

Geochemical Fingerprinting of Conflict Minerals using LIBS



Application Note

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Summary

Conflict minerals are commercially valuable resources mined in areas of armed conflict or human rights abuses. Recently, the United States Securities and Exchange Commission (SEC) proposed new rules requiring manufacturers to disclose whether conflict minerals from the Democratic Republic of Congo (DRC) are used in their products [1-3].

This application note describes how Applied Spectra's RT100-HP Laser-Induced Breakdown Spectroscopy (LIBS) system provides a simple and rapid solution for distinguishing between columbite-tantalite (coltan) mineral ores from different geographical regions.

Introduction

The exploitation of commercially valuable resources in areas of armed conflict and human rights abuses has received much attention recently. In compliance with the 2010 passage of the Dodd-Frank Wall Street Reform and Consumer Protection Act, the United

States SEC has proposed a new set of rules which will require manufacturers to disclose whether or not specific minerals originated from the Democratic Republic of Congo (DRC) or its surrounding regions where human rights violations are well-documented [1-3].

All companies that manufacture goods containing gold, tin, tungsten and tantalum will be affected. These so-called "conflict minerals" are used in a wide variety of products, such as mobile phones, laptops, medical devices and jewelry.

The proposed rules require "reasonable inquiries" into the country of origin of these rare earth metals and minerals. In many cases, tracing the supply chain back to the smelter facility can be extremely difficult and time-consuming.

This application note describes a simple, rapid and environmentally friendly method for classifying naturally occurring columbite-tantalite mineral ores by geographical



location using Applied Spectra's RT100-HP LIBS Instrument.

LIBS has previously been used to determine the chemical composition in a number of geological materials, including silicates, carbonates and lithium [4-7]. Columbite-tantalite mineral ores, also known as coltan, contain significant quantities of tantalum and niobium. These highly valuable ores are mined and their minerals are extracted for use in consumer electronics and other goods. The ores used in this study were collected from different geographical regions in North America. Significant statistical differences between sample ores were seen by analyzing LIBS emission spectra.

Samples

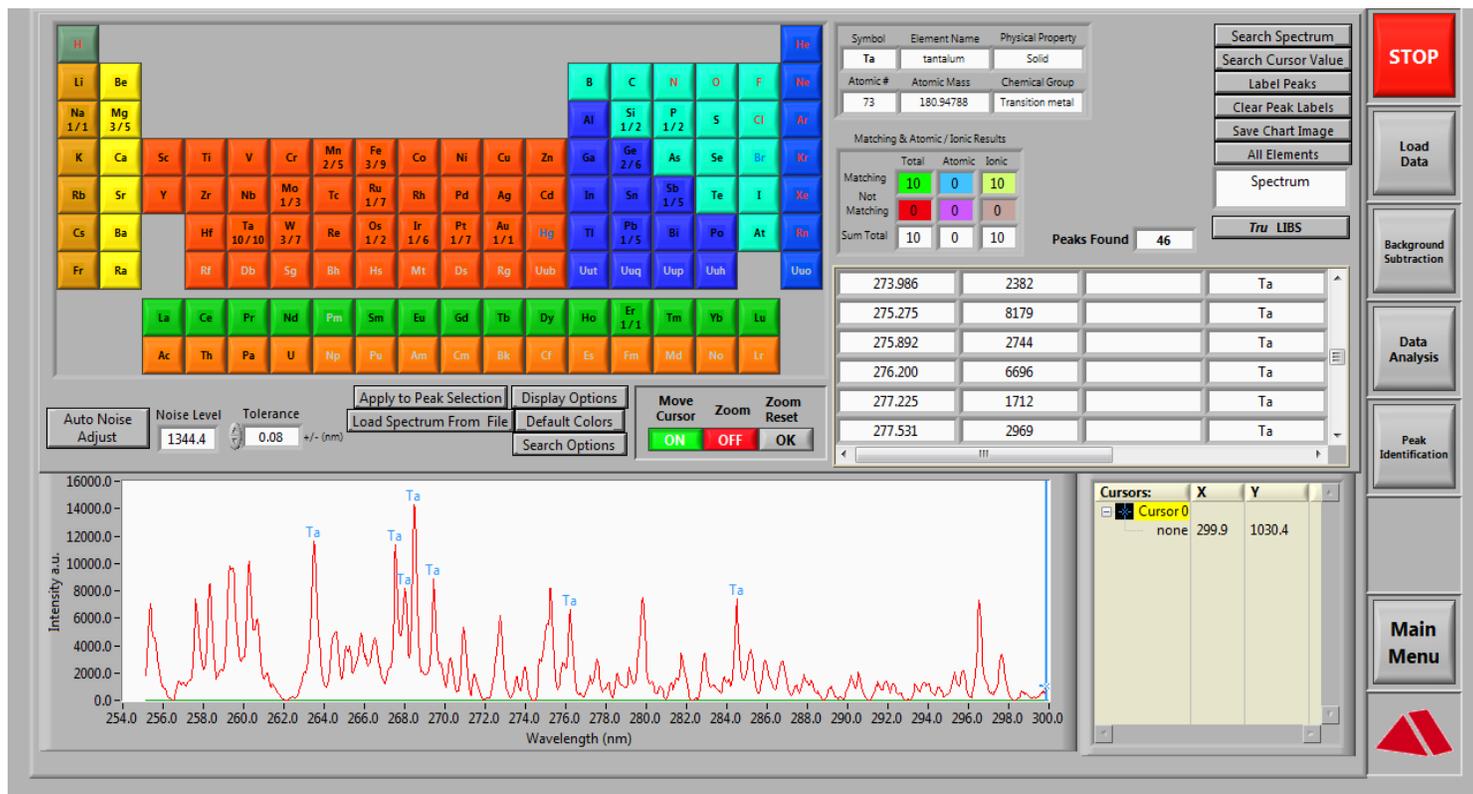
The coltan samples selected for this pilot study were collected from three fractionated granitic pegmatite fields in North America: (1) the Starrett pegmatite in the central Maine, U.S.; (2) the Pack Rat and Beebe Hole pegmatite fields of San Diego County, California, U.S.; and (3) the Moose pegmatite in Northwest Territories, Canada. Note: Samples from the Pack Rat and Beebe locations were combined for PLSDA statistical analyses since they represent a single locality.

Experimental Method

Spectral data were collected using Applied Spectra's pre-installed Axiom software package. Spectra of Nb, Ta, Mn, Fe, W, and Ti metal standards and columbite-tantalite ore samples were taken using an automatically translating stage with auto-focusing camera and auto-focusing laser system. Each 2 x 2 acquisition grid contained four locations with 0.5mm spacing between each sampling location so very small ore chips could be analyzed (Figure 4). The laser output energy was 23 mJ, gate width 3 μs, gate delay 2 μs, and repetition rate 3Hz.

Forty laser pulses were applied at each location on the sample. The first fifteen laser pulses at each location were used to self-clean the surface of the ore. The spectra from the remaining 25 laser shots were averaged for analysis, thus providing superior signal to noise performance (Figure 4). Data were taken with a central wavelength at 370 ± 120 nm (Figure 2) and a 600 grooves/mm grating to maximize the number of emission lines of interest in the spectral window range. Emission wavelengths of the elements of interest are shown in Table 1.

Figure 1. Identification of tantalum (Ta) peaks using the integrated Axiom software package.



Statistical Analysis

The data were analyzed using chemometric methods to generate cluster plots and classification results. Partial least squares discriminant analysis (PLSDA) was the statistical method used to discriminate between columbite-tantalite of different geographic origins. Figure 3 shows the PCA scatter plots. Each individual point in the figure is the projection of a single spectrum, with 100 spectra per sample. The two-dimensional scatter plots show that most of the within-class spectra cluster together, with only a single substantial outlier in the samples from location 2 (Pack Rat/Beebe). There was good separation between the location 2 cluster and the remaining samples.

Table 1. Elements and wavelength regions of interest.

Element	Wavelength, λ (nm)
Fe	274.65, 275.57, 274.95
Mn	257.61, 259.37, 260.57
Nb	309.42, 405.89, 313.08
Ta	266.57, 268.52, 284.45
W	248.88, 257.93, 257.22
Ti	334.94, 376.13, 375.93
Zr	343.82, 339.20, 327.31

Table 2. Sample Classification Results. Percentage of spectral data from each sample assigned to a particular geographical location. ★ indicates 75-100% correct classification; ✓ indicates 50-74% correct classification.

	Location 1 Starrett	Location 2 BeeBee, Pack Rat	Location 3 Moose
BeeBee 3	0%	100% ★	0%
Moose 102	0%	33%	67% ✓
Moose 104	0%	0%	100% ★
Moose 113	0%	0%	100% ★
Moose 114	0%	0%	100% ★
Moose 117	0%	0%	100% ★
Moose 121	0%	0%	100% ★
Pack Rat 12	25%	73% ✓	2%
Pack Rat 20	0%	100% ★	0%
Starrett 4	100% ★	0%	0%
Starrett 5	100% ★	0%	0%
Starrett 12	100% ★	0%	0%
Starrett 21	100% ★	0%	0%
Starrett 23	100% ★	0%	0%

The classification study used a leave-one-sample-out (LOSO) cross-validation approach. In each pass, the spectra from the i^{th} sample are held out of the training data. This i^{th} sample was then used as the test data. Only four PLSDA components were needed to achieve near perfect classification of spectra into correct sampling group.

Table 2 lists the percentage of shots from each sample that were assigned to each possible class (i.e. geographic origin). The PLSDA results used 20 components, a value that was chosen after a preliminary investigation indicated robust performance. The PLSDA classifier then assigned a label to each LIBS spectrum. Using such an approach, there was a perfect 16 out of 16 classification result achieved for the correct identification of samples to their geographical location.

Summary

The Applied Spectra RT100-HP LIBS system demonstrates the ability of LIBS to distinguish between columbite-tantalite ores collected from different regions of North America.

Three coltan samples sets were analyzed by LIBS and statistically analyzed to rapidly distinguish ores originating from different geographic sources of this economically important mineral series. Individual spectral emission lines and line ratios for Fe, Mn, Nb, Ta, W, Ti, and Zr were used as features in a Partial Least Squares Discriminant Analysis (PLSDA).

Outstanding performance, with 100% correct classification, was achieved for the LIBS spectra collected with a central wavelength at 370 ± 120 nm and a 600 grooves/mm grating. Statistical analysis of LIBS spectra identified the geographical origin of the ores with 100% accuracy.

Figure 2. Offset plot using spectral range of 370 ± 120 nm for the three locations: (a) Starrett, (b) Moose, and (c) Pack Rat-Beebe locations.

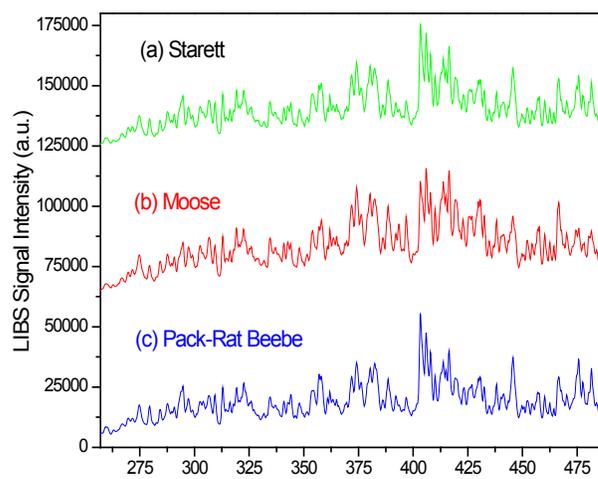


Figure 3. PCA Analysis. Scatter plot of the 1st and 2nd latent variables components of LIBS data sets. Each symbol corresponds to one spectrum projected into the two-dimensional latent variable space.

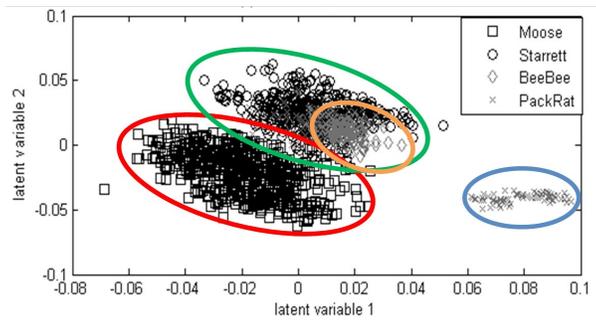
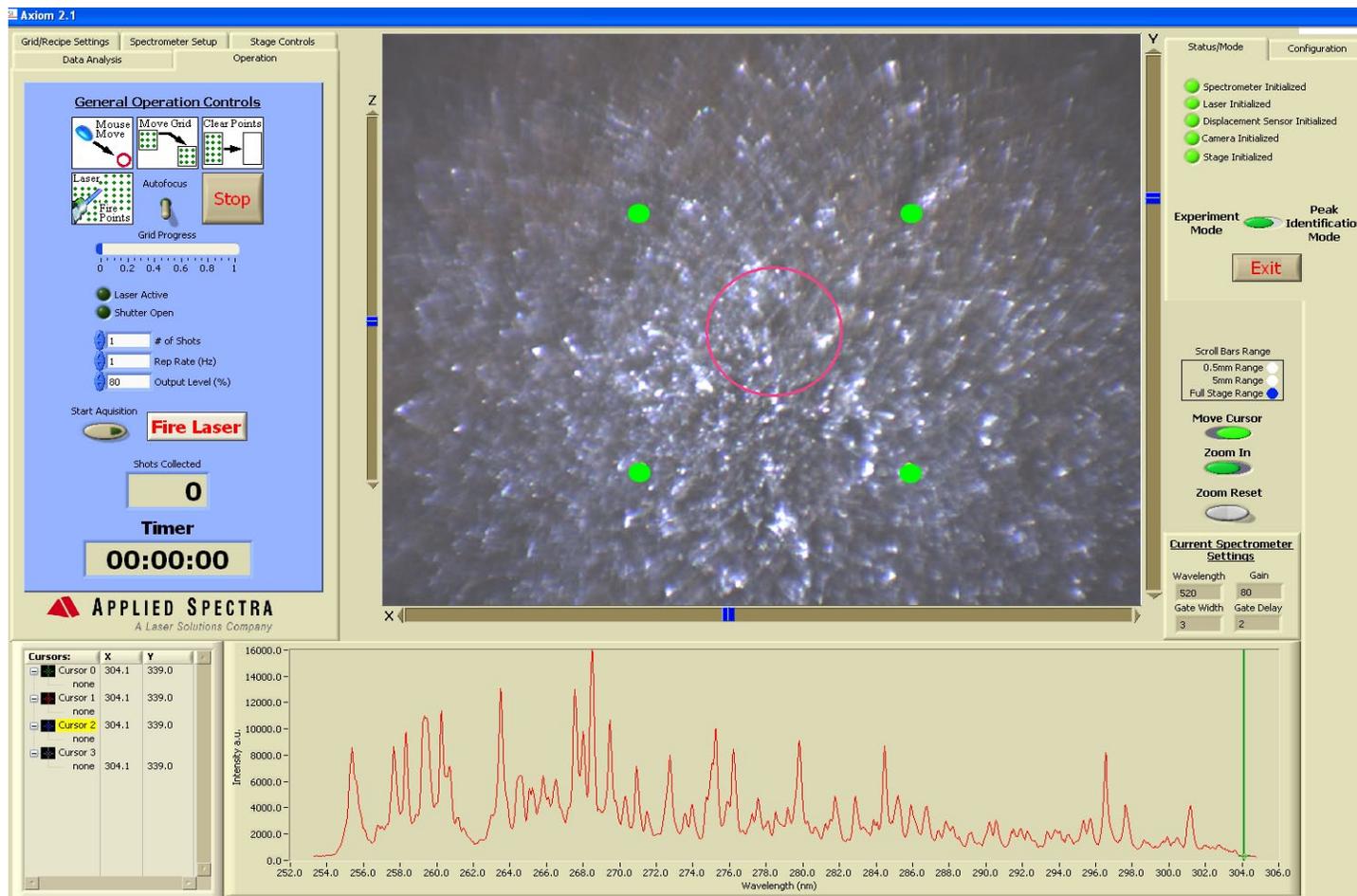


Figure 4. Photomicrograph of a tantalum ore, locations of laser sampling (green dots), and tantalum ore spectrum using Applied Spectra's Axiom software.



References

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