Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), A New Method for Gemstone Analysis

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最新之**Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)**是一項新而強的技術，利用鐳射消融細小部分的寶石表面，再對寶石進行分析，其中對寶石之化學性分析，可從微量元素濃度中進行檢測。本文利用於**SSEF Swiss Gemmological Institute**的樣本檢測例子，介紹該檢測技巧及與其他化學分析方法的比較，並描述該法之各可行性及局限性。

Abstract

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) has only recently come into use as a tool for gemstone analysis. LA-ICP-MS is a powerful method for applying spatially resolved chemical analysis down to very low trace element concentrations. This article describes the testing techniques and compares LA-ICP-MS with other methods that are used for the chemical analysis of gemstones. The possibilities and limitations of the method are described using examples of current research using LA-ICP-MS at the SSEF Swiss Gemmological Institute.

Introduction

Gemmological laboratories provide a service for the gem trade. They ensure the confidence of the consumer in the product by issuing gemstone reports, which disclose the nature of the item (Fig. 1) in question. As new gem materials, new treatments and new gem deposits emerge onto the market, gemstone reports will become increasingly important. International gemmological laboratories such as the SSEF Swiss Gemmological Institute not only test gemstones in large quantities, much more importantly, they are the driving force behind any research on gemstones for the benefit of the trade (SSEF was the first lab to offer the identification of HPHT treated diamonds and beryllium diffusion treated sapphires as a routine service to our clients). To meet the demand of the trade and consumers to be able to detect any new developments (e.g. new treatments) in gemmology, the labs are constantly evaluating new analytical tools for gemstone analysis. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is one of these new, fancy tools, which have a great potential for chemical analysis of gemstones. But it is not only the name of this instrument that sounds sophisticated, the method itself is too. In the paragraphs that follow, the authors would hope to give a brief insight into this new testing method and to discuss the possibilities and limitations of LA-ICP-MS in gemmology.

LA-ICP-MS, The method

LA-ICP-MS provides a very sensitive method for the spatially resolved chemical analysis of solid samples. A pulsed ultraviolet laser beam is focused on the surface of the sample to be investigated. The laser drills a tiny ablation pit onto the surface of the sample (Fig. 2). Generally, the size of the ablation pit (60-100 µm or 0.06 - 0.1 mm) is smaller than the diameter of a hair and thus nearly invisible to the naked eye. The ablated material is then transported by a carrier gas (usually argon or helium) towards an inductively coupled torch, where it forms an ionic plasma. The ions are then injected into a mass spectrometer, where they are separated according to their mass and charge. With LA-ICP-MS, it is possible to determine the chemical composition (and isotopes) of any solid by measuring, simultaneously, major element concentrations (up to 100 wt %) and ultra trace element concentrations (ppb, parts per billion).

Nowadays, LA-ICP-MS is used in a wide range of applications such as, forensic analysis for criminal investigations, in biology and environmental sciences, in material sciences and geosciences, including mineralogy and most recently gemmology (Guillong & Günther 2000, Hänni & Pettke 2002, Rankin et al. 2003, Abduriyim et al. 2006). As detailed above, LA-ICP-MS is a slightly destructive method compared to other techniques commonly used for gemstone testing (e.g. XRF). However, by positioning the ablation pit on the girdle of a gemstone, and given its very small dimensions, the "damage" to the stone can be minimised and the beauty of the stone remains intact.

The SSEF Swiss Gemmological Institute started its first LA-ICP-MS analyses on gemstones in 1999 with a series of corundum samples. Since then, we have analysed a large range of gemstones using LA-ICP-MS including untreated and treated sapphire and ruby, chrysoberyl, beryl, pezzottaite, tourmaline (Paraiba), musgravite, taaffeite, and pearls.

Currently, the SSEF Swiss Gemmological Institute is cooperating closely with the geochemical laboratory of the Mineralogical Institute, the University of Bern (Switzerland) in its use of LA-ICP-MS analyses (Fig. 3) using a setup developed specifically for analysis of mineral samples. The system operates with a pulsed ArF excimer laser with a homogenised beam profile (MicroLas, Germany), which produces highly geometric, pan-shaped ablation pits. This laser type uses a combination of an inert gas (argon) and a reactive gas (fluorine) for the emission of laser radiation at 193 nm (shortwave ultraviolet). The UV light from an excimer laser is well absorbed by gemstones, thus resulting in a very effective ablation without any tension features caused by localised heating. With a microscope, the laser spot can be adjusted precisely on the surface of the investigated sample. The instrument is equipped with a Perkin Elmer Elan DRC II quadrupole mass spectrometer. Our operation parameters, which have been chosen carefully for consistent data acquisition, follow the procedures described by Longerich et al., 1996. Each LA-ICP-MS analysis actually takes place over a certain period of time during which the laser drills minimally into the sample. Routinely, we start with a 60 seconds interval during which only the instrumental background signal is registered. Only after this does the pulsed laser start the ablation process, registering the elemental (mass/charge) information during the ablation interval (again about 60 seconds, see Fig. 4). The registered raw data (counts) is later corrected against the background signal and integrated over the chosen analytical time and processed to gain quantitative chemical data. Considerable time and experience is required for this analysis in order that all possible information may be gained from the LA-ICP-MS and misinterpretation of the results be avoided. It is obvious from this description of the process, that this highly sensitive technique requires scientifically trained staff both for operation of the instrument and data processing.

Other techniques for the chemical analysis of gemstones

For many years, the analysis of the chemical composition of gemstones has been effected by X-ray fluorescence (XRF) analysis. By this method, it is possible to gain semi-quantitative chemical analyses of gemstones for elements not lighter than sodium (Fig. 5). Very light elements such as lithium, boron, carbon, and beryllium cannot be detected by XRF. However, the transition metals such as titanium, iron, chromium, and the heavy elements such as lead, caesium and silver are readily analysed even at low concentrations (down to about 100-10 ppm). The analytical spot of the XRF is generally several millimetres in diameter so the results reflect an average chemical composition of a stone rather than a spot analysis. In many cases, this is more conclusive than knowing the chemical composition of just a tiny spot of the sample (as is generated with e.g. LA-ICP-MS). XRF needs no sample preparation and is a fast and reliable, non-destructive method. It has been integrated into the analytical routine of many gemmological laboratories. The chemical information gained by XRF may help to identify a gemstone, detect a treatment (e.g. silver nitrate staining of pearls) or indicate the geographic origin of a gemstone (e.g. a ruby from Burma versus a ruby from Thailand). X-ray fluorescence remains the key method for chemical analysis of gemstones in a gemmological laboratory despite the development of new and more sophisticated technology such as LA-ICP-MS.

The electron microprobe (EMP) and the scanning electron microscope coupled with an energy dispersive spectrometer (SEM-EDS) both use a focused electron beam to provide local excitation of the atoms of a test gemstone. They do provide a spot analysis and allow chemical zoning in a gemstone to be mapped, however both methods require a conductive coating (e.g. carbon) to prevent static electric charge in the sample. Consequently, these methods are only rarely applied in gemstone testing.

Recently, the SSEF Swiss Gemmological Institute introduced LIBS (Laser Induced Breakdown Spectroscopy) to gemmology (Krzemnicki et al. 2004, and 2006). This technology uses a pulsed ultraviolet laser to vaporise a minute part of the gemstone (Fig 6). Unlike in LA-ICP-MS, the ablated material is analysed on the spot by optical emission spectroscopy (EOS). The superheated, ablated material is transformed immediately into plasma; a form of matter in which the original chemical bonds of the substance are broken apart and the resulting atoms are converted into a mixture of neutral atoms, ions, and electrons. The atoms and ions within the expanding plasma lose some of their energy by emitting light, which produces a characteristic emission spectrum in the ultraviolet, visible, and near-infrared spectral range. The spectrum is then recorded with a spectrometer. Due to complex plasma dynamics, LIBS does not yield quantitative data. By using reference standards of known composition, it is sometimes possible to calibrate the instrument to generate semi-quantitative data, such as for beryllium in a corundum matrix. LIBS has proved to be a rather easy-to-use and versatile method especially for beryllium detection at low trace element concentrations (2 ppm Be) in diffusion treated corundum (Fig. 7, Krzemnicki et al. 2004).

Other methods used for chemical analysis of gemstones include PIXE (Proton Induced X-ray Emission Spectroscopy) and SIMS (Secondary Ion Mass Spectrometry). However, both of these highly sophisticated methods have as yet been used only rarely for gemstone analysis.

Possibilities and limitations of LA-ICP-MS

With LA-ICP-MS, chemical analysis of gemstones is taken to a new level. The possibility of analysing up to 40 elements simultaneously (using our setup) and over several orders of magnitudes (from main elements to ultra trace elements) is one of the main advantages of this method. Furthermore, it is possible to analyse most chemical elements down to very low concentrations; even such light elements as beryllium, lithium and boron. As the laser drill pits are very small, it is even possible to gain information about the chemical zoning of a gemstone. However, LA-ICP-MS does have some drawbacks. First of all, some clients may not find even the tiniest laser drilling pit on their sample acceptable (e.g. if it is a historical piece), so LA-ICP-MS cannot be used on their stone. Also, due to the limited size of the sample chamber, it is generally impossible to analyse any mounted stone using LA-ICP-MS. There are also quite a lot of analytical factors such as the gas flow, the geometry of the sample chamber, the ICP torch and instrumental drift, which have to be controlled to avoid lower resolutions, interference by recombined molecules and contamination effects. Each LA-ICP-MS analysis produces a large quantity of raw data, which has to be processed adequately to gain quantitative chemical analyses of a gemstone. The LA-ICP-MS is also quite an expensive instrument (minimum about US$ 300,000) with high operation and maintenance costs. It requires scientifically trained and specialised staff for its operation.

In 1999, SSEF started to use LA-ICP-MS on corundum since when we have analysed more than a hundred sapphires with this method. Calculating the quantity of beryllium particularly in diffusion treated sapphires, but also in untreated sapphires has been the focus of our recent research. In Figure 8, a series of blue beryllium diffusion treated sapphires are shown. These were analysed by SSEF to gain more data on the stones. Just recently we came across a very uncommon sample of basaltic sapphire from Northern Madagascar (Diego Suarez), which is intergrown with yellow chrysoberyl (Fig 9). LA-ICP-MS analysis on this sample was exemplary in providing new insights into the presence of beryllium in untreated sapphires and the correlation of Be with tantalium, niobium, tin, and thorium. Based on these analyses, the beryllium traces in untreated sapphires are probably due to nano inclusions in the milky zones of some sapphires (Fig 10). Another focus of our research has been the analysis of copper bearing elbaite tourmalines (Paraiba tourmalines) from Brazil, Nigeria, and Mozambique. LA-ICP-MS has revealed that it is possible to identify the different origins of at least some of these tourmalines, based on their trace element chemistry. Although there is a considerable overlapping in the chemical composition of the three geographic origins, as seen in figure 11, most samples will plot in three "distinct clouds" in such a diagram of the elements, each origin dependent. Taking into account not only one plot, but a whole series of plots with different elements increases the statistical probability for a specific origin determination on such a tourmaline.

Current research at SSEF includes the LA-ICP-MS analysis of pearls (see Fig 4).

Conclusion and Outlook

LA-ICP-MS will become an important technique in the field of gemmology because of its sensitivity and versatility for trace element analysis in gemstones. The SSEF Swiss Gemmological Institute regularly analyses gemstones with LA-ICP-MS. Currently, this is mostly for research purposes and only rarely as a lab service for a client's stone. However, in the future, it may well be applied to some extent as a routine analysis (rather qualitatively, without data processing) in gemmological laboratories.

It has to be stressed, that chemical data of a gemstone is, in many cases, not sufficient to provide a full assessment of a stone. The LA-ICP-MS is not a black box into which you simply place your stone and after a short period of analysis get a full identification and breakdown of what it is you own. Some gemstone dealers use the term LA-ICP-MS as a synonym for accuracy and as a solution for all problems in gemstone testing, ignoring the fact that the detection of heat treatment in a corundum is still readily done by using a microscope. The authors also consider that an origin determination of a gemstone relying only on chemical data is not feasible in most cases. Gemstone analyses in the future will rely on a logical combination of techniques, which include the correct interpretation of microscopic features with trace element analysis (e.g. by LA-ICP-MS) and spectroscopic (absorption and luminescence) data.

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Fig. 1 A heated ruby from Siam (Thailand) mounted in a ring with diamonds. © M.S. Krzemnicki, SSEF

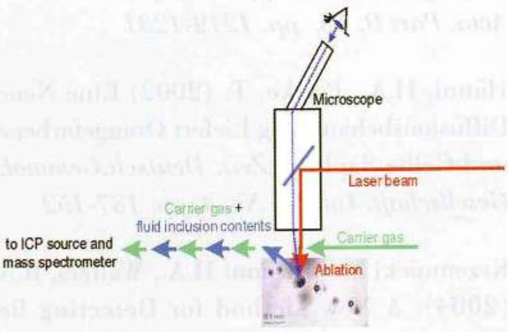

Fig. 2 Scheme showing the laser drilling with LA-ICP-MS. © T. Pettke, University Bern, Switzerland

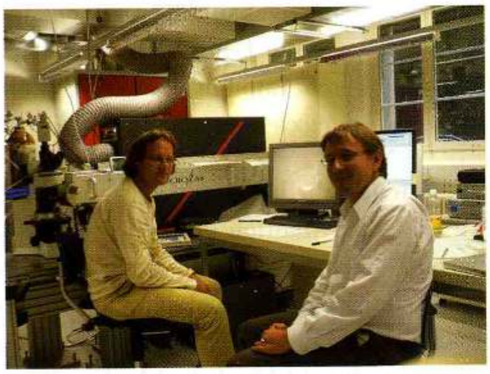

Fig. 3 Two of the authors, Prof. Dr. T. Pettke (University Bern, Switzerland) and Dr. M.S. Krzemnicki (SSEF) using the LA-ICP-MS instrument at the geochemical laboratory of the Mineralogical Institute of the University of Bern (Switzerland). © M.S. Krzemnicki, SSEF

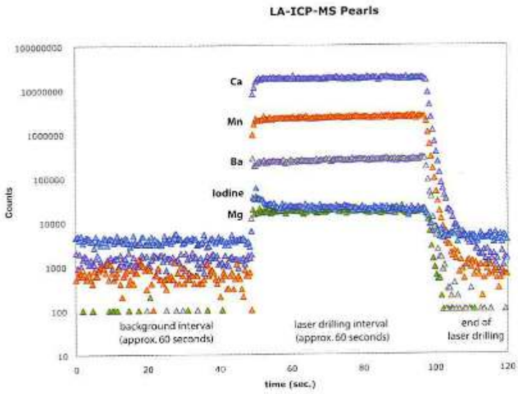

Fig. 4 LA-ICP-MS signal against laser drilling time (approx. 1 minute). The displayed element (mass/charge) signal represents one laser drilling on a freshwater pearl. Element concentrations values are calculated by integrating the signal over the drilling interval © M.S. Krzemnicki, SSEF 2007

Fig. 5 XRF instrument at the SSEF Swiss Gemmological Institute. © H.A. Hänni, SSEF

Fig. 6 LIBS system at the SSEF using a pulsed 266 nm Nd:YAG laser. © M.S. Krzemnicki, SSEF

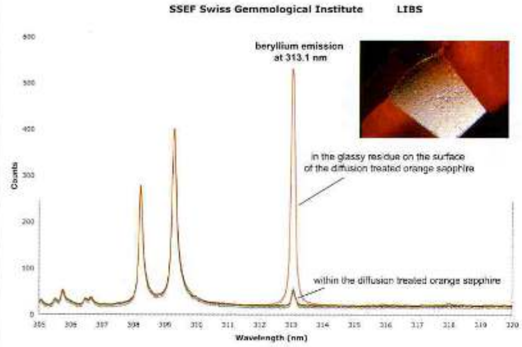

Fig. 7 LIBS spectrum showing beryllium emission peak at 313.1 nm in a diffusion treated sapphire (strong beryllium peak from glassy residues at the surface, small peaks from the diffusion treated sapphire). © M.S. Krzemnicki, SSEF

Fig. 8 Blue beryllium diffusion treated sapphires prepared in a sample holder for analyses with LA-ICP-MS. Under the microscope, most but not all of these stones show characteristic "diffusion clouds". © M.S. Krzemnicki, SSEF 2007

Fig. 9 Intergrowth of sapphire with yellow chrysoberyl. LA-ICP-MS data shed new light on the concentration and distribution of beryllium in untreated sapphire. © H.A. Hänni, SSEF

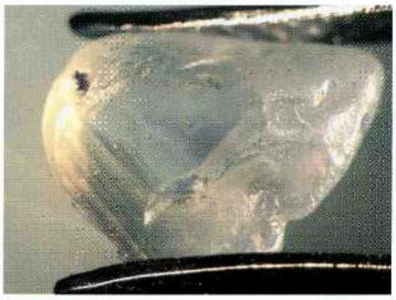

Fig. 10 LA-ICP-MS drill holes on an untreated sapphire with milky zones, showing trace amounts of beryllium (up to 3.2 ppm). © M.S. Krzemnicki, SSEF

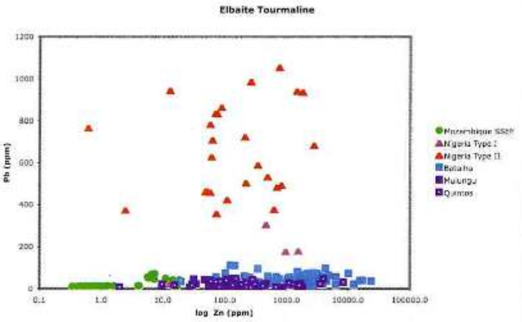

Fig. 11 Plot showing zinc (log Zn) versus lead (Pb) concentrations in Paraiba tourmalines from Brazil (in blue: Batalha, Mulungu, Quintos), Nigeria (red and purple: type I and II) and Mozambique (green). © M.S. Krzemnicki