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*X-Ray Conference Norway 15 september 2010*

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

Dr. Pascal Lemberge - Renaat Van Geel
ThermoFisher Scientific, Ecublens, Switzerland

Renaat Van Geel
SID Commercial Marketing Manager BEA

# 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 (α-Alumina, $Al_2O_3$)
  - Ruby - red or dark pink variety of corundum (Cr)
  - Sapphire – any other color variety of corundum (Cr, Fe and Ti)
- Beryl ($Be_3Al_2(SiO_3)_6$)
  - 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

    laser excitation, f.e.

# 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

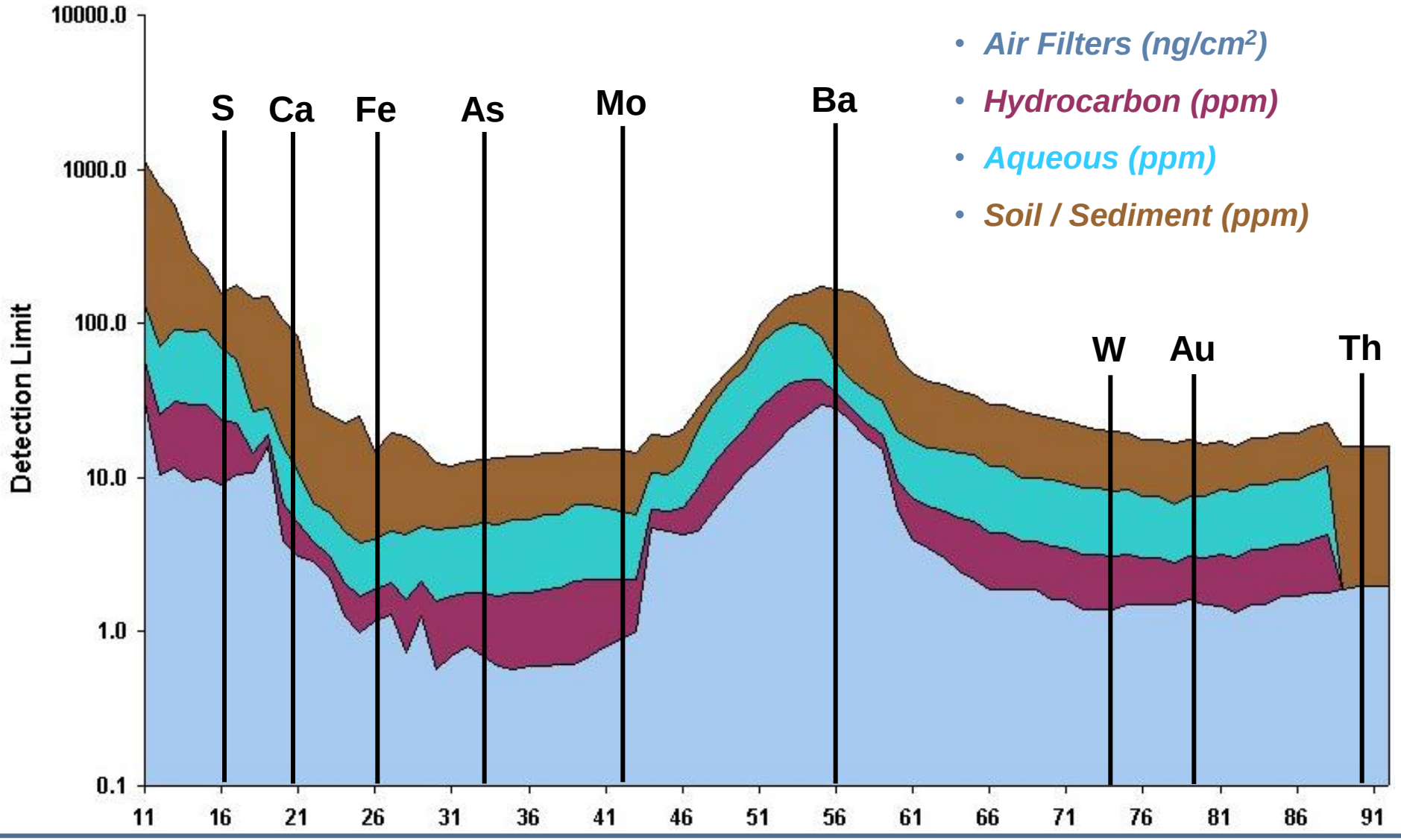
- Rubies & Sapphires
  - Cr, Fe & Ti determine color
  - Presence of Ga, V, Zr tells something about origin

- 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

# Typical Sensitivity of EDXRF



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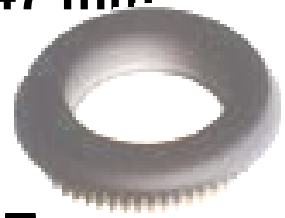
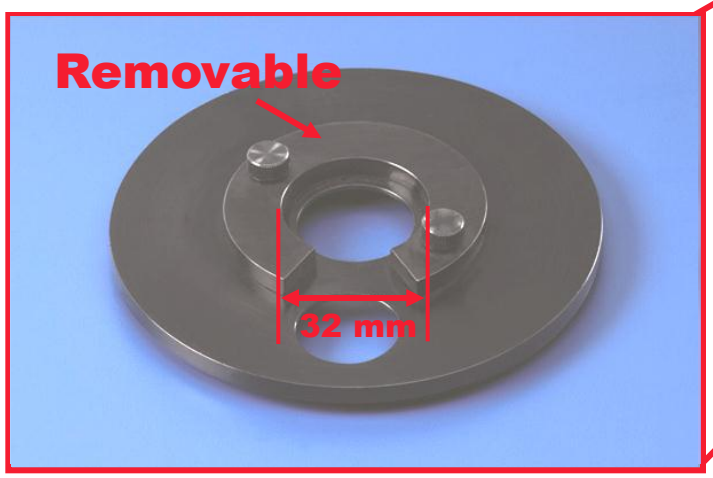
# Sample Stages for Bulk Analysis

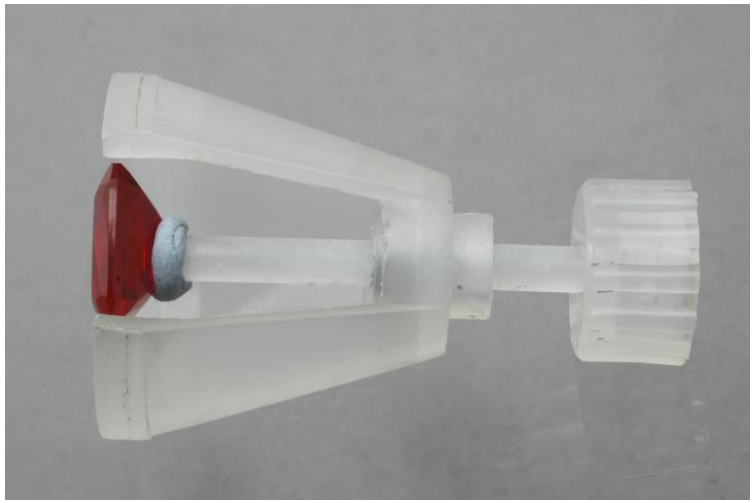
- **Interchangeable auto-samplers**
  - 20 position for 32 mm
  - 10 position for 32 - 47 mm
  - Sample spinning



- **Single-sample stage**

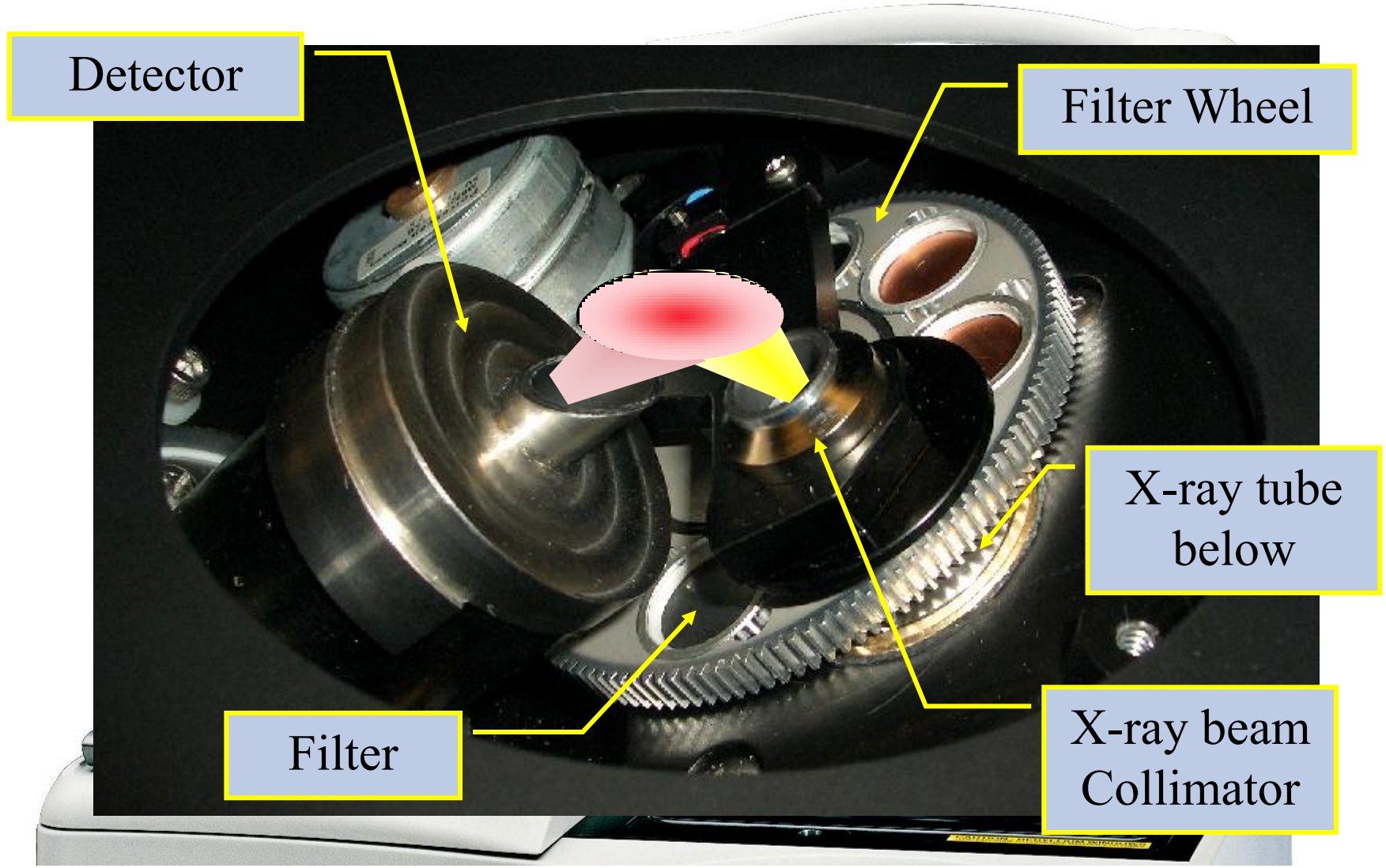



# Sample Presentation

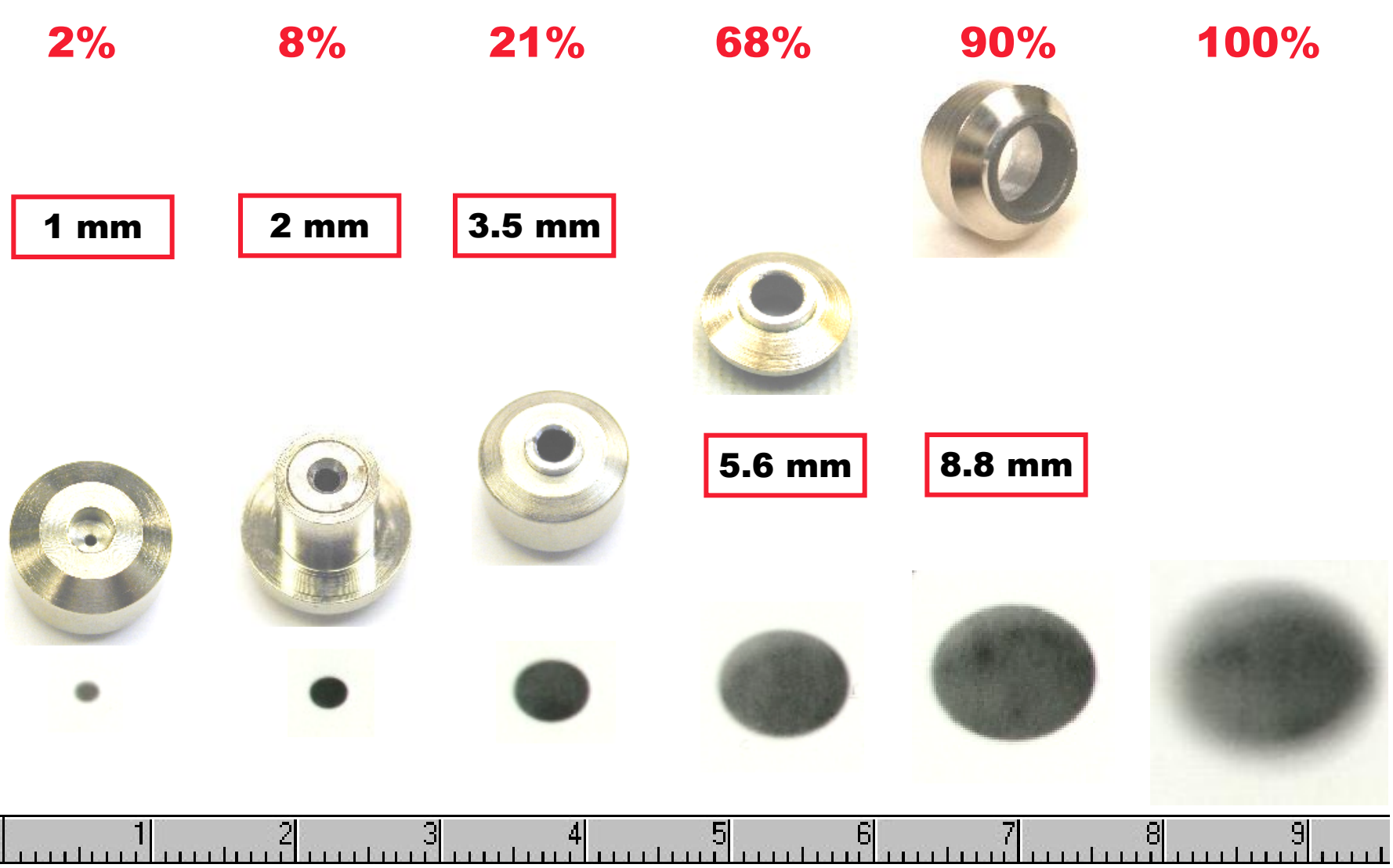


- Gemstones come in a variety of sizes or are imbedded in a piece of jewelry
- Accurate quantitative results require reproducible sample positioning
- Use of collimators to excite gemstone material only
  - Improves analysis results
  - 1 mm to 3 mm spot size
    - Sensitivity suffers at very small spot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

# Inside the Quant'X



# Collimators



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# Camera…

- Camera
- Lights
- Aperture/Collimator
- Beam Filters
- Detector
- Sample
- X-rays...

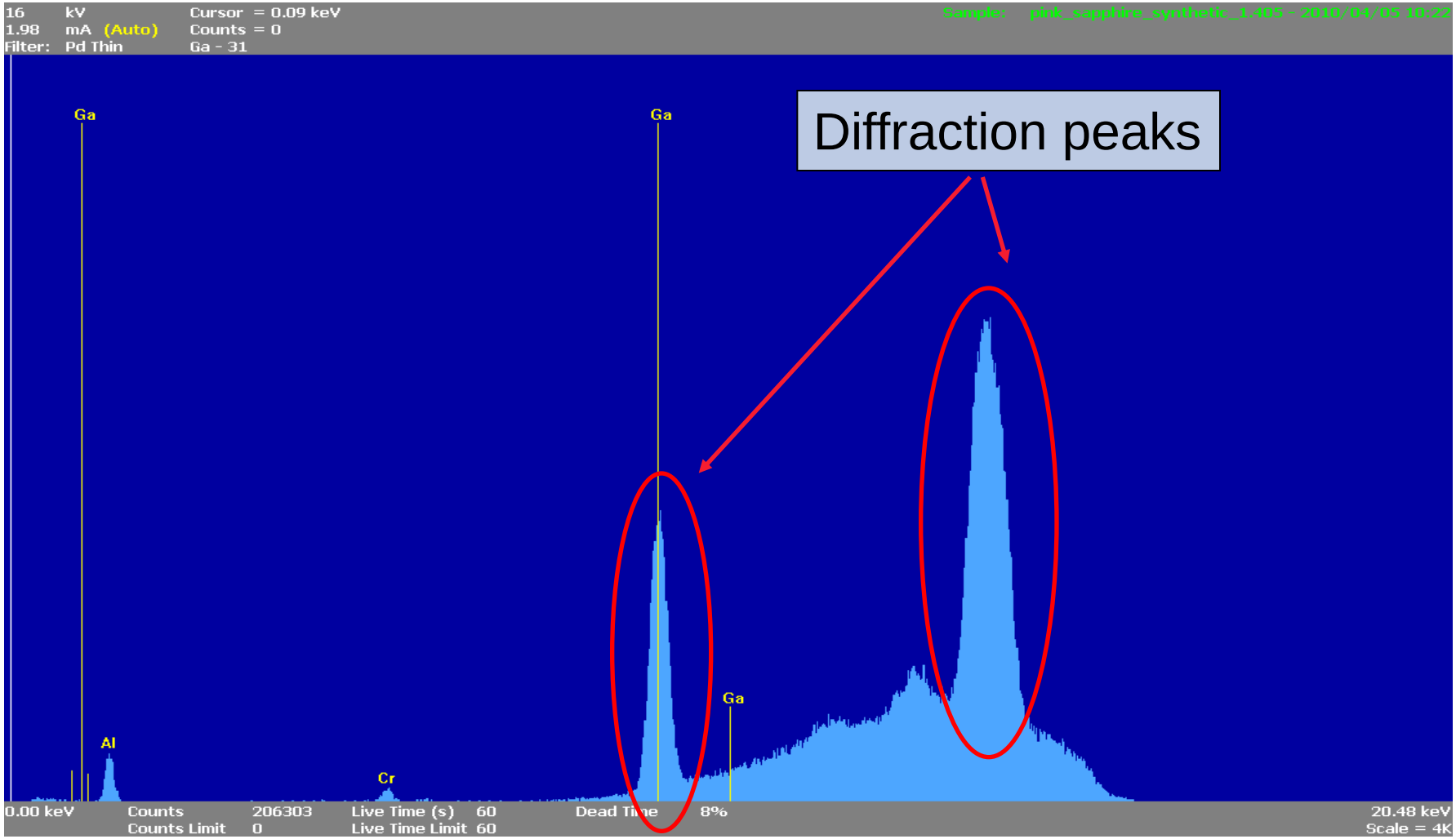
# Lights…

# 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



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# 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 ($Al_2O_3$), Quartz ($SiO_2$), Rutile ($TiO_2$), Vanadinite ($V_2O_3$), Hematite ($Fe_2O_3$), Scheelite ($CaWO_4$)…
    - Presence of diffraction peaks
  - Calibration using amorphous compounds – pressed pellets
    - $SiO_2$, $NaHCO_3$, $MgCO_3$, $Cr_2O_3$, Fe, $Ga_2O_3$…
    - 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

| Condition | Filter | Voltage | Atmosphere | Count Rate | Live Time | Analytes |
|---|---|---|---|---|---|---|
| High Za | Cu Thin | 40 kV | Vacuum | High | 30 sec | Ag, Pd, Sn |
| Low Za | No Filter | 4 kV | Vacuum | Medium | 120 sec | Na, Mg, Al, Si |
| Low Zb | Cellulose | 8 kV | Vacuum | Medium | 60 sec | Ca |
| Low Zc | Aluminum | 12 kV | Vacuum | Medium | 60 sec | Ti, V, Cr, Mn, Fe |
| Mid Za | Pd Thin | 16 kV | Vacuum | Medium | 60 sec | Fe, Mn, Cr, Ni, Cu |
| Mid Zb | Pd Medium | 20 kV | Vacuum | Medium | 30 sec | Ni, Cu, Zn, Ga, W, Pt, Re, Ir, Au |
| Mid Zc | Pd Thick | 28 kV | Vacuum | Medium | 30 sec | Pb, Pt, Au, Zr, Mo |

# Case Study – Analysis of Rubies & Synthetic Sapphires (II)

| | Al2O3 | TiO2 | | V2O3 | | Cr2O3 | | Fe2O3 | | Ga2O3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Synthetic ruby Douros, 4.80 ct** | Conc. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev | Conc. | Std. Dev. | Conc. | Std. Dev. |
| **LA-ICP-MS** | 99.5 | 0.0015 | 0.0001 | 0.0000 | 0.0001 | 0.883 | 0.428 | 0.048 | 0.006 | 0.043 | 0.003 |
| **ED-XRF - Pure compounds** | *Diff.* | 0.0029 | 0.0016 | 0.00 | | 0.792 | 0.004 | 0.024 | 0.001 | 0.032 | 0.001 |
| **ED-XRF - Minerals** | *Diff.* | [illegible] | | | | 1.409 | 0.006 | 0.070 | 0.002 | 0.041 | 0.002 |

| | Al2O3 | | | | | Cr2O3 | | Fe2O3 | | Ga2O3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **[illegible]hetic pink sapphire, 1.405 ct** | Conc. | | | | Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. |
| **LA-ICP-MS** | 99.5 | | | | 0001 | 0.0299 | 0.0002 | bd | - | 0 | |
| **ED-XRF - Pure compounds** | *Diff.* | | | | | 0.0334 | 0.001 | 0.00 | | 0.002 | 0.001 |
| **ED-XRF - Minerals** | *Diff.* | | | | | 0.0335 | 0.001 | 0.00 | | 0.003 | 0.001 |

| | Al2O3 | TiO2 | | V2O3 | | Cr2O3 | | Fe2O3 | | Ga2O3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **[illegible]ire Shadong (China), 1.784 ct** | Conc. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev |
| **LA-ICP-MS** | 99.5 | 0.0208 | 0.0014 | 0.0030 | 0.0003 | 0.0045 | 0.0032 | 1.182 | 0.043 | 0.029 | 0.002 |
| **ED-XRF - Pure compounds** | *Diff.* | 0.0195 | 0.0015 | 0.0028 | 0.0008 | 0.0034 | 0.0006 | 1.043 | 0.006 | 0.027 | 0.001 |
| **ED-XRF - Minerals** | *Diff.* | 0.0125 | 0.0010 | 0.0029 | 0.0008 | [illegible] | | [illegible] | 005 | 0.025 | 0.001 |

| | Al2O3 | TiO2 | | V2O3 | | | | | | Ga2O3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Synthetic brow[illegible]** | Conc. | Conc. | Std. Dev. | Conc. | Std. Dev. | | | | Dev. | Conc. | Std. Dev. |
| **LA-ICP-MS** | 99.5 | 0.096 | 0.006 | 0.398 | 0.015 | | | | - | 0.0000 | 0.0001 |
| **ED-XRF - Pure compounds** | *Diff.* | 0.110 | 0.003 | 0.349 | 0.004 | | | | | 0.00 | |
| **ED-XRF - Minerals** | *Diff.* | 0.072 | 0.002 | 0.397 | 0.004 | | | | | 0.00 | |

| Cr2O3 | |
|---|---|
| Conc. | Std. Dev. |
| 0.883 | 0.428 |
| 0.792 | 0.004 |
| 1.409 | 0.006 |

| Ga2O3 | |
|---|---|
| Conc. | Std. Dev. |
| 0.029 | 0.002 |
| 0.027 | 0.001 |
| 0.025 | 0.001 |

***Concentrations expressed as % w/w***

# Case Study – Analysis of Emeralds (I)

| V2O3 | | Cr2O3 | | Fe2O3 | |
|---|---|---|---|---|---|
| Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. |
| 0.074 | 0.005 | 1.40 | 0.27 | 0.256 | 0.007 |
| 0.082 | 0.003 | 1.75 | 0.01 | 0.322 | 0.005 |
| 0.080 | 0.002 | 2.00 | 0.01 | 0.318 | 0.004 |

| V2O3 | | Cr2O3 | | Fe2O3 | |
|---|---|---|---|---|---|
| Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. |
| 0.072 | 0.004 | 0.363 | 0.007 | 0.046 | 0.001 |
| 0.094 | 0.003 | 0.396 | 0.005 | 0.062 | 0.003 |
| 0.092 | 0.002 | 0.436 | 0.001 | 0.062 | 0.002 |

| | Na2O | | MgO | | Al2O3 | | SiO2 | | Sc2O3 | | V2O3 | | Cr2O3 | | Fe2O3 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. |
| LA-ICP-MS | 1.95 | 0.04 | 2.37 | 0.03 | 14.25 | 0.36 | 65.22 | 0.40 | 0.461 | 0.032 | 0.074 | 0.005 | 1.40 | 0.27 | 0.256 | 0.007 |
| ED-XRF - Pure compounds | 2.98 | 0.16 | 3.09 | 0.05 | 13.18 | 0.04 | 62.75 | 0.08 | 0.761 | 0.008 | 0.082 | 0.003 | 1.75 | 0.01 | 0.322 | 0.005 |
| ED-XRF - Minerals | 2.04 | 0.16 | 2.33 | 0.06 | 12.86 | 0.10 | 65.74 | 0.10 | 0.500 | 0.005 | 0.080 | 0.002 | 2.00 | 0.01 | 0.318 | 0.004 |

| Synthetic emerald, Gilson flux grown, 1.43 ct | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Na2O | | MgO | | Al2O3 | | SiO2 | | Sc2O3 | | V2O3 | | Cr2O3 | | Fe2O3 | |
| | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. | Conc. | Std. Dev. |
| LA-ICP-MS | 0.104 | 0.002 | 0.0033 | 0.0001 | 19.35 | 0.22 | 67.12 | 0.40 | 0.00023 | 0.00001 | 0.072 | 0.004 | 0.363 | 0.007 | 0.046 | 0.001 |
| ED-XRF - Pure compounds | bd | | bd | | 18.84 | 0.05 | 64.76 | 0.09 | bd | | 0.094 | 0.003 | 0.396 | 0.005 | 0.062 | 0.003 |
| ED-XRF - Minerals | bd | | bd | | 19.29 | 0.08 | 67.22 | 0.11 | bd | | 0.092 | 0.002 | 0.436 | 0.001 | 0.062 | 0.002 |

***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*


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