensifier coupled to photodiode array in the mid 80’s and coupled to CCD in the beginning of 90’s.
Detectors

- Interline CCD, Gated CCD

Larger wavelength coverage, high quantum efficiency, 12-14 bits dynamic range, less expensive.

Cost: 1-20 k$

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Typical Range</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-well capacity</td>
<td>10000-500000 electrons</td>
<td>Defines dynamic range</td>
</tr>
<tr>
<td>Pixel dimensions</td>
<td>6-30µm</td>
<td>Dictate spectral or spatial resolution</td>
</tr>
<tr>
<td>Array format</td>
<td>Related to pixel size and number</td>
<td>Dictates the active area</td>
</tr>
<tr>
<td>Number of pixels</td>
<td>58X512 to 2048X2048</td>
<td>Dictates number of resolution elements and acquisition time</td>
</tr>
<tr>
<td>Quantum efficiency</td>
<td>0-80%</td>
<td>Defines ultimate sensitivity limit</td>
</tr>
<tr>
<td>Blooming</td>
<td>Present with materials having strong lines in the range 200-900nm</td>
<td>Cannot observe weak lines near strong lines, ghost lines</td>
</tr>
<tr>
<td>Read noise</td>
<td>Few electrons</td>
<td>Excess noise limits weak light detection</td>
</tr>
</tbody>
</table>
Detectors

- Photomultiplier PM

Monochromatic, low quantum efficiency, bulky, larger wavelength coverage, high dynamic range, cheap.

Cost: 1-3 k$

• Aluminum spectra
Échelle spectrometer LIBS spectrum from copper ore sample

Fe 306.73

Bi 306.77
Typical evolution of echelle spectrometer response in a given diffraction order

- It needs calibration for absolute measurements
LIBS components: échelle spectrometer/detector

Echelle spectrometer ESA3000, LLA
http://www.lla.de/echelle.html

Echelle spectrometer SE200
Catalina with Roper, http://www.libs.info/

Andor spectrometer 7500
http://www.andor-tech.com/

LTB echelle spectrometer
http://www.ltb-berlin.de/

Cost: 35-80k$
LIBS equipment

Ocean Optics and Spectrolaser use gated CCD

Pharmalaser uses an interline CCD
http://www.pharmalaser.com/

ARL laser spark;
Pachen-Runge spectrometer with PM; www.arl.ch

Pachen Runge LS-5 with MCI of up to 64 PM, 1000Hz

Marwan Technology uses echelle spectrometer and dual pulse laser
Detectors

• Intensified CCD or Intensified PDA
  Poor quantum efficiency (below 20%), limited wavelength coverage, high gain, 16 bits dynamic range, simultaneous measurements, high cost.

• Interline CCD, Gated CCD
  Larger wavelength coverage, high quantum efficiency, 13 bits dynamic range, less expensive.

• Photomultiplier PM
  Monochromatic, low quantum efficiency, bulky, larger wavelength coverage, high dynamic range, cheap.

• New EMCCD and EBCCD in the market but not presently appropriate for LIBS applications.

Cost: 1-35 k$
Advantages

- Very high resolution equivalent to 2m Czerny-Turner spectrometer with 2400 grooves/mm
- Enhanced spectral range
- Powerful tool for identification of complex matrix
- Compactness
- Choice of several lines for the same element
  - Increase the dynamic range
  - Flexibility to choose a line for analysis
  - Rapidity of measurements, normalization
  - Complete analysis by single shot
Limitations

- Correction of the instrument response within an order of diffraction and between orders for absolute measurements
- Blooming
  - Ghost line apparition
  - Difficulties in measuring weak line close to strong line
- Dynamic range
- Small gap for the low orders (in the visible)
- Acquisition rate, 1Hz (ICCD limitation)
- High cost
Recent interest in LIBS has focused on the miniaturisation of the components and the development of compact, low power, portable systems. This direction has been pushed along by interest from groups such as NASA, ESA as well as the military. Portable LIBS systems are more sensitive, faster and can detect a wider range of elements (particularly the light elements) than competing techniques such as portable x-ray fluorescence.
- LIBS is portable; it may weigh less than 1 kg.
- Battery powered
- Multi-element analysis for any element
Advantages

- It can be applied on:
  - solid, liquid or gaseous
- No sample preparation
- Small mass required (sub-µg)
- Ambient air at atmospheric pressure
- Remote and real time analysis
- Single step for vaporization and excitation
- High spatial resolution (2 µm)
- Simultaneous multi-element analysis
- Portable system
Drawbacks

- Small volume of analysis
- Destructive technique
- Surface analysis could be different from bulk
- Sensitivity is in the ppm range
Comparison of some methods based on plasma spectrochemistry

<table>
<thead>
<tr>
<th>Attribute</th>
<th>LIBS</th>
<th>ICP-AES</th>
<th>LA-MS</th>
<th>LA-ICP-MS</th>
<th>ICP-MS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detection limits</td>
<td>Low ppm high ppb</td>
<td>mid to low ppb</td>
<td>10^{-20} g</td>
<td>ppb</td>
<td>ppb to ppt</td>
</tr>
<tr>
<td>Preparation</td>
<td>Little or none</td>
<td>Must be liquid</td>
<td>Little or none</td>
<td>Little or none</td>
<td>Must be liquid</td>
</tr>
<tr>
<td>Atmospheric conditions</td>
<td>Air, He, Ar or vacuum</td>
<td>Air, Ar High vacuum</td>
<td>High vacuum</td>
<td>High vacuum</td>
<td>High vacuum</td>
</tr>
<tr>
<td>Cost</td>
<td>50k$+</td>
<td>50k$-200k$</td>
<td>120k$-500k$</td>
<td>170k$-300k$</td>
<td>120k$-300k$</td>
</tr>
<tr>
<td>Commercially available</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
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</table>
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Influence of the various components of the LIBS system on the analytical performances

<table>
<thead>
<tr>
<th></th>
<th>laser</th>
<th>optics (spectro)</th>
<th>detection detector</th>
<th>atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>precision</td>
<td>x</td>
<td></td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>selectivity</td>
<td></td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>limits of detection</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>stability</td>
<td>x</td>
<td>x</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Procedure to evaluate the LIBS analytical performance

- Ionic to atomic line intensity ratio measurements
- Sampling approach and optimization
- Practical resolution measurements
- Scale of limit of detection
- Drift diagnostics
- Figures of merit
Analysis of aluminum and iron in molten zinc for the galvanizing process
Problems and difficulties

• *Problems related to the laser-liquid interaction*
  – Splashing of the liquid caused by powerful laser pulses
  – Generation of waves perturbing the surface
  – Aerosols and particles ejected

• *Difficulties related to the molten metal*
  – Surface is not representative of the bulk
  – Diffusion of some elements to the surface
  – The sensor should be sufficiently rugged for plant use
Laser-liquid interaction

Laser pulse

liquid

aerosol

bubble

splashing

waves

lens
LIBS for Continuous Analysis of Liquids

Fiber optic and power cables

Fan to purge aerosols

Laser and LIBS Optics

Exit Window

LIPS Plasma

Laser power supply
Spectrometer & Computer

Liquid in

Measurement Cell

Liquid out
Profilometry
Spatial distribution of the laser beam

\[ D(r) = Y \cdot F(r) \]

\[ F(r) = \frac{1}{\Gamma\left(1 + \frac{2}{\alpha}\right)} \frac{E}{\pi R^2} \exp\left[-\left(\frac{r}{R}\right)^\alpha\right] \]

\( R \) is the radius of the beam at 1/e

Ablation threshold (\( \text{cm}^3/J \))

empiric parameter

LIBS

Zinc line intensity (counts)
LIBS setup for depth profilometry
Profilometry using 2 diaphragms

Step 1: Ablation

Step 2: Measurement
Profilometry

Profile obtained by using the measurement (small) diaphragm

Profile obtained by using the ablation (larger) diaphragm

Zn intensity a.u.

Zn coating

Steel

Depth (µm)

Wavelength (nm)
# Detection of Gold: moisture effect

<table>
<thead>
<tr>
<th>Gold concentration (ppm)</th>
<th>Measurement conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>64.8</td>
<td>Dry sample</td>
</tr>
<tr>
<td>2.2</td>
<td>Immediately after watering</td>
</tr>
<tr>
<td>68.3</td>
<td>After 5 minutes</td>
</tr>
<tr>
<td>63.2</td>
<td>After 10 minutes</td>
</tr>
<tr>
<td>65.4</td>
<td>Watering followed by blowing</td>
</tr>
</tbody>
</table>
Approaches to enhance the LIPS sensitivity

1. Laser for ablation
   - Dual Pulse mode
   - Laser for reheating
   - Laser for selective excitation
   - UV followed by visible, IR laser pulse or IR followed by IR etc.

2. Laser for ablation
   - LIF
   - Laser for resonance excitation
   - Second laser tuned for selective excitation of trace element.

3. Laser for ablation
   - RELIPS
   - Laser for resonance excitation
   - Second laser tuned for resonance excitation of major element.
Enhanced LIPS using mixed wavelength laser pulses

![Bar chart showing silicon line intensity (counts) for different conditions: NIR, UV, NIR+UV, UV+NIR, and UV+NIR+UV with time intervals ∆t=0 and ∆t=1 µs. The bars indicate the intensity levels with error bars for each condition.]
Conclusion

• The LIBS technique is a useful tool for quantitative analysis of materials.
• The results obtained in terms of accuracy are comparable to conventional techniques.
• LIBS will gain a wide acceptance for process control in a broad range of industrial applications.
• The advent of new detectors and spectrometers promises a bright future for the LIBS technique.
• The LIBS sensitivity can be enhanced by different approaches but at additional cost.
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Thank you for your attention