Introduction to Laser Induced Breakdown Spectroscopy (LIBS) for Glass Analysis
Module 4
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Outline
- LIBS theory and background
- LIBS setup and practice
- Glass as a model analysis matrix
- Comparison of LIBS to other elemental analysis methods in forensic science
- LIBS data analysis

LIBS Background
First reported by Maker, Terhune and Savage in 1963
- A focused laser pulse interacts with a target material to generate a practically totally ionized gas (plasma).
- The plasma then excites the substrate’s atoms and ions.
- A characteristic emission is detected.
- The emission spectrum is spectrally resolved to provide qualitative and (semi) quantitative analysis of the material.
- Direct sampling of gases, liquids and solids to determine elemental composition.

LIBS Developments
Number of publications over the last 40 years (but still less mature than ICP and XRF as an analytical method)
Source: M. Sabsabi from Cremers and Radziemski, 2006

Atomic Emission Spectroscopy
- Ability to detect all elements
- Simultaneous multi-element detection
- Fast and easy to operate
- No sample preparation
- Almost non-destructive
- Good sensitivity for a wide range of elements (down to 5 ppm)
- Capability of field and stand-off analyses

LIBS Overview
- Remote sensing
  - Potential hazardous materials at long distance (80m)
  - Aerosol identification
- Quality control
  - Pharmaceutical
  - Steel and alloy company
- Non destructive analysis on materials
  - Art pieces
  - Precious gems
- Biological and environmental safety
  - Discrimination of bacterial species
  - Environmental pollution in fish, plant, and paint
Plasma as an Excitation Source

ICP Plasma:
- ~ cm in length
- sustained and controlled with gas flow
- n_e ~ 1 x 10^{15}/cm^3
- Temperature ~ 8000 K

LIBS Laser Plasma:
- ~ mm in length
- created with ns laser pulse
- ~ microseconds lifetime
- n_e ~ 1 x 10^{16}/cm^3
- Temperature ~ 10000 K

Source of photo: Cremers and Radziemski 2006

Emission Process in Plasma

Jablonski diagram:
Fluorescence: S_1 \rightarrow S_0
Phosphorescence: T_1 \rightarrow S_0

Vibrational relaxation

Three Non-radiative Processes
1. Internal conversion
2. Intersystem crossing
3. Vibrational relaxation

EMISSION LINES

GAS PHASE ATOMS, NO VIBRATIONS & ROTATIONS
SHARP LINES (~ 5 pm WIDE)

M^+* (0) LINES, +1 ION
M^+ + e^-
M^* (0) LINES, NEUTRAL ATOM
M

*Intensity of line from level j
\propto\ population of level j
\propto e^{-E_j/kT}

Laser-sample interaction time scale

Plasma temporal analysis

Source: Cremers and Radziemski 2006.
**Plasma creation**

- Laser Pulse
- Hot, high-pressure strongly absorbing Plasma
- Shock Wave
- Radiation
- Sample

**Plasma Evolution**

- t = 50ns scale = 0.5mm

**Experimental Setup**

- **Continuum MiniLite Nd:YAGs**
  - Two lasers (PIV) system
  - 2nd harmonic 532nm
  - 22 mJ max energy per pulse
  - 6.87 Hz Rep Rate

- **New Wave Tempest**
  - 4th harmonic 266 nm
  - 27 mJ max energy per pulse
  - 6.87 Hz Rep Rate
  - Focal length = 150 mm
  - Varying focus positions wrt sample surface
  - Delay between laser pulses varied from 0.2 - 10.0 µs

- **Spectrometer**
  - Mechelle 200-900nm
  - Resolving power 5000

- **Detector**
  - Andor ICCD Camera

**FIU Setup**

**Advantages of LIBS**

- Qualitative and (semi) quantitative analysis
- Almost non-destructive direct solid sampling
- Minimal (or no) sample preparation
- Speed, versatility, ease of operation and portability
- Good detection limits (~ 5 ppm - 50 ppm)
- Good discrimination power ??
- Affordability in comparison to LA-ICPMS

**Challenges of LIBS**

- Calibration for quantitative analysis
- Matrix effects
Some Analytical Applications of LIBS

- Trace metal detection (1999)
- Trace metal accumulation in teeth (1999)
- Glass composition (2000)
- Detecting gunshot residue (2002)
- Hair tissue mineral analysis (2003)
- Detection of trace elements in liquids (2003)

Commercial LIBS Systems

Avantes
Ocean Optics
Foster and Freeman
PhotonMachines
NewWave Research

Avantes Spectrometer

NIST 614 (~2 ppm)
NIST Standard Reference Materials
610 = 515 ppm Sr
1831 = 112 ppm Sr

NIST 1831 Float Glass Standard
1064 nm 10 laser shots
1.5 µs detector delay
100 µs integration time
220 - 950 nm spectral range
Resolution ~ 5000 over range

NIST 610 Glass Standard
266 nm 10 laser shots
1.5 µs detector delay
100 µs integration time
[Sr] 515.5 ppm (~ 0.05%)

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1.5 µs detector delay
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XRF spectra and figures of merit

Rh x-ray tube
40 keV beam potential
300 micron diameter monocapillary focusing collimator
Li drifted silicone EDS with beryllium window
beam current adjusted to achieve a 35% dead time factor (approximately 760 microamps)
17 microsecond-time constant
resolution approximately 156 eV

LIBS spectra (NIST Glass)

LIBS & LA-ICP-MS (strontium)
Double pulsed LIBS: UV followed by IR reheating

LIBS & LA-ICP-MS (strontium)

Correlation of LA-ICPMS and μ XRF

LA-ICP-MS, μ XRF and LIBS

210 ways to compare 6 element ratios between pairs

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<th>sample A</th>
<th>vehicle make</th>
<th>vehicle model</th>
<th>year</th>
<th>sample location</th>
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<tr>
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<td>Grand Cherokee</td>
<td></td>
<td>2001</td>
<td>inside windshield</td>
</tr>
</tbody>
</table>

150 combinations (of the possible 210) produced no Type I or Type II errors

Using a 1000 ppm Sr solution – 1 drop contains ~117 pL and 117 pg of Sr.

Using a 500 ppm Sr solution, 1 drop contains ~52.3 pg of Sr.

Jetlab IV by MicroFab Technologies, TX

Deposition of ~117 pg of Sr on an Al surface

Signal accumulation over 20 laser shots

S/N ~ 70 for ~100 pg deposited
LoD ~ 4.3 pg Sr
Deposition of 1, 2, 4, 6, 8 and 12 drops of 500 ppm [Sr] on Al

Microdrop printing of standards

215 μm spot size (20 shot accumulation)

Future of LIBS

• Move towards standardization of the technique
• Combined techniques- (Raman/LIBS, LIBS/Mirowave)
• Micro-LIBS - spatial mapping of elemental composition (3-10 μm diameter craters)
• Portable LIBS

LIBS Components

• Laser Fluence : Energy/Area (J/cm²)
  \[ F_1 > F_2 > F_3 \]
• Laser \( \lambda \) : (Nd:YAG -1064nm, 532nm, 355nm, 266nm)
• Damage threshold of optics (mirrors & lens)
• Mirror (polarization, angle of incidence, coatings)
• Antireflection Coatings (AR coatings on lens)
• Optical Transmission of materials
  • BK7: 350-2100nm
  • UV-Fused Silica: 170nm-2100nm