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**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 ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$)
 - 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

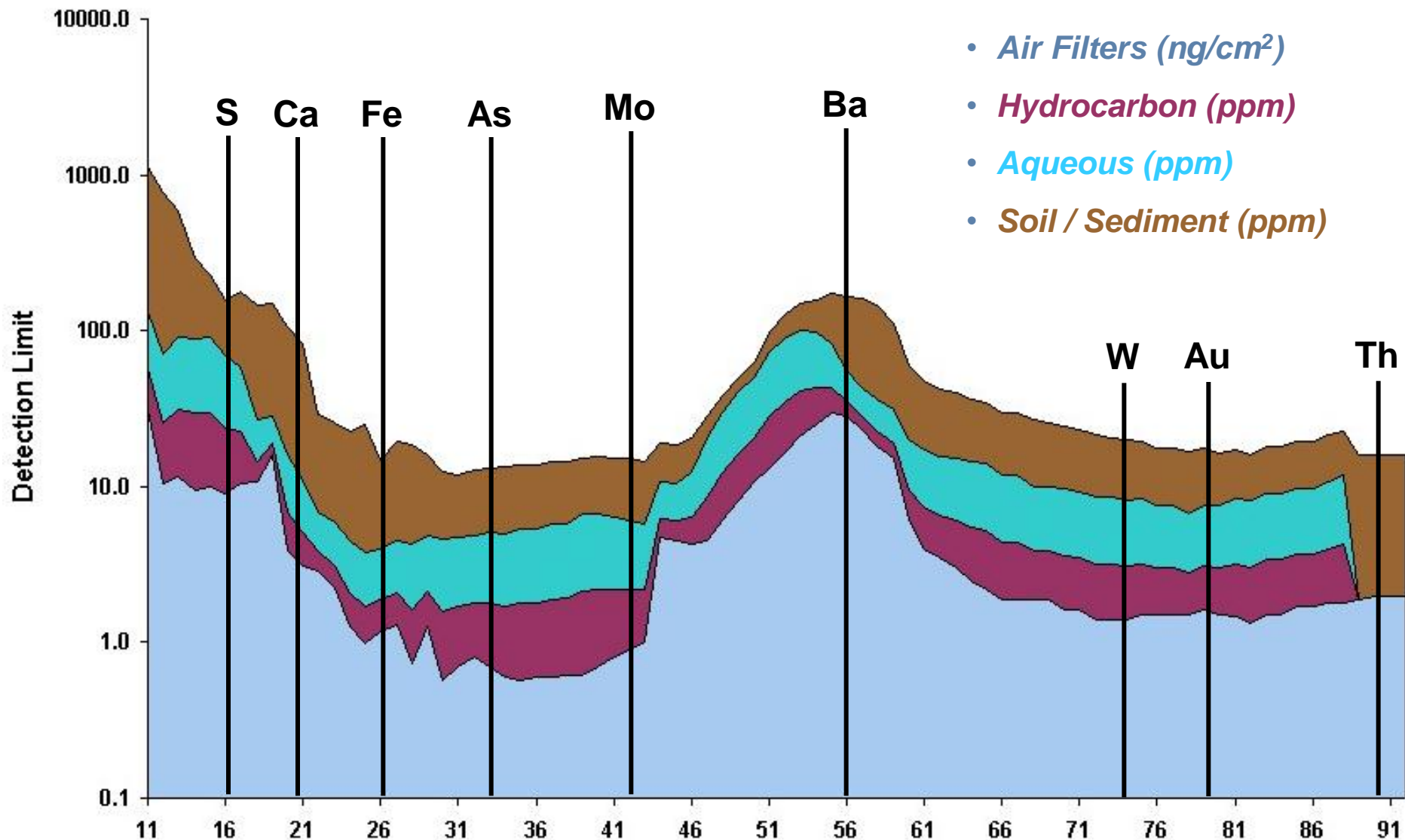
Chemical Fingerprinting

- 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

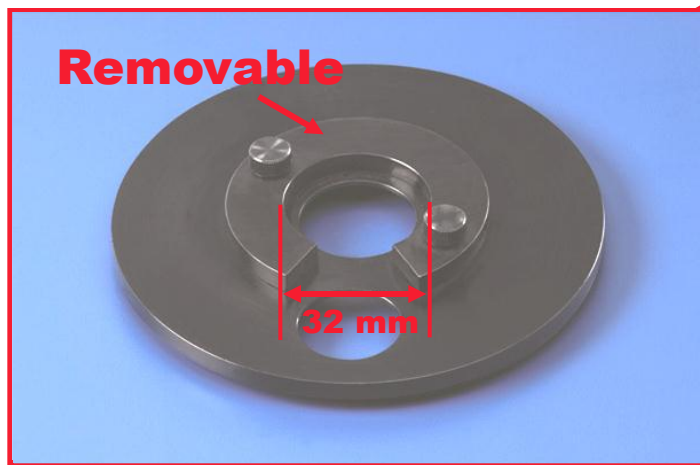


Sample Stages for Bulk Analysis

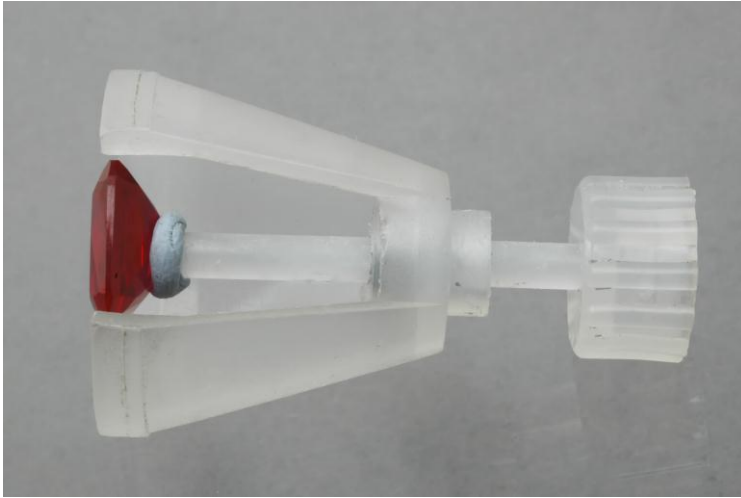
- ▶ **Interchangeable auto-samplers**

- ▶ 20 position for 32 mm
- ▶ 10 position for 32 - 47 mm
- ▶ Sample spinning

- ▶ **Single-sample stage**

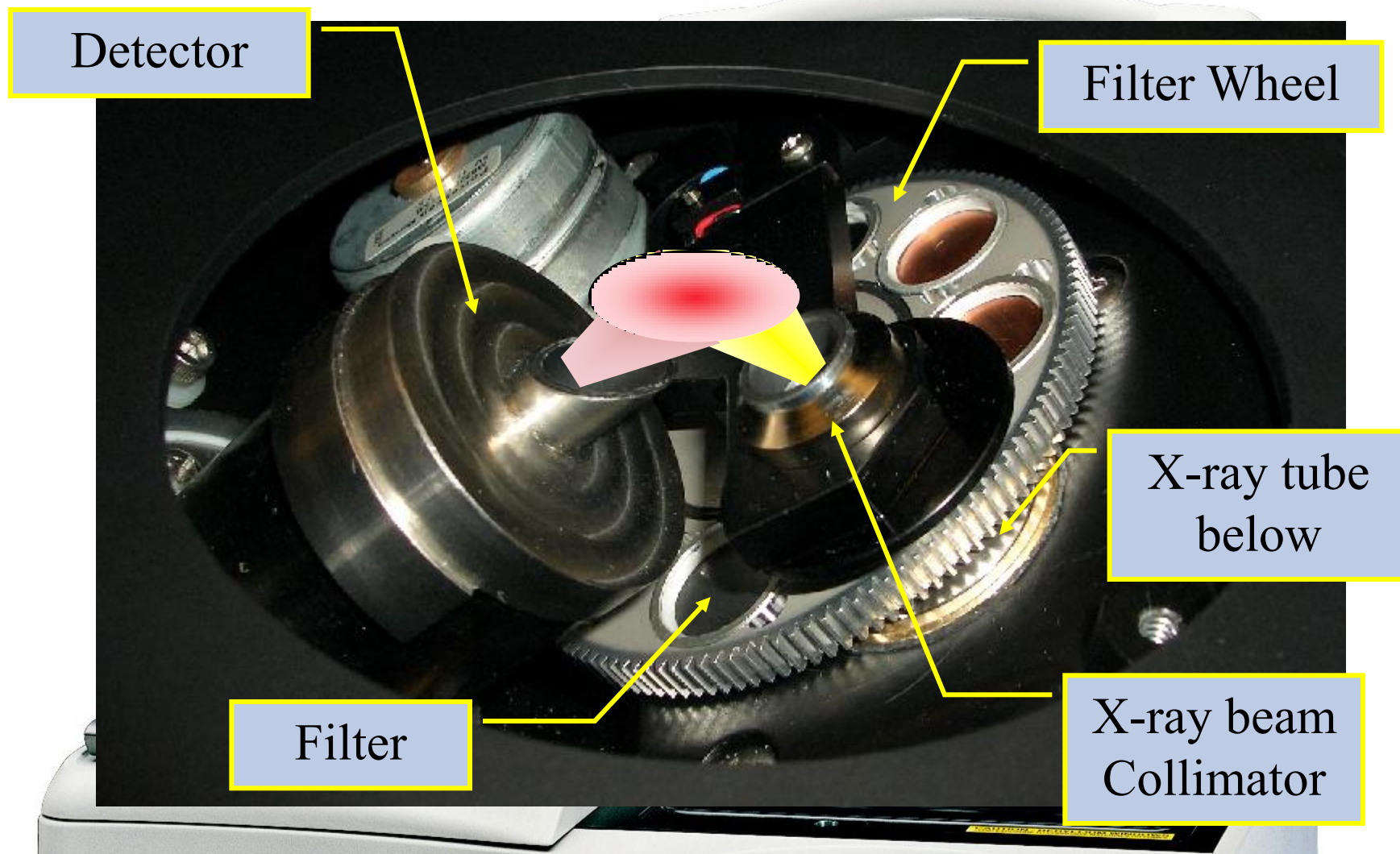


Sample Presentation



- 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

2%

8%

21%

68%

90%

100%

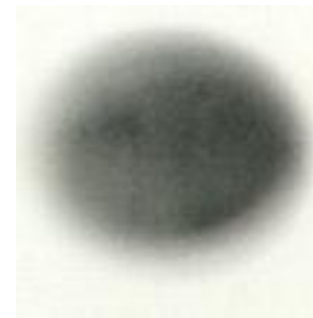
1 mm

2 mm

3.5 mm

5.6 mm

8.8 mm



Camera...

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



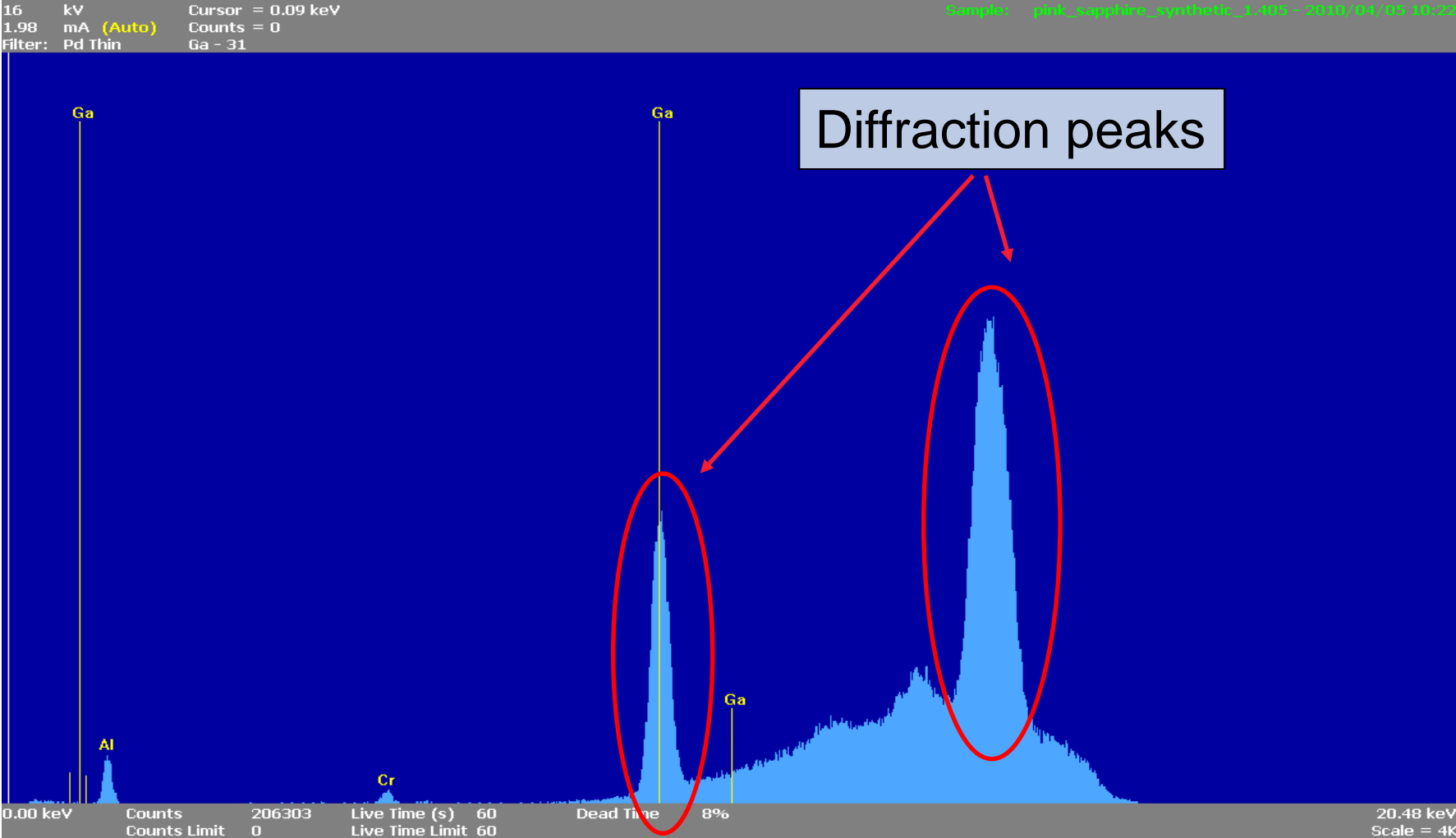
Lights...



Calibration Techniques & Standards

- Empirical calibration (α -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



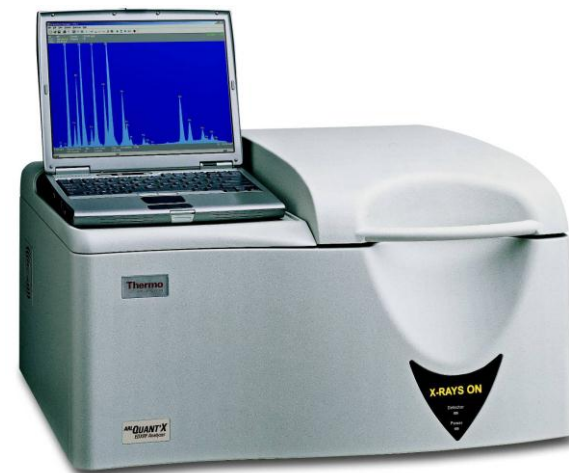
Calibration Techniques & Standards

- Empirical calibration (α -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

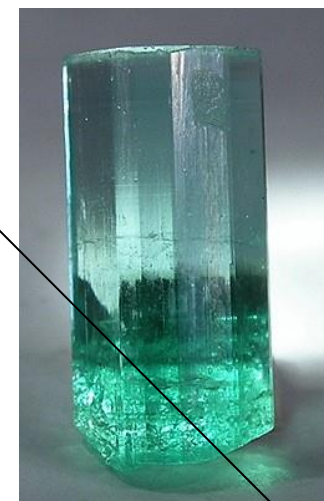
Condition	Filter	Voltage	Atmosphere	Count Rate	Live Time	Analytes
High Za	Cu Thin	40 kV	Vacuum	High	30 sec	Ag, Pd, Sn
Low Za	No Filter	4 kV	Vacuum	Medium	120 sec	Na, Mg, Al, Si
Low Zb	Cellulose	8 kV	Vacuum	Medium	60 sec	Ca
Low Zc	Aluminum	12 kV	Vacuum	Medium	60 sec	Ti, V, Cr, Mn, Fe
Mid Za	Pd Thin	16 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 & Sapphires (II)

Synthetic ruby Deures, 4.90 ct											
	Al ₂ O ₃	TiO ₂		V ₂ O ₃		Cr ₂ O ₃		Fe ₂ O ₃		Ga ₂ O ₃	
	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.	0.0000	0.0000	0.00		1.409	0.006	0.070	0.002	0.041	0.002
Synthetic pink sapphire, 1.405 ct											
	Al ₂ O ₃	Cr ₂ O ₃		Fe ₂ O ₃		Ga ₂ O ₃					
	Conc.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.
LA-ICP-MS	99.5	0.883	0.428	0.0001	0.0290	0.0002	bd	-		0	
ED-XRF - Pure compounds	Diff.	0.0334	0.001	0.00		0.002		0.002		0.001	
ED-XRF - Minerals	Diff.	0.0335	0.001	0.00		0.003		0.003		0.001	
Synthetic brown sapphire Shadong (China), 1.784 ct											
	Al ₂ O ₃	Cr ₂ O ₃		Fe ₂ O ₃		Ga ₂ O ₃					
	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	0.0024	0.0005	0.892	0.005	0.025	0.001
Synthetic brown sapphire											
	Al ₂ O ₃	TiO ₂		V ₂ O ₃		Ga ₂ O ₃					
	Conc.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.	Conc.	Std. Dev.
LA-ICP-MS	99.5	0.096	0.006	0.398	0.015	0.029	0.002	0.0000		0.0001	
ED-XRF - Pure compounds	Diff.	0.110	0.003	0.349	0.004	0.027	0.001	0.00			
ED-XRF - Minerals	Diff.	0.072	0.002	0.397	0.004	0.025	0.001	0.00			

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

	V2O3		Cr2O3		Fe2O3		V2O3		Cr2O3		Fe2O3					
	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	0.46	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

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