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Application News

UV-VIS-NIR Spectrophotometer SolidSpec™-3700i
Energy Dispersive X-ray Fluorescence Spectrometer EDX-8100

Multifaceted Evaluation of Gemstones Using UV-Vis and EDXRF

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User Benefits

- The color of gemstones can be quantitatively evaluated using an ultra-violet and visible light spectrophotometer (UV-Vis).
- Qualitative and quantitative analysis of trace elements can be performed with the energy dispersive X-ray fluorescence spectrometer (EDXRF).
- By using UV-Vis and EDXRF, the relationship between differences in the color of gemstones and trace elements can be investigated.

■ Introduction

Various types of gemstones are in circulation, and the types and geographical origins of the gems that are traded are diverse. In recent years, interest in gemstones has grown, and it is expected that the number traded will increase. Gem identification involves considering various things such as the origin, color, and cutting. Methods to evaluate the color of gemstones include ultra-violet and visible light spectrophotometry (UV-Vis) and energy dispersive X-ray fluorescence spectrometer (EDXRF). With UV-Vis, the color can be directly evaluated, and with EDXRF, trace elements that cause color can be evaluated. This article introduces examples of evaluating gemstone colors using UV-Vis and EDXRF for the green and blue gemstones zoisite and tanzanite.

■ Epidote Group Gemstones

The epidote group includes various gemstones that are types of silicate minerals and whose chemical composition can be expressed by the formula $Ca_2(M1,M2,M3)Si_3O_{12}(OH)$. Here M1 to M3 represent metal elements, mostly aluminum (Al). When the elements in M3 change, the color of the gemstone also changes. If the M3 element is Al, the mineral is referred to as zoisite, and if it is Mn^{3+}, it is referred to as piemontite (see Table 1).

Table 1 Main Epidote Group Gemstones

	M1	M2	M3	Color of the Gemstone
Zoisite	Al	Al	Al	Green, blue, yellow, purple, etc.
Epidote	Al	Al	Fe^{3+}	Yellow, green
Piemontite	Al	Al	Mn^{3+}	Peach, red
Allanite	Al	Al	Fe^{2+}	Black, brown, purplish brown

Zoisite mainly found in Tanzania, with a part of the Al replaced with vanadium (V), and the deep blue color with vivid purple is referred to as tanzanite.[2] It has been selected as one of the birthstones for December. Note that raw tanzanite stones that contain V can have a brownish-red or green color. But by heat treating the stone the valence of the V is changed, which brings out the vivid deep blue color.

■ Samples

The UV-Vis and EDXRF measurements were performed on six types of loose stone samples (1) to (6) that are sold commercially as zoisite or tanzanite.

Fig. 1 shows the external appearance, the number of carats, and the size of gemstones obtained by observing through a stereoscopic microscope. Comparing samples (1) to (3) with samples (4) to (6), it can be seen more bluish, so it is assumed that the content of vanadium is higher.

Sample	External Appearance	Sample	External Appearance
(1) 0.25 ct 3.5 × 5.1 mm		(4) 0.36 ct 3.9 × 5.1 mm	
(2) 0.30 ct 4.0 × 5.8 mm		(5) 0.75 ct 4.3 × 5.8 mm	
(3) 0.42 ct 4.4 × 6.5 mm		(6) 0.28 ct 3.8 × 4.8 mm	

Fig. 1 Sample Appearance, Number of Carats, and Diameter of Loose Stone Samples Measured

1. Color Measurement by UV-Vis

The loose stone samples were fixed in a commercially available sponge and set in the UV-Vis instrument, as shown in Fig. 2. Due to the extremely small sizes of the loose stone samples, as indicated in Fig. 1, the UV-VIS-NIR spectrophotometer SolidSpec-3700i, which allows the most focused light beam, was used for the measurement. The size of the light beam was narrowed down to φ2 mm using the included beam narrowing mask. Additionally, the centers of the samples were irradiated and the measurements were conducted by the relative diffuse reflection method (hereafter described as "diffuse reflection"), which does not include the specular reflection component. The measurement conditions are shown in Table 2.

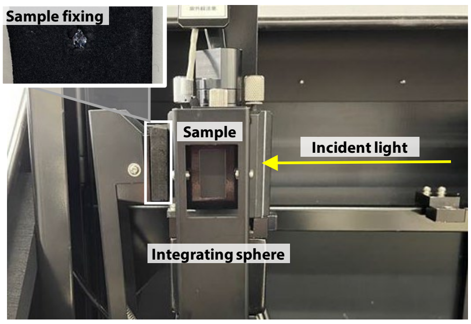

Fig. 2 View within Sample Chamber when Measuring Sample

Table 2 UV-Vis Measurement Conditions

Instrument:	SolidSpec-3700i
Wavelength Range:	300 - 800 nm
Data Interval:	1.0 nm
Scan Speed:	Medium speed
Slit Width:	5.0 nm

The diffuse reflection spectra obtained are shown in Fig. 3. Note that the surface condition of the samples varied for each sample, as shown in Fig. 1, so the reflectance fluctuated depending on the sample placement.

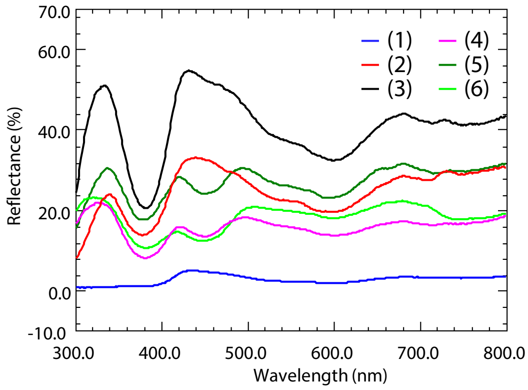

Fig. 3 Diffuse Reflection Spectra of Samples

Therefore, an x-y chromaticity diagram was prepared using the diffuse reflection spectra obtained. The coordinates of the chromaticity diagram show the proportions of red (R), green (G), and blue (B). If the relative values of the horizontal axis x (red) and the vertical axis y (green) are determined, the proportion of blue can be determined from R + G + B = 1. These values indicate the proportions of each color, so they are less affected by the surface condition or placement method of the samples. Note that the color calculation software (optional) of the LabSolutions™ UV-Vis for control of the UV-Vis spectrophotometer was used for the calculations. The results obtained for the x-y values are shown in Table 3, and the chromaticity diagram is shown in Fig. 4.

Table 3 Calculation Results of the Color Values (x-y Values)

Sample		x	y
(1)	Blue	0.26	0.25
(2)		0.28	0.29
(3)		0.28	0.29
(4)	Green	0.31	0.34
(5)		0.31	0.33
(6)		0.33	0.37

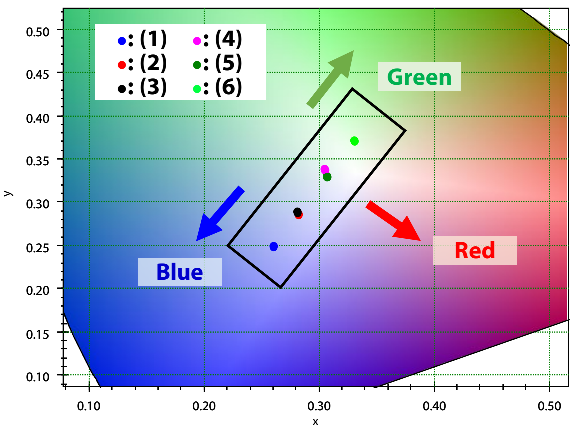

Fig. 4 x-y Chromaticity Diagram of Samples

From Table 3 and Fig. 4, it is possible to quantify and visualize that samples (1) to (3) were blue, and samples (4) to (6) were green. Among samples (1) to (3) and samples (4) to (6), it was difficult to distinguish the colors visually, as shown in Fig. 1, it turned possible to quantitatively distinguish the colors numerically from the x-y values.

2. Qual-Quant Analysis by EDXRF

Qual-Quant analysis was performed by EDXRF. The EDX-8100, which is capable of performing light element analysis with high sensitivity, was used for the measurements. The measurement conditions are shown in Table 4. For the quantitative analysis, a fundamental parameter (FP) method was used, assuming the compound form to be oxides.

Table 4 EDXRF Measurement Conditions

Instrument:	EDX-8100
Elements:	$_{11}$Na to $_{92}$U
Analysis Group:	Qualitative quantitative
Detector:	SDD
X-Ray Tube:	Rh target
Tube Voltage:	50 [kV] (Ti-Y) (Zr-Ba), 15 [kV] (Na-P) (S-Sc)
Tube Current:	Auto [µA]
Collimator:	3 [mmφ]
Primary Filter:	Non (Na-P), #2 (S-Sc), #4 (Ti-Y), #1 (Zr-Ba)
Atmosphere:	Vacuum
Integration Time:	#4 (Ti-Y): 240 [sec.], others 3 Ch: 60 [sec.]
Dead Time:	Maximum 30 [%]

■ Sample Pretreatment

The samples were sandwiched between 5 µm thick polypropylene film, fixed in a sample cell facing downward, and measured. Fig. 5 shows the appearance, and Fig. 6 shows an image of the sample observed using PCEDX Navi software.

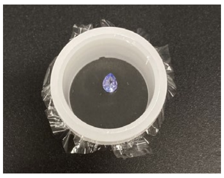

Fig. 5 View of Sample Fixed in Sample Cell

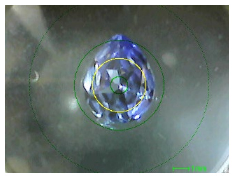

Fig. 6 Image of Sample Observed Using PCEDX Navi Software

■ Qual-Quant Analysis Results

The EDXRF qualitative analysis results are shown in Fig. 7, and the quantitative analysis results are shown in Table 5.

It was found that the six samples measured in this case were all silicate minerals (epidote) with Si, Al, and Ca being the main components. Fig. 8 shows the quantitative values of V_2O_5 and TiO_2 in each sample. It can be seen that the concentration of vanadium is higher in the blue samples, and the titanium is dominant in the green samples. Other trace elements are usually not added to synthetic stones, so the six loose stone samples measured here were considered as natural stones.

■ Conclusion

Multifaceted evaluations of loose gemstones sold commercially under the names “zoisite” and “tanzanite” were performed using with UV-Vis and EDXRF. By performing color measurement with the UV-Vis, it was possible to quantitatively distinguish gemstones whose color was difficult to distinguish visually. Also, in the qual-quant analysis using with EDXRF, a correlation was found between the vanadium and titanium content of the gemstones and their visual color. This suggests that the valence of the vanadium that causes the blue-purple color was changed by heat treatment.[3] Note that the types and quantities of the elements contained in the gemstones varied depending on their geographical origin. Therefore, analysis of the trace elements in gemstones is useful for determining their geographical origins. For details see Shimadzu Application News No. X276.

Acknowledgements
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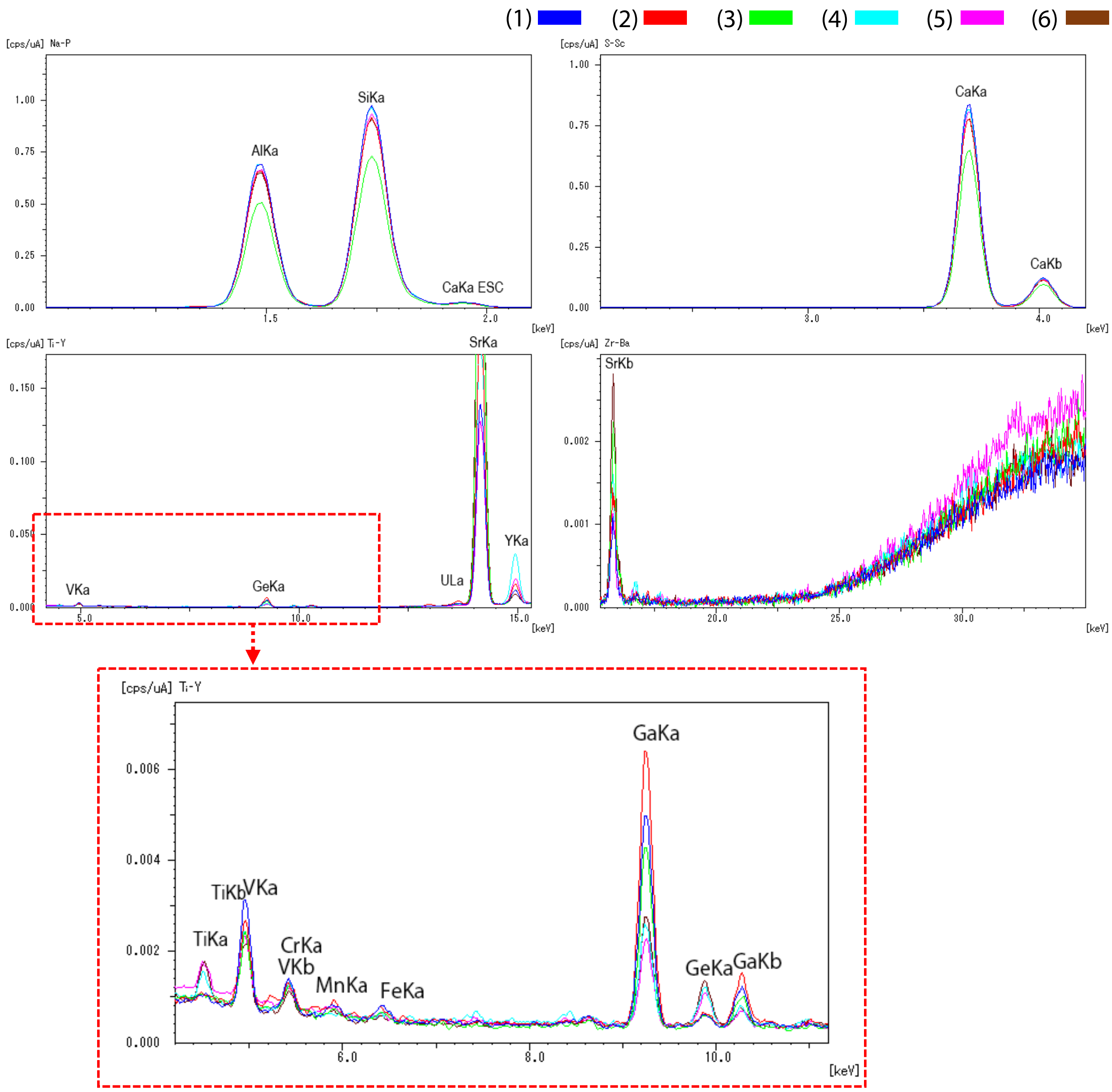

Fig. 7 EDXRF Profiles

Table 5 Quantitative Analysis by EDXRF

(wt%)

Analysis Target	(1)	(2)	(3)	(4)	(5)	(6)
SiO_2	39.999	40.164	39.831	40.096	40.018	40.013
Al_2O_3	32.045	32.206	31.137	32.265	31.916	31.980
CaO	27.397	27.059	28.194	27.047	27.582	27.178
V_2O_5	0.289	0.225	0.245	0.210	0.160	0.176
SrO	0.151	0.225	0.471	0.203	0.140	0.412
TiO_2	0.036	0.031	0.031	0.105	0.132	0.179
Cr_2O_3	0.029	0.022	0.026	0.023	0.022	0.022
Ga_2O_3	0.022	0.030	0.031	0.011	0.009	0.012
MnO	0.010	0.015	0.014	0.036	0.019	0.007
Y_2O_3	0.008	0.010	0.011	-	-	0.010
Fe_2O_3	0.003	0.005	0.003	0.002	-	0.002
U_3O_8	0.010	0.005	0.006	-	-	0.003
GeO_2	0.001	0.001	0.002	0.003	0.003	0.004
ThO_2	-	0.002	-	-	-	-

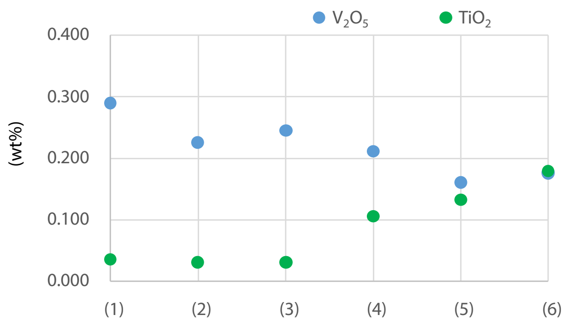

Fig. 8 Quantitative Values of V_2O_5 and TiO_2 in Each Sample

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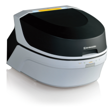

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