Application note

Studying the homogeneity of tourmalines with the ARL QUANT'X EDXRF Spectrometer

Introduction

Tourmalines are well-known, valuable gemstones available in a variety of colors. Chemically, tourmalines belong to the family of silicate minerals, and their general chemical formula* can be written as $XY_3Z_6(T_6O_{18})(BO_3)_3V_3W$, where:

- **X** = Ca, Na, K, or a vacancy
- **Y** = Li, Mg, Fe^{2+}, Mn^{2+}, Al, Cr^{3+}, V^{3+}, Fe^{3+}, (Ti^{4+})
- **Z** = Mg, Al, Fe^{3+}, Cr^{3+}, V^{3+}
- **T** = Si, Al, (B)
- **B** = B, (or a vacancy)
- **V** = OH, O
- **W** = OH, F, O

Species in parentheses are, as yet, not proven to occur at these sites.

*Reference for definition and chemical formula: Hawthorne, F.C. & Henry, D.J. (1999). "Classification of the minerals of the tourmaline group" European Journal of Mineralogy, 11, pp. 201–216.

This wide range of potential combinations explains how there are 37 generally accepted tourmaline species, with schorl as the most common, followed by dravite and elbaite. Each species can occur in several different color varieties. (E.g., rubellite, indicolite, and verdelite are varieties of elbaite.)

Besides the major elements, tourmalines might contain a variety of trace elements such as Mn, Ni, Cu, Zn, Ga, Sr, Sn, Ba, and Pb, which can be used to identify the geographical origin of the stone.

Energy-dispersive X-ray fluorescence

Energy-dispersive X-ray fluorescence (EDXRF) can be used to quantify major, minor, and trace elements in gemstones and serves as a cost-effective alternative to laser-ablation inductively coupled-plasma mass spectrometry (LA-ICP-MS). EDXRF is an entirely non-destructive technique and allows for quick analysis with limited operator training. Note that the suitability of EDXRF for the analysis of gemstones was previously discussed in a different application note (AN41958).

Condition	Filter	Voltage, kV	Atmosphere	Live Time, s	Elements
Low Za	No Filter	4	Vacuum	60	Na, Mg, Al, Si
Low Zb	C	8	Vacuum	120	K, Ca
Low Zc	Al	12	Vacuum	120	Ti, V, Cr
Mid Za	Pd Thin	16	Vacuum	120	Mn, Fe
Mid Zb	Pd Medium	20	Vacuum	120	Ni, Cu, Zn, Ga
Mid Zc	Pd Thick	30	Vacuum	120	Sr, Pb, Bi
High Za	Cu thin	50	Vacuum	120	Nb
High Zb	Cu Thick	50	Vacuum	120	Ag, Sn, Ba

Table 1. EDXRF excitation conditions used for tourmaline analysis.

Gemstone homogeneity

Obtaining representative and quantitative compositional data is a common challenge in gemstone analysis, particularly for tourmalines, as composition can vary throughout the stone's volume. To address this with LA-ICP-MS, multiple analyses would be required, since the analysis spot size can only cover a very small volume of material (i.e., micrometer scale). Compared to LA-ICP-MS an EDXRF analysis spot is much larger, covering millimeters instead of micrometers. As such, a single EDXRF analysis can already provide a representative, average composition. In this application note, the repeatability of tourmaline EDXRF analysis is determined (by analyzing the same stone multiple times from a single orientation) and is then compared to the average composition from several different orientations. This comparison can provide both the reliability of the technique as well as the general homogeneity of the stone.

Instrumentation

The Thermo Scientific™ ARL QUANT'X™ EDXRF Spectrometer is a benchtop instrument equipped with an air-cooled end-window X-ray tube with 50 watt power and a maximum voltage of 50 kV. While a silver tube target was used in this experiment, a rhodium target is also available. Nine primary beam filters ensure optimized excitation for every element. A latest-generation silicon drift detector, equipped with a thin graphene window, allows for the detection of all periodic table elements, from carbon (Z = 6) onwards. Several collimators are available to control the size of the excitation spot down to 1 mm. A camera aids in positioning the sample to precisely set the excitation spot.

Excitation conditions

Table 1 shows the different excitation conditions used to analyze the tourmaline sample, which are combined with a 3.5 mm collimator. This collimator generates an elliptical excitation spot which measures 5.8 mm by 4.5 mm. Total analysis time is approximately 20 minutes, including dead time and the time required to evacuate the sample chamber.

Results and discussion

The blue tourmaline used for this experiment is a larger stone weighing ~60 g. It was analyzed at 5 different orientations (i.e., 5 distinct surfaces). The first orientation (orientation A) was analyzed 7 times without repositioning the stone in order to establish the instrument's repeatability (Table 2). The tourmaline was then analyzed from four additional orientations (B, C, D and E) (Table 3). Finally, the standard deviations (variations) obtained for the different elements at one orientation were compared to the variations obtained by averaging all five orientations.

Since XRF cannot detect all elements present in tourmaline, fixed concentrations of B_2O_3, Li_2O, and H_2O were used at 11%, 3%, and 4% w/w respectively. We used a fundamental parameters (FP) calibration to calculate the composition of tourmaline. Using the general chemical formula we calculate Si as SiO_3 while other detectable elements are in elemental form.

Comparing Tables 2 and 3 revealed a notable increase in variation when averaging the different orientations of the tourmaline, particularly for certain elements such as Mn. Closer inspection of the data reveals that orientation E is the main contributor to this variance. However, variation remains significantly higher between orientations, even when orientation E is excluded. Except for trace elements with concentrations close to the detection limit, the relative standard deviation due to orientation is ≤10%. Variability is 5 to 10 times less when repeatedly measuring at the same orientation. Overall, this seems to indicate that the instrument's analytical variability is much smaller than the natural variation in the gemstone's composition.

	Na	Al	SiO_3	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Ga	Nb	Sn	Pb	Bi
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Orientation A Rep 1	2.22	22.76	52.57	0.143	0.371	0.0222	0.0005	0.0025	3.225	0.075	0.0009	0.485	0.0589	0.0006	0.0004	0.0070	0.0403
Orientation A Rep 2	2.18	22.69	52.69	0.146	0.365	0.0212	0.0008	0.0021	3.230	0.069	0.0009	0.487	0.0589	0.0004	0.0012	0.0074	0.0409
Orientation A Rep 3	2.23	22.74	52.61	0.144	0.362	0.0233	0.0005	0.0021	3.219	0.069	0.0009	0.490	0.0598	0.0004	0.0015	0.0080	0.0407
Orientation A Rep 4	2.18	22.73	52.63	0.146	0.368	0.0225	0.0000	0.0024	3.232	0.070	0.0011	0.490	0.0593	0.0006	0.0011	0.0074	0.0407
Orientation A Rep 5	2.19	22.72	52.66	0.146	0.364	0.0241	0.0002	0.0026	3.208	0.072	0.0009	0.484	0.0591	0.0007	0.0010	0.0079	0.0406
Orientation A Rep 6	2.15	22.68	52.74	0.143	0.366	0.0226	0.0003	0.0027	3.214	0.071	0.0013	0.484	0.0586	0.0006	0.0000	0.0074	0.0403
Orientation A Rep 7	2.14	22.64	52.83	0.141	0.365	0.0226	0.0001	0.0022	3.194	0.069	0.0010	0.486	0.0584	0.0005	0.0003	0.0071	0.0397
Average	*2.19*	*22.71*	*52.68*	*0.144*	*0.366*	*0.0226*	*0.0003*	*0.0024*	*3.217*	*0.071*	*0.0010*	*0.487*	*0.0590*	*0.0005*	*0.0008*	*0.0075*	*0.0405*
1-Sigma	*0.03*	*0.04*	*0.09*	*0.002*	*0.003*	*0.0009*	*0.0003*	*0.0002*	*0.013*	*0.002*	*0.0002*	*0.003*	*0.0005*	*0.0001*	*0.0006*	*0.0004*	*0.0004*
% RSD	*1.6*	*0.2*	*0.2*	*1.3*	*0.8*	*4.0*	*80.5*	*10.2*	*0.4*	*3.3*	*15.3*	*0.5*	*0.8*	*20.9*	*70.3*	*5.0*	*1.0*

Table 2. EDXRF repeatability for blue tourmaline, measured from orientation A.

	Na	Al	SiO_3	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Ga	Nb	Sn	Pb	Bi
	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Orientation A	2.19	22.7	52.7	0.144	0.37	0.023	0.0003	0.0024	3.2	0.071	0.0010	0.49	0.059	0.0005	0.0008	0.0075	0.040
Orientation B	2.01	22.1	53.2	0.129	0.39	0.026	0.0000	0.0024	3.4	0.068	0.0009	0.55	0.067	0.0007	0.0009	0.0079	0.045
Orientation C	2.23	22.4	52.9	0.125	0.34	0.020	0.0013	0.0022	3.3	0.046	0.0009	0.50	0.058	0.0004	0.0004	0.0071	0.039
Orientation D	2.02	22.2	53.5	0.117	0.32	0.025	0.0000	0.0004	3.2	0.044	0.0007	0.48	0.056	0.0003	0.0009	0.0062	0.035
Orientation E	2.19	21.7	52.8	0.112	0.42	0.044	0.0012	0.0018	4.1	0.044	0.0000	0.46	0.046	0.0002	0.0014	0.0094	0.038
Average	*2.13*	*22.2*	*53.0*	*0.125*	*0.37*	*0.028*	*0.0006*	*0.0018*	*3.5*	*0.055*	*0.0007*	*0.49*	*0.057*	*0.0004*	*0.0009*	*0.0076*	*0.040*
1-Sigma	*0.10*	*0.4*	*0.3*	*0.012*	*0.04*	*0.009*	*0.0006*	*0.0008*	*0.4*	*0.013*	*0.0004*	*0.03*	*0.007*	*0.0002*	*0.0004*	*0.0012*	*0.004*
% RSD	*4.7*	*1.8*	*0.6*	*9.8*	*11.2*	*34.3*	*112.3*	*45.6*	*11.4*	*24.6*	*58.0*	*6.5*	*12.8*	*46.1*	*40.7*	*15.5*	*9.1*

Table 3. Compositional variation of blue tourmaline measured from five different orientations.

Conclusion

This application note illustrates the capabilities of the ARL QUANT'X EDXRF Spectrometer for the analysis of tourmalines, including the typical repeatability for different elements at different concentrations. This data was compared to the variability in stone composition due to inhomogeneity.

A 5- to 10-fold increase in standard deviation was observed for compositional variation relative to instrument repeatability. Though this is a significant difference, it also demonstrates the excellent reproducibility of the technique. With EDXRF, you can be sure that any compositional differences found when analyzing a stone at various orientations are due to its natural inhomogeneity.

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