The daily work of gemmologists

- Identification: what is it?
- Natural or synthetic?
- Treated or not?
- The origin: Where does it come from?

Apart from microscopic observations and spectroscopic analyses (UV-Vis, NIR, FTIR, Raman) it is important to have chemical data.
Options for chemical analysis

- X-ray fluorescence (ED-XRF and WD-XRF)
- Energy dispersive spectroscopy coupled with scanning electron microscope (SEM EDS)
- Electron microprobe (EMP)
- Laser induced breakdown spectroscopy (LIBS)
- Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)

Features of LA ICP MS

Chemical analysis of specimens

+ nearly all chemical elements can be analysed
+ up to 50 elements at the same time
+ point analysis (zoning)
+ only minor sample preparation
+ large dynamic range of analysis
  (from sub-ppm to main element concentrations)
+ quantitative data

- slightly destructive analysis (laser drill holes diameter ca 100 μm)
- how representative are point analyses for the whole stone?
- raw data (qualitative) has to be processed to get quantitative data
- contamination effects
- spike filtering
- highly sophisticated instrument

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The LA-ICP-MS instrument

Microlas system:
Beam modulation optics to homogenize laser beam energy profile

Lambda Physics, Coherent:
Pulsed nanosecond ArF excimer laser (193 nm)

Perkin Elmer:
DRC-e quadrupole mass spectrometer

Laser ablation:

Local heating and vaporization
Laser ablation

Important factors for analysis:
- laser wavelength (e.g. 193 nm)
- laser energy (mJ)
- ablation spot geometry
- ablation spot diameter and depth
- ablation pulse length and rate

Inductively Coupled Plasma

Important factors:
- plasma flame stability
- carrier gas
- particle size
- ± complete combustion of particles
Mass spectrometer

Important factors:
- Ions (isotopes) are detected on the basis of their mass/charge ratio
- Beware of superpositions by recombinated molecules
  (e.g. ArO interferes with $^{55}\text{Mn}$, and $^{56}\text{Fe}$)

Quadrupole MS

Measuring

- the samples are positioned in the sample chamber together with the standards.
- the sample chamber is then connected with the tubes for floating with the carrier gas.

Paraiba-tourmalines from Brazil, prepared for testing with LA ICP MS

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What do we get?

Chemical concentration signal versus time

Raw data has to be processed...

Data processing

Using Lamtrace program by S.E. Jackson

homogeneous signal

Careful setting of integrals for data processing is important
Data processing

Surface contamination

Spike filtering

Saltwater pearl (Pteria Sterna)

Kashmir sapphire

zoned signal

Included

What do we get?

Quantitative chemical data

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Research at SSEF using LA-ICP-MS

- Beryllium-diffusion treated orange sapphires
- Beryllium diffusion treated blue sapphires
- Beryllium in untreated sapphires
- Chrysoberyl grown on sapphire
- Alexandrite from different origins
- Emeralds from different origins
- Pezzottaite from Madagascar and Afghanistan
- Shells, Pearls and treated pearls
- Musgravite and Taaffeite
- Vanadium tourmaline from Madagascar
- Cu-Mn bearing tourmaline from Brazil, Nigeria and Mozambique
- Colour zoning in corundum
- Spinels from different origins

1. Example: beryllium diffusion treated orange sapphire

| Comments    | Ba  | Na  | Mg  | Al2O3 | Si  | P  | Ti  | V   | Cr  | Mn  | Fe  | Zn  | Ga  | Zr  |
|-------------|-----|-----|-----|-------|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|             | ppm | ppm | ppm | ppm   | ppm | ppm| ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| Saph K. profile, rim | 0.00 | 23.00 | 25 | 21.0 | 29 | 31 | 40 | 61 | 53.0 | 55.00 | 57 | 66.0 | 71 | 95.000 |
| Saph K. profile | 0.65 | 0.37 | 65 | 90.8 | 222 | 12 | 76 | 12.6 | 423.2 | 0.15 | 1516 | 0.6 | 64 | <0.013 |
| Saph K. profile | 0.57 | 0.37 | 63 | 90.6 | 159 | 10 | 75 | 12.5 | 413.5 | <0.30 | 1516 | 0.6 | 54 | <0.008 |
| Saph K. profile | 0.02 | 0.37 | 71 | 90.6 | 173 | 11 | 76 | 13.4 | 453.9 | <0.31 | 1702 | 0.7 | 57 | <0.015 |
| Saph K. profile | 4.74 | 1.41 | 74 | 90.6 | 193 | 12 | 80 | 14.2 | 493.1 | <0.40 | 1550 | 0.9 | 62 | <0.016 |
| Saph K. profile | 3.31 | 6.2 | 71 | 90.6 | 251 | 13 | 79 | 14.2 | 468.0 | <0.39 | 1550 | 0.6 | 62 | 0.019 |
| Saph K. profile | 4.22 | 0.80 | 72 | 90.6 | 212 | 16 | 82 | 14.6 | 476.8 | <0.31 | 1910 | 0.7 | 62 | <0.026 |
| Saph K. profile | 3.10 | <0.62 | 69 | 90.6 | 197 | 14 | 82 | 14.9 | 459.6 | <0.68 | 1866 | 1.0 | 63 | <0.027 |
| Saph K. profile, core | 1.95 | <0.74 | 67 | 90.6 | 243 | 16 | 74 | 14.5 | 474.9 | <0.41 | 1550 | 0.9 | 62 | 0.017 |
| Saph K. profile, core | 2.88 | 0.74 | 68 | 90.6 | 200 | 13 | 77 | 14.1 | 466.0 | <0.54 | 1842 | 1.1 | 60 | <0.022 |
| Saph K. profile | 2.50 | 0.74 | 72 | 90.6 | 237 | 13 | 61 | 14.4 | 503.1 | <0.31 | 1912 | 1.2 | 64 | <0.024 |
| Saph K. profile | 4.16 | 1.41 | 66 | 90.6 | 218 | 13 | 79 | 14.1 | 476.0 | <0.49 | 1550 | 0.7 | 61 | 0.029 |
| Saph K. profile | 4.28 | 0.89 | 66 | 90.6 | 176 | 10 | 77 | 13.3 | 441.6 | <0.39 | 1757 | 0.7 | 57 | <0.013 |
| Saph K. profile | 0.11 | 1.19 | 64 | 90.6 | 151 | 11 | 77 | 15.3 | 464.5 | <0.51 | 1702 | 1.0 | 55 | <0.013 |

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Copper-bearing Tourmaline („Paraiba“)

LA ICP MS analysis of „Paraiba“ tourmaline:

Pb versus Zn (ppm)

The effect of a logarithmic scale
LA ICP MS analysis of „Paraiba“ tourmaline:

Pb versus Ga (ppm)

Pb versus Bi (ppm)
LA ICP MS analysis of Pearls

Saltwater pearl (Pteria Sterna)

freshwater pearl (China, Hyriopsis)

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LA ICP MS analysis of Pearls

Freshwater bead in saltwater cultured pearl

Saltwater pearls

freshwater pearls

© SSEF Swiss Gemmological Institute
Unheated sapphire from Kashmir of 42.29 ct

Colour zoning in corundum

Corundum from Winza, Tanzania
Beryllium in sapphire

3-dimensional jellyfish-like internal structures in Be-diffusion treated sapphires.
© GAAJ

Planar curved structures in basaltic sapphire

© SSEF Swiss Gemmological Institute

Beryllium in diffusion treated sapphire

© SSEF Swiss Gemmological Institute
Beryllium in untreated sapphire

Some saphires may contain locally low amounts of beryllium.

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Chrysoberyl on Sapphire

LA ICP MS data

ca. 200 μm from chrysoberyl contact

ca. 1 mm from chrysoberyl contact

© SSEF Swiss Gemmological Institute
Chrysoberyl on Sapphire

SEM micrographs (backscattered electrons), showing a dense syngenetic intergrowth of chrysoberyl with sapphire

© SSEF Swiss Gemmological Institute

Last week in Sri Lanka...
Thank you for your attention

Prof. Thomas Pettke, dipl. min. Pierre LeFèvre, and Dr. Michael S. Krzemnicki at the LA-ICP-MS in the Institute of Geological Sciences, University of Bern (Switzerland).

before... ...and after a LA-ICP-MS session

SSEF offers LA-ICP-MS course for gemmologists in August 2009!