GemLIBS: A New Analytical Instrument To Analyse Beryllium In Orange Sapphires

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Abstract

With the identification of Be diffused corundum it became obvious that laboratory gemmology needed up-to-date analytical technology in order to analyse even light chemical constituents in gemstones down to low trace concentrations. Be detection was achieved with micro mass spectrometry, a technology which is costly and not always in the reach of gemmological laboratories. A new method, based on laser induced optical emission spectroscopy, offers a feasible and affordable way for trace elemental analysis of gemstones. Laser induced breakdown spectroscopy (LIBS) is now successfully used for the identification of Be diffused corundum, and Be concentrations down to a few ppm can be identified. A focused pulse of an Nd:YAG laser transforms some micrograms of the sample into plasma. The light emission is diffracted and recorded by a multi-channel analyser, and the line spectrum can be used for qualitative and quantitative analysis. Almost all chemical elements are detectable, and the method allows a precise chemical fingerprinting of gem materials. A quantitative analysis is possible when reference samples are used whose contents have been determined previously by LA ICPMS or SIMS. The new method is slightly destructive in that a tiny burning spot remains after a laser shot. Precise targeting is a precondition when damage should be avoided.

Introduction

Chemical information about gemstones may be important for a mineral identification because an analysis of the major and minor elements can provide the necessary data. We differentiate between qualitative analysis which indicates the present elements, and quantitative analysis which goes further and determines the concentrations of the detected elements. Trace element analysis identifies any chemical element that is at a lower concentration than 0.1 weight percent. It is challenging to identify chemical constituents at trace levels in gemmology. Such data may help to differentiate between natural and synthetic, to determine provenance or to detect treatments.

Regarding the identification of analysis of light elements such as Li, Be, B, an analytical problem exists for classical chemical analysis with EDXRF or microprobe because the energy emitted by these elements is too weak to be registered. Alternative methods such as LA ICPMS or SIMS are necessary for measuring light elements. These techniques are, however, expensive and the instruments are often not available. The method presented here is much more affordable and the technique identifies low concentrations, especially for the element beryllium. The new GemLIBS instrument displays virtually all chemical constituents simultaneously by their elemental emission lines. An earlier related analytical technique is optical emission spectroscopy. A theoretical background of the presented method may be seen with Barnes, (1981). An emission spectrum recorded on film from a geological sample is shown in Fig. 1.

GemLIBS

The new instrument is a combination of parts, which constitutes a most effective system (Fig. 2). The excitation energy is provided by an Nd:YAG laser which is vertically focused on the sample surface. The sample is kept on a sample stage which is an x-y table with vertical control. This allows perfect spot focusing. The sample stage is housed in a transparent chamber with transparent protective walls (Fig. 3). The focused pulse of the laser transforms some micrograms of the sample into plasma from which the excited sample ions emit their characteristic energies. Optical fibres conduct the emission signals to the spectrometers which sort the radiation according to the wavelength. A number of CCD spectrometers cover the spectral area from 200 to 980 nm. A computer with special software governs the settings and the management of the spectra. On a PC the final spectrum can be displayed and evaluated (Fig. 4). A gemmological application of optical emission spectral analysis was demonstrated by Kuhlmann (1983) for natural and synthetic rubies, sapphires, emeralds and alexandrites.

Analytical experience with GemLIBS

During the last year SSEF has evaluated a number of LIBS systems from different producers. Large differences exist not only in the price, but also in the practical use of the instruments. Laser wavelength and power determines the impact the produced spark has on the sample. Incorrect parameters may create major damage to the sample. A good combination of laser parameters results in an acceptable trace on the surface and a low detection limit at the same time (Fig. 5). There are also big differences in the sample holders provided by the LIBS systems available on the market. While some holders are made for larger industrial samples, others are sold without a sample holder. For gemmological applications it is important to have a sample holder and targeting device since the analysis spot has to be placed precisely on a selected area on the gemstone under test. Another important point is the quality of the spectrometer. High resolution ensures a separation of a great number of possible emission lines from different elements.

So far, Be has been identified in all samples that have previously been analysed quantitatively with LA ICPMS. We expect the detection limit for Be in corundum to be around 3 ppm. A presence of Be at this level or lower will have no influence on the colour of a stone.

References

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Figure 1 : An optical emission spectrum from a geological sample, produced by a spectrograph and recorded on film. Each line corresponds to a chemical element, and each element may have a great number of lines.

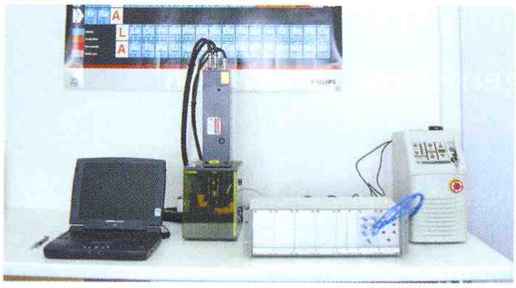

Figure 2 : An SSEF Gem LIBS system ready for application (Photo H.A. Hänni, SSEF)

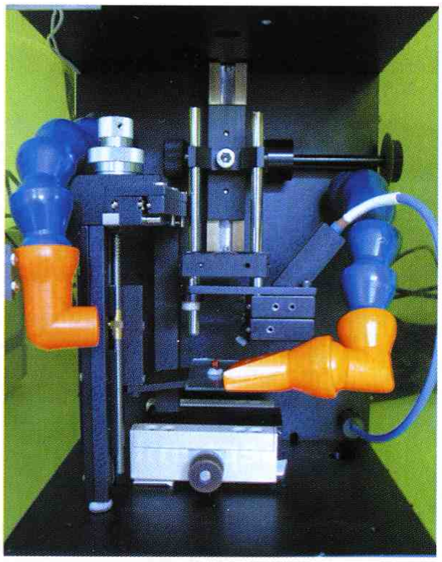

Figure 3 : A GemLIBS sample chamber with x-y-z stage (Photo H.A. Hänni, SSEF)

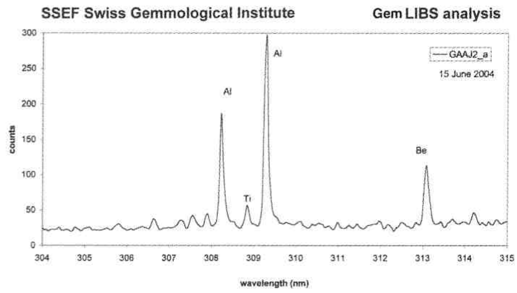

Figure 4 : An optical emission spectrum (304 - 315 nm) of a Be treated orange sapphire, presenting a Be signal which corresponds to a concentration of 5 ppm (Photo H.A. Hänni, SSEF)

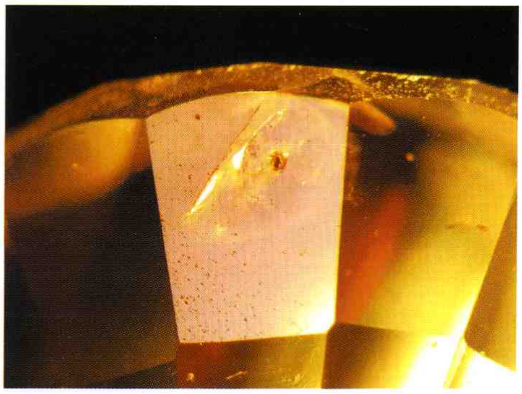

Figure 5 : Burning spot on an orange sapphire. By careful focusing and setting the parameters of the GemLIBS damage can be controlled and kept to a minimum. The pit is placed on an inclusion and has a diameter of 0.1 mm. (Photo H.A.Hänni, SSEF)