ED-XRF analysis to determine the origin and authenticity of gemstones

P. Lemberge
Thermo Fisher Scientific, Ecublens, Switzerland

EXRS 2010, Figueira da Foz, Portugal
June 20th – 25th, 2010
Overview

• Gemstones
  • Background & classification
  • Certification
  • Analysis tools
    • Chemical fingerprinting

• ED-XRF methodology for the analysis of gemstones

• Case studies
  • Rubies & Sapphires
  • Emeralds
Gemstones

• A wide variety of precious and semi-precious stones exist

• Traditional classification not always logical and goes back to Ancient Greeks
  • Precious stones are diamond, ruby, sapphire and emerald
  • Sometimes also pearls and opal are classified as precious stones
  • Everything else is called semi-precious

• Corundum ($\alpha$-Alumina, Al$_2$O$_3$)
  • Ruby - red or dark pink variety of corundum (Cr)
  • Sapphire – any other color variety of corundum (Cr, Fe and Ti)
• Beryl (Be$_3$Al$_2$(SiO$_3$)$_6$)
  • Emerald (green)
  • Aquamarine (blue)
  • Heliodor (gold)
• Spinel, turquoise, amethyst, peridot…
Certification of Gemstones

• Value of gemstones
  • Natural
  • Color, clarity, cut and carat
  • Unusual optical phenomena within the stone
    • Color zoning
    • Asteria (star effects)
  • Origin & associated history
    • Kashmir, Burma…

• Treated ordinary gemstones or glass sold as precious stones

• Synthetic gemstones
  • Synthetic rubies might look more bright and colorful but are almost worthless
  • Synthetic gemstones have other applications
    • Ruby laser
Tools of the Gemologist

- It becomes increasingly more difficult to determine the authenticity of gemstones
  - Visual inspection is far from sufficient

- Multi-disciplinary approach
  - Inclusion features (cavity fillings, growth features, solid inclusions)
  - Chemical fingerprinting (major, minor and trace elements)
    - Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)
      - Energy-Dispersive X-ray Fluorescence (ED-XRF)
  - Spectral fingerprinting (UV Vis nIR range)
  - Optical properties (e.g. refractive index)
  - Infrared characteristics
  - Luminescence behavior
Chemical Fingerprinting

- Presence or absence of trace elements is an indication of authenticity and origin of the gemstone

- Rubies & Sapphires
  - Cr, Fe & Ti determine color
  - Presence of Ga, V, Zr tells something about origin

- Emeralds (Beryl)
  - Cr & V determine color
  - Presence of Ga, Sc, Rb, Cs determines origin and authenticity
  - Presence of Pt might point to a synthetic stone
    - Flux growth
Chemical Fingerprinting with ED-XRF

• LA-ICP-MS
  • Excellent detection limits & spot analysis
  • Complex technique requiring a trained & dedicated operator
  • *Semi*-non-destructive
    • Leaves behind a “crater” of up to 200 microns in size

• ED-XRF
  • True non-destructive analysis technique
  • Once calibrated fairly straightforward to use by any operator

• A specific methodology is required for ED-XRF analysis of gemstones
  • Sample presentation
  • Inhomogeneous nature of samples → not an ideal XRF sample
  • Availability of calibration standards → Quantification
Sample Presentation

- Gemstones come in a variety of sizes or are imbedded in a piece of jewelry
- Accurate quantitative results require reproducible sample positioning
- Use of collimators to excite gemstone material only
  - Improves analysis results
  - 1 mm to 3 mm spot size
    - Sensitivity suffers at very small spot sizes
- Camera assisted positioning
  - Selection of a flat surface
Calibration Techniques & Standards

- Empirical calibration ($\alpha$-coefficients)
  - Requires many standards which are not available
  - Not applicable

- Fundamental Parameters Method
  - Calibration using minerals
    - Periclase (MgO), Corundum (Al2O3), Quartz (SiO2), Rutile (TiO2), Vanadinite (V2O3), Hematite (Fe2O3), Scheelite (CaWO4)…
  - Presence of diffraction peaks
Presence of Diffraction Peaks

Diffraction peaks
Calibration Techniques & Standards

• Empirical calibration ($\alpha$-coefficients)
  • Requires many standards which are not available
  • Not practical

• Fundamental Parameters Method
  • Calibration using minerals
    • Periclase (MgO), Corundum (Al2O3), Quartz (SiO2), Rutile (TiO2), Vanadinite (V2O3), Hematite (Fe2O3), Scheelite (CaWO4)…
    • Presence of diffraction peaks
  • Calibration using amorphous compounds – pressed pellets
    • SiO2, NaHCO3, MgCO3, Cr2O3, Fe, Ga2O3…
    • Avoiding diffraction peaks during calibration
  • Additional NIST Glass standards, e.g. NIST 610, NIST 612
    • To add elements of interest at lower concentrations
  • Calibration with gemstones previously analyzed by LA-ICP-MS
Case Study – Analysis of Rubies & Sapphires (I)

- Instrument - ARL Quant’X EDXRF Analyzer
  - 50 watt Rh target X-ray tube
  - 8 primary beam filters
  - Collimator – 3 mm spot
  - Peltier cooled Si(Li) detector

- FP Calibration based on pure crystals & selected rubies/sapphires
  - Multiple spectra per sample recorded with different excitation conditions
  - Each spectrum optimized towards series of elements

<table>
<thead>
<tr>
<th>Condition</th>
<th>Filter</th>
<th>Voltage</th>
<th>Atmosphere</th>
<th>Count Rate</th>
<th>Live Time</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>High Za</td>
<td>Cu Thin</td>
<td>40 kV</td>
<td>Vacuum</td>
<td>High</td>
<td>30 sec</td>
<td>Ag, Pd, Sn</td>
</tr>
<tr>
<td>Low Za</td>
<td>No Filter</td>
<td>4 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>120 sec</td>
<td>Na, Mg, Al, Si</td>
</tr>
<tr>
<td>Low Zb</td>
<td>Cellulose</td>
<td>8 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>60 sec</td>
<td>Ca</td>
</tr>
<tr>
<td>Low Zc</td>
<td>Aluminum</td>
<td>12 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>60 sec</td>
<td>Ti, V, Cr, Mn, Fe</td>
</tr>
<tr>
<td>Mid Za</td>
<td>Pd Thin</td>
<td>16 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>60 sec</td>
<td>Fe, Mn, Cr, Ni, Cu</td>
</tr>
<tr>
<td>Mid Zb</td>
<td>Pd Medium</td>
<td>20 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>30 sec</td>
<td>Ni, Cu, Zn, Ga, W, Pt, Re, Ir, Au</td>
</tr>
<tr>
<td>Mid Zc</td>
<td>Pd Thick</td>
<td>28 kV</td>
<td>Vacuum</td>
<td>Medium</td>
<td>30 sec</td>
<td>Pb, Pt, Au, Zr, Mo</td>
</tr>
</tbody>
</table>
# Case Study – Analysis of Rubies & Sapphires (II)

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>TiO₂</th>
<th>V₂O₃</th>
<th>Cr₂O₃</th>
<th>Fe₂O₃</th>
<th>Ga₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conc.</strong></td>
<td>99.5</td>
<td>0.0015</td>
<td>0.0001</td>
<td>0.0000</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td><strong>Std. Dev.</strong></td>
<td>0.0029</td>
<td>0.0016</td>
<td>0.00</td>
<td>0.00</td>
<td>1.409</td>
<td>0.006</td>
</tr>
<tr>
<td><strong>Conc.</strong></td>
<td>99.5</td>
<td>0.0208</td>
<td>0.0014</td>
<td>0.0030</td>
<td>0.0003</td>
<td>0.0045</td>
</tr>
<tr>
<td><strong>Std. Dev.</strong></td>
<td>0.0125</td>
<td>0.0010</td>
<td>0.0029</td>
<td>0.0008</td>
<td>0.0034</td>
<td>0.0006</td>
</tr>
<tr>
<td><strong>Conc.</strong></td>
<td>99.5</td>
<td>0.096</td>
<td>0.006</td>
<td>0.398</td>
<td>0.015</td>
<td>0.029</td>
</tr>
<tr>
<td><strong>Std. Dev.</strong></td>
<td>0.110</td>
<td>0.003</td>
<td>0.349</td>
<td>0.004</td>
<td>0.0000</td>
<td>0.0000</td>
</tr>
</tbody>
</table>

**Concentrations expressed as % w/w**

---

**Synthetic ruby - Douro, 4.80 ct**

**Synthetic pink sapphire, 1.460 ct**

**Sapphire Shadong (China), 1.784 ct**

**Synthetic brown star sapphire, 3.935 ct**

---

**Case Study – Analysis of Rubies & Sapphires (II)**

- **Synthetic ruby - Douro, 4.80 ct**
  - LA-ICP-MS
  - ED-XRF - Pure compounds
  - ED-XRF - Minerals

- **Synthetic pink sapphire, 1.460 ct**
  - LA-ICP-MS
  - ED-XRF - Pure compounds
  - ED-XRF - Minerals

- **Sapphire Shadong (China), 1.784 ct**
  - LA-ICP-MS
  - ED-XRF - Pure compounds
  - ED-XRF - Minerals

- **Synthetic brown star sapphire, 3.935 ct**
  - LA-ICP-MS
  - ED-XRF - Pure compounds
  - ED-XRF - Minerals
Case Study – Analysis of Emeralds (I)

Emeralds belong to the Beryl group (Be₃Al₂(SiO₃)₆)
- Be not detectable by ED-XRF
- BeO concentration fixed at 13% w/w
- H₂O concentration fixed at 2% w/w
- Excitation conditions similar to Ruby/Sapphire method
- More elements
- Longer measurement time for Low Z condition

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂O₃</td>
<td>0.074</td>
<td>0.005</td>
<td>1.40</td>
<td>0.27</td>
<td>0.256</td>
<td>0.007</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.082</td>
<td>0.003</td>
<td>1.75</td>
<td>0.01</td>
<td>0.322</td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.080</td>
<td>0.002</td>
<td>2.00</td>
<td>0.01</td>
<td>0.318</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.094</td>
<td>0.003</td>
<td>0.363</td>
<td>0.007</td>
<td>0.046</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.092</td>
<td>0.002</td>
<td>0.436</td>
<td>0.001</td>
<td>0.062</td>
<td>0.003</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Concentrations expressed as % w/w

Synthetic emerald, Gilson flux grown, 1.43 ct

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.104</td>
<td>0.002</td>
<td>0.0033</td>
<td>0.0001</td>
<td>19.35</td>
<td>0.22</td>
<td>67.12</td>
</tr>
<tr>
<td>MgO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sc₂O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Concentrations expressed as % w/w
Short Summary

• ED-XRF can be successfully applied for the analysis of gemstones

• Methodology of analysis should focus on
  • Sample presentation
  • Calibration technique
  • Selection of standards

• Case studies demonstrated that FP calibration based on amorphous bulk samples or minerals both produce results which correspond well with LA-ICP-MS data
Acknowledgement

- F. Herzog and M.S. Krzemnicki
  Swiss Gemmological Institute SSEF, Basel, Switzerland