

Application News

X-Ray Analysis

Analysis of Precious Stones by EDX-8100:

Differentiation of Natural Stones/Synthetic Stones, Determination of Geographic Origin of Natural Stones

No. X276

Various instruments are used in appraisals of precious stones, including not only general gemstone appraisal tools such as the stereoscopic microscope, but also various analytical instruments ⁽¹⁾.

For example, the Fourier transform infrared spectrophotometer (FT-IR) is used to determine whether heat treatment/resin impregnated treatment have been applied or not, and the UV-Vis spectrophotometer (UV-Vis) is used to judge the presence or absence of coloring treatment.

The energy dispersive X-ray fluorescence spectroscope (EDXRF) is also a necessary and indispensable instrument that enables quick, nondestructive composition analysis. For example, EDXRF can clearly detect the lead used in lead glass-filling treatment of gemstones.

Here, a Shimadzu EDX-8100 was used in a composition analysis of rubies, emeralds, and Paraiba tourmalines, which are commonly seen gemstones and strongly loved by many people, and effective results for distinguishing natural stones and synthetic stones and identifying the geographic origin of natural stones were obtained.

T. Nakao, H. Nakamura

Samples

The precious stones (natural and synthetic stones) and rough gemstones shown below were used.



Fig. 1 Types and Origins of Precious Stones and Gemstones

Elements

11Na - 02U

Sample Preparation

 $Samples\ were\ set\ to\ enable\ direct\ X-ray\ irradiation\ and\ measured.$

Ruby

1. Measurement results

Fig. 2 shows the qualitative analysis and quantitative analysis results for the natural stone (mined from Tanzania) and the synthetic stone.

2. Differences between natural stone and synthetic stone

A trace amount of gallium was not detected in the synthetic stone, and in comparison with the natural stone (Tanzania), the synthetic stone had a high content of chromium. As one example, natural stones and synthetic stones can be distinguished by this kind of difference. However, elements originating from a catalyst may also be detected in synthetic stones in some cases.

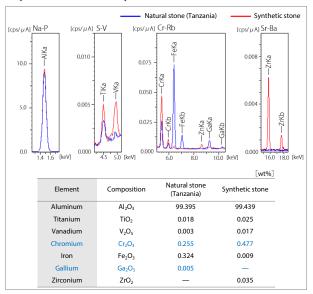


Fig. 2 Results of Qualitative Analysis/ Quantitative Analysis of Rubies

Emerald

1. Measurement results

Fig. 3 shows the qualitative analysis and quantitative analysis results for the two types of natural stones (mined from Colombia and Zambia) and the synthetic stone.

2. Identification of natural or synthetic stone

Chromium, iron, and vanadium are elements that give emeralds their color, and the hues of stones changes depending on the contents of the respective elements. In the results in Fig. 3, the Zambian stone has high contents of chromium and iron and a low content of vanadium in comparison with the Colombian stone. Comparatively large amounts of sodium, magnesium, and potassium and trace amounts of rubidium and cesium were also detected in the Zambian stone, providing one indicator for distinguishing this stone from the Colombian stone. Although the price of emeralds is mainly determined by their transparency, hue, and depth of color (color strength), the geographic origin is also a factor in the price. As distinctive features of the respective geographic origin, Colombian emeralds display a bright green color, while Zambian stones are characterized by high transparency, and the price of Colombian stones is generally higher. Since it is difficult to distinguish deep green Zambia emeralds from Colombian emeralds, elemental analysis is used as a technique for determining the geographic origin. The synthetic stone was identified based on detection of rhodium, which was estimated to originate from a catalyst, and the absence of sodium and magnesium in the detection results.

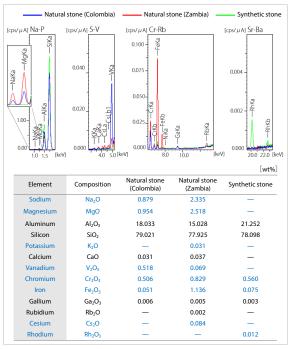


Fig. 3 Results of Qualitative Analysis/ Quantitative Analysis of Emeralds

Paraiba Tourmaline

1. Measurement results

Fig. 4 shows the qualitative analysis and quantitative analysis results for the rough gemstone and the cut stone (both produced in Brazil).

2. Geographic origin

From the results in Fig. 4, the main components are oxides of aluminum and silicon, and the samples also contain manganese and copper, indicating that both samples are natural Paraiba tourmalines. Although Paraiba tourmaline is produced in three areas (Brazil, Nigeria, and Mozambique), these stones are estimated to be of Brazilian origin because their copper contents exceed 0.6 w% (CuO). A detailed analysis was also conducted using LA-ICP-MS ⁽²⁾.

3. Hue

The results in Fig. 4 showed that the cut stone had a high manganese content of 4 wt% (MnO) in comparison with the 0.5 wt% (MnO) content of the rough stone. Stones generally have a strong green hue if the Mn content is high, but the hues of both stones appeared to be the same neon blue when examined with the naked eye (Fig. 5). Therefore, the samples were observed with an OLS5000 3D measuring laser microscope, as shown in Fig. 6. Green areas were observed in the interior, and these are thought to be a factor in the high content of Mn.

Table 1 Measurement Conditions

Instrument : EDX-8100 (EDX-8000) Elements Na - U Analysis group Qualitative analysis and quantitative analysis Detector SDD X-ray tube : Rh target Tube voltage : 15 [kV] (Na-V), 50 [kV] (Cr-U) Tube current : Auto [µA] Collimator : 3 [mm o] Primary filter, channel : Non [Na-P], #1 [Sr-Ba], #2 [S-V], #4 [Cr-Rb]

Atmosphere : Vacuum
Integral time : 50 [s] × 4 Ch
Dead time : Maximum 30 [%]

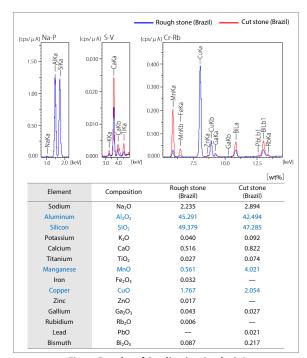
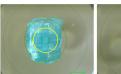
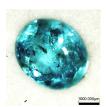


Fig. 4 Results of Qualitative Analysis/ Quantitative Analysis of Paraiba Tourmaline







Rough stone (Brazil) Cut sto

Fig. 5 Observation Images of EDX Samples (: X-Ray Irradiation Range 3 mm φ)

Fig. 6 Observation Image of Cut Stone (OLS5000)

Conclusion

As demonstrated by these results, Identification of natural stone or synthetic stone and determination of the geographic origin of natural stones can be roughly estimated from the types of elements, differences in their contents, and trace detection. In comparison with measurements using only EDX, higher accuracy can be expected in appraisals of gemstones by using EDX measurement in combination with other analytical instruments (FT-IR, UV-Vis) ⁽³⁾.

<References>

- Dr. Ahmadjan Abduriyim: The Science of Gemstones, ARK PUBLISHING INC.
- (2) Ahmadjan Abduriyim, Hiroshi Kitawaki, Masashi Furuya, and Dietmar Schwarz: "Paraiba"-Type Copper Bearing Tourmaline from Brazil, Nigeria, and Mozambique: Chemical Fingerprinting by LA-ICP-MS
- (3) Ahmadjan Abduriyim and Hiroshi Kitawaki: Applications of Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to Gemology

Acknowledgement

We wish to express our deep appreciation to Dr. Ahmadjan Abduriyim, who is the Representative of Tokyo Gem Science LLC and Director of the GSTV Gemological Laboratory, for various advice in connection with gemology and gemstone appraisal.

First Edition: Sep. 2020



Shimadzu Corporation

www.shimadzu.com/an/

For Research Use Only. Not for use in diagnostic procedures

This publication may contain references to products that are not available in your country. Please contact us to check the availability of these products in your country.

The content of this publication shall not be reproduced, altered or sold for any commercial purpose without the written approval of Shimadzu. Shimadzu disclaims any proprietary interest in trademarks and trade names used in this publication other than its own. See http://www.shimadzu.com/about/trademarks/index.html for details.

The information contained herein is provided to you "as is" without warranty of any kind including without limitation warranties as to its accuracy or completeness. Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to the use of this publication. This publication is based upon the information available to Shimadzu on or before the date of publication, and subject to change without notice.