Application note

Determining the origin and authenticity of gemstones with ARL QUANT'X EDXRF Spectrometer

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Keywords

ARL QUANT'X, Emerald, Gemstones, Ruby, Sapphire, SDD, X-Ray Fluorescence

Introduction

Energy Dispersive X-Ray Fluorescence (EDXRF) is an important tool for the determination of the authenticity of colored gemstones and their geographical origin. Depending on the geological setting, precious gemstones like rubies, emeralds or sapphires from different origins often exhibit a characteristic combination of trace elements at different concentrations. As an example, identification and quantification of such elements may allow tracking an emerald down to its location of origin such as Colombia, Brazil, Afghanistan, Zambia or Zimbabwe. Similarly the presence of certain trace elements also helps to distinguish between a valuable naturally formed gemstone (e.g. ruby) and a quasi-worthless synthetic crystal (e.g. synthetic ruby).

Instrumentation

The Thermo Scientific™ ARL™ QUANT'X EDXRF Spectrometer is perfectly suited for the non-destructive analysis of gemstones. Its large area (30 mm^2) Silicon Drift Detector (SDD) offers excellent detection efficiencies for characteristic elements such as gallium (Ga), an important trace element of rubies. In addition, the direct excitation geometry and adjustable X-ray beam collimation allows analysis with small analysis spots while retaining most of the analytical sensitivity. X-ray beam collimators of various sizes are available to adjust the spot size. The sample imaging CCD camera allows positioning of small gemstones for efficient excitation and analysis.

Voltage (kV)	Tube filter	Atmosphere	Live time (s)	Elements
4	No Filter	Vacuum	120	Na, Mg, Al, Si
8	C	Vacuum	60	Ca
12	Al	Vacuum	60	Ti, V, Cr, Mn
16	Pd Thin	Vacuum	60	Fe, Ni
20	Pd Medium	Vacuum	30	Cu, Zn, Ga, W, Ir, Pt, Au
28	Pd Thick	Vacuum	30	Pb, Zr, Mo
40	Cu Thin	Vacuum	30	Ag, Pd, Sn

Table 1. Analytical settings.

Excitation conditions

The ARL QUANT'X Spectrometer is equipped with a 50 Watt X-ray tube offering a vast range of excitation voltages (4-50 kV) which are controllable in steps of 1 kV. Together with multiple primary beam filters (nine) for optimal background control, elemental sensitivity is improved while reducing the background providing improved peak-to-background ratios and better performance.

Table 1 shows the set of excitation conditions used for the analysis of rubies and emeralds. The tube current is automatically adjusted to optimize the detector's dead time. The total counting time per analysis is less than 10 minutes. All measurements are performed in vacuum.

Sample preparation and presentation

Gemstones are analyzed as such not to damage the sample in any way. Small gemstones are mounted on a custom made sample holder or placed in an XRF cup sealed with a 4 µm thick polypropylene film.

Calibration

A Fundamental Parameter (FP) approach was used to perform the calibrations. This method is included in the standard quantitative package of the ARL QUANT'X Spectrometer. To calibrate the spectrometer, a total of 20 readily available pure element and compound standards are used. As these are amorphous materials such standards do not show any diffraction peaks in the spectrum and are therefore preferred over pure minerals or gemstones of known composition, but of crystalline nature. A dedicated set of standards together with the calibration methods specifically developed for gemstone analysis is now available from our company.

Analysis results

A number of synthetic and natural rubies, sapphires and emeralds have been analyzed with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), a semi non-destructive and reliable analysis technique often used as reference technique for gemstone analysis. The results of these analyses are compared with those obtained on the ARL QUANT'X Spectrometer. Table 2 compares the concentrations found for several rubies and sapphires. Table 3 shows the results for the analysis of emeralds. All analyses have been performed with a 2 mm X-ray beam collimator. The data shows a good agreement between EDXRF and LA-ICP-MS results. In most cases the difference in concentrations falls within the uncertainty interval as dictated by the standard deviation.

Synthetic ruby Douros, 4.80 ct											
	Al_20_3	$Ti0_2$		V_20_3		Cr_20_3		Fe_20_3		Ga_20_3	
	Conc.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.
LA-ICP-MS	99.5	0.0015	0.001	0.0000	0.0001	0.883	0.428	0.048	0.006	0.043	0.003
ARL QUANT'X	*Diff.*	0.0029	0.0016	0.000	-	0.792	0.004	0.024	0.001	0.032	0.001

Synthetic pink sapphire, 1.405 ct											
	Al_20_3	$Ti0_2$		V_20_3		Cr_20_3		Fe_20_3		Ga_20_3	
	Conc.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.
LA-ICP-MS	99.5	0.0027	0.0002	0.0000	0.0001	0.0299	0.0002	<DL	-	0.0000	0.0001
ARL QUANT'X	*Diff.*	0.0029	0.0008	0.000	-	0.0334	0.001	0.000	-	0.002	0.001

Natural Shadong sapphire, 1.784 ct											
	Al_20_3	$Ti0_2$		V_20_3		Cr_20_3		Fe_20_3		Ga_20_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
ARL QUANT'X	*Diff.*	0.0195	0.0015	0.0028	0.0008	0.0034	0.0006	1.043	0.006	0.027	0.001

Synthetic brown star sapphire, 3.935 ct											
	Al_20_3	$Ti0_2$		V_20_3		Cr_20_3		Fe_20_3		Ga_20_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	0.0112	0.0004	< DL	-	0.0000	0.0001
ARL QUANT'X	*Diff.*	0.110	0.003	0.349	0.004	0.0130	0.0012	0.000	-	0.000	-

Table 2. Analysis results for rubies and sapphires (conc. expressed as % w/w).

Natural emerald, Pakistan, 1.022 ct								
	Na_20		$Mg0$		Al_20_3		$Si0_2$	
	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
ARL QUANT'X	2.04	0.16	2.33	0.06	12.86	0.10	65.74	0.10
	Sc_20_3		V_20_3		Cr_20_3		Fe_20_3	
	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.
LA-ICP-MS	0.461	0.032	0.074	0.005	1.40	0.27	0.256	0.007
ARL QUANT'X	0.500	0.005	0.080	0.002	2.00	0.01	0.318	0.004

Synthetic emerald, Gilson flux grown, 1.43 ct								
	Na_20		$Mg0$		Al_20_3		$Si0_2$	
	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
ARL QUANT'X	<DL	-	<DL	-	19.29	10.08	67.22	0.11
	Sc_20_3		V_20_3		Cr_20_3		Fe_20_3	
	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.	Conc.	Std Dev.
LA-ICP-MS	0.00023	0.00001	0.072	0.004	0.363	0.007	0.046	0.001
ARL QUANT'X	<DL	-	0.092	0.002	0.436	0.001	0.062	0.002

LA-ICP-MS data generated by and property of Dr. M.S. Krzemnicki, Swiss Gemmological Institute SSEF.

Table 3. Analysis results for emeralds (conc. expressed as % w/w).

Conclusion

This application note illustrates how the ARL QUANT'X EDXRF Spectrometer is used for the analysis of gemstones. A straightforward calibration using pure elements or compounds yields results which show very good agreement with LA-ICP-MS data. As such, the ARL QUANT'X Spectrometer proves to be a cost efficient and a truly non-destructive analysis tool for the gemological lab. Next to rubies, sapphires and emeralds a similar approach can be implemented for the analysis of other precious stones such as spinels, chrysoberyls and even pearls.

Acknowledgment

Thermo Fisher Scientific would like to thank Dr. F. Herzog and Dr. M.S. Krzemnicki of the Swiss Gemmological Institute SSEF, Basel, Switzerland for sharing the LA-ICP-MS data as well as offering their valuable expertise regarding gemstone authenticity, origin and chemical fingerprinting.