

Simultaneous High Sensitivity Trace-Element and Isotopic Analysis of Gemstones Using Laser Ablation Inductively Coupled Plasma Time-of-Flight Mass Spectrometry

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GemTOF, installed at the Swiss Gemmological Institute SSEF, is a next-generation chemical analysis technique for gemmology: laser ablation inductively coupled plasma time-of-flight mass spectrometry (LA-ICP-TOF-MS). The system enables full elemental mass-spectrum acquisition at an ultra-high acquisition speed. Nearly all elements in the periodic table can be simultaneously acquired with low limits of detection. Major-to-trace (and even ultra-trace) element compositions can be accurately quantified, and slight concentration differences can be distinguished. The data can be processed with multivariate statistical analysis, thereby increasing the reliability of origin determination as well as the detection of potentially new diffusion treatments. Additionally, higher precision for isotopic analysis is expected than with sequential-acquisition LA-ICP-quadrupole-MS (LA-ICP-Q-MS), especially for short transient signals. Novel research directions in gemstone age dating, analysis of inclusions and chemical zoning will benefit from the advantages of this system.

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Introduction

In the past several decades, gem testing has evolved from a rather basic characterization of physical properties (e.g. RI, SG, absorption and fluorescence) into advanced materials science, using sophisticated instrumental technologies for detailed chemical and structural analyses. As gemmology is primarily an applied science, this

analytical evolution was driven by challenging issues confronting the gem trade rather than by fundamental research. From the use of X-ray radiography and X-ray diffraction to detect beaded cultured pearls in the early 20th century (Anderson, 1932), additional technological innovations in gemmology include the chemical characterization of synthetic coloured stones by



Figure 1: Six blue sapphires (various client stones weighing approximately 2–36 ct) are shown on an historical map of the famous gem locality of Mogok, Myanmar. Quantitative chemical data can be helpful for determining the geographic origin of sapphires. Map from Gordon (1888); photo by L. E. Cartier and Julien Xaysongkham, SSEF.

energy-dispersive X-ray fluorescence (EDXRF; Stern and Hänni, 1982; Muhlmeister et al., 1998) and the detection of fissure-filling treatments using Fourier-transform infrared (FTIR) spectroscopy and micro-Raman spectroscopy (Kiefert et al., 1999). Subsequently, the undisclosed appearance of Be-diffusion-treated sapphires, high-pressure, high-temperature (HPHT)-treated diamonds and beadless cultured pearls at the turn of the millennium had major impacts on the evolution of analytical methods in gem laboratories. New and highly sensitive methods have proven very helpful for gemstone and pearl testing, many of them applied for the first time or in a very early stage in the field of gemmology and in actual testing cases. These techniques include photoluminescence spectroscopy at liquid-nitrogen temperature (-196°C) of HPHT-treated diamonds (Chalain et al., 1999; Fisher and Spits, 2000), atomic force microscopy of pearl surfaces (Gutmannsbauer and Hänni, 1994), laser-induced breakdown spectroscopy (LIBS) of Be-diffused corundum (Krzemnicki et al., 2004), X-ray computed microtomography of pearls (Wehrmeister et al., 2008; Krzemnicki et al., 2010), age dating of pearls using accelerator mass spectrometry (Hainschwang et al., 2010; Krzemnicki and Hajdas, 2013), DNA-fingerprinting of pearl species (Meyer et al., 2013), X-ray phase contrast and X-ray scattering imaging of pearls (Krzemnicki et al., 2015; Revol et al., 2016) and neutron imaging of gemstones and pearls (Hanser, 2015; Mannes et al., 2016).

Throughout this period, the chemical analysis of gem materials has been very important not only for material identification (e.g. to identify species within the garnet-group solid solution), but also for identifying synthetics and treatments (e.g. Ti-diffusion of corundum). The main driving force for detailed trace-element analysis of gem materials, however, has been the demand from the trade for laboratories to deliver a scientifically based opinion of geographic origin, particularly for higher-end stones (see, e.g., Figure 1 and the cover of this issue). The demand has resulted from value factors attributed to certain origins (e.g. sapphires from Kashmir), but also from the growing need for traceability of gems due to political (trade bans) or ethical (fair trade) reasons (Dickinson DeLeon, 2008; Cartier, 2010).

Semi-quantitative to quantitative chemical analysis of trace elements in gem materials is typically performed using EDXRF spectroscopy. For the past 15 years, LA-ICP-MS has proven to be a very sensitive and versatile method for trace-element analysis of gem materials (Guillong and Günther, 2001), despite being only quasi-non-destructive. This technique provides access not only to a distinctly wider range of elements than traditional XRF methods, but also to much lower detection limits (especially for light elements such as Li, Be, B and Na) and to different isotopes of the same element. During the past several years, various publications have focused on the chemical characterization of gems from different origins (Giuliani et al., 2000; Rankin et al., 2003; Abduriyim



Figure 2: This LA-ICP-TOF-MS system, named GemTOF, was installed at SSEF in July 2016. The ICP-TOF-MS instrumentation is on the left and the LA unit is on the right. Photo by Vito Lanzafame, SSEF.

and Kitawaki, 2006; Sutherland et al., 2009; Halicki, 2013).

Recently, a novel analytical technique, LA-ICP-TOF-MS, was introduced into the market. In late 2015, the SSEF laboratory in Basel, Switzerland, initiated an evaluation project with three leading companies focusing on implementing such a system for gemstone analysis. The final instrumentation was installed at SSEF in July 2016 (Figure 2) and will be fully operational in winter 2016. This article discusses the capabilities of LA-ICP-TOF-MS compared to conventional ICP-Q-MS. Various potential applications of this new instrumentation are described, and a preliminary case study of sapphire origin determination is briefly presented.

Introduction to LA-ICP-TOF-MS

In general, LA-ICP-MS is a well-known and versatile analytical method for major- to trace-elemental analysis of solids. It consists of a material sampling part (LA) and a chemical analysis part (ICP-MS). The gemstone is placed within a sealed sample chamber in the LA instrument, with no need for sample preparation. Then a high-power pulsed UV laser is focused on the surface of the gem (normally on the girdle). The high laser energy accumulates on a tiny spot, and the ablated particles are instantaneously ejected into the sealed chamber. The resulting crater is too small (commonly less than 100 µm in diameter) to be visible to the naked eye and too shallow (e.g. 18 µm for a 30 s ablation on sapphire; Guillong and Günther, 2001) to produce any significant weight loss. The released particles are transported in a

flow of He gas into the plasma source. Inductively coupled plasma (ICP), created from Ar gas, is a robust ionization source. The temperature of this plasma is comparable with the surface temperature of the sun, causing almost all fine particles to become dissociated, atomized and finally ionized. The stream of ions is then extracted into the mass spectrometer (MS), which separates them based on their mass-to-charge ratio (m/Q). Most ions measured by ICP-MS have a charge of +1, and therefore m/Q is of equal value to mass m . A detector separately registers the intensities of ions with different m/Q values. External calibration is performed using standard reference materials, through which quantitative results for various elements can be calculated. The capability to precisely quantify multiple elements in a wide range of concentrations is the key benefit of LA-ICP-MS.

Commonly, LA instruments are equipped with either a 213 nm solid-state Nd:YAG laser or a 193 nm ArF excimer laser. An excimer laser is preferred for universal applications because finer particles are produced during ablation (Guillong et al., 2003).

There are several types of ICP-MS instruments based on different mass-separation schemes. The quadrupole type is one of the most popular, and is typically used for gemstone research. In such instrumentation, only one selected m/Q is collected by the detector at a time, while others are deflected and lost. To measure several isotopes, the mass spectrometer has to jump from one selected m/Q (isotope) to another.

ICP-TOF-MS is one of the latest and most advanced technologies in the ICP-MS family. The key difference between TOF and quadrupole setups is the mass-separation scheme. TOF uses the principle that the ‘flight’ duration for one ion passing through a fixed flight tube is related to its m/Q . Lighter ions take less time to travel the same distance compared to their heavier counterparts with the same charge, provided they have identical kinetic energy; hence mass separation is achieved. The flight time difference between the lightest and the heaviest ions travelling to the detector is so minimal that one may even consider them to arrive at almost the same time (i.e. simultaneously) at the detector. Benefiting from recent developments in ultra-fast electronics and optimized ion optics, ICP-TOF-MS acquires spectra from the lightest to the heaviest isotopes at a

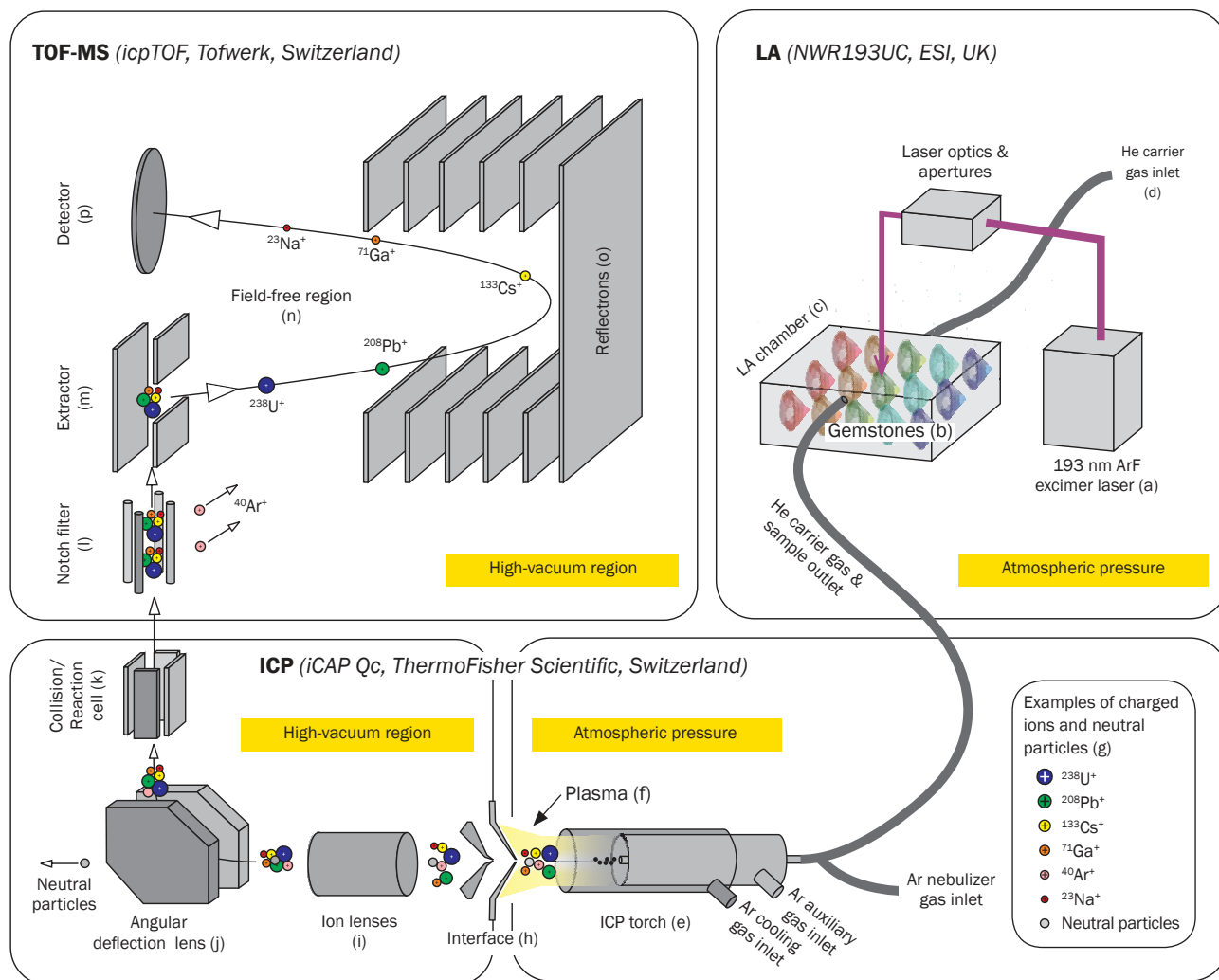


Figure 3: This schematic diagram shows a typical LA-ICP-TOF-MS setup (e.g. GemTOF at SSEF). The beam from a 193 nm ArF excimer laser (a) is focused on the gemstone or pearl (b) that is sealed in a sample chamber (c). The LA chamber is flushed by He gas (d), which transports the ablated particles to the ICP torch (e). The plasma (f) dissociates, atomizes and ionizes the particles into preferably singly-charged ions (g), which are sampled at an interface (h) from atmospheric pressure to a high-vacuum region. The stream of ions is extracted through a series of ion lenses (i), and neutral particles are separated from ions by an angular deflection lens (j). A collision/reaction cell (k) can be used to reduce interferences. At the entrance to the TOF-MS, a notch filter (l) first rejects selected dominant ions (e.g. Ar⁺) from the ion stream, and then the extractor (m) pushes the ions orthogonally at a high frequency into the field-free time-of-flight region (n). The ions are mirrored by reflectrons (o) and finally registered at a detector (p).

higher speed as well as achieving a better resolving power (or higher mass resolution) than conventional Q-MS (see www.tofwerk.com/icp). A schematic diagram showing the components and procedures of the LA-ICP-TOF-MS instrumentation at SSEF is shown in Figure 3.

Key Features of LA-ICP-TOF-MS

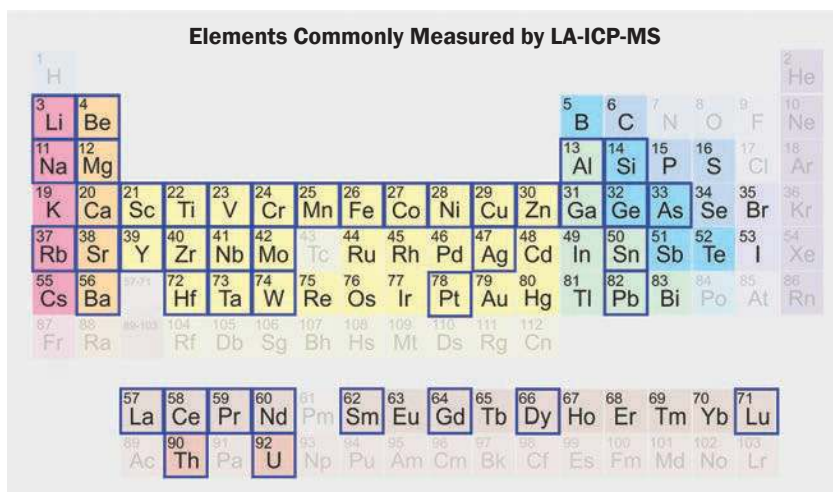
Full Mass-Spectrum Acquisition

Argon ICP has a high ionization potential, so almost all elements can be ionized efficiently. But to detect all these elements, an adequate mass

spectrometer should be employed. Conventional Q-MS has limitations. Because of sequential acquisition, it measures the intensity of one m/Q during a certain dwell time (integration time) before jumping to the next one. Although Q-MS is able to scan the full mass range by hopping through the entire spectrum, it is time consuming. Therefore, in practice, elements from Li to U (Figure 4) are commonly measured using only a selected number of isotopes within a limited measurement time. After measurement, if the selection of isotopes needs to be readjusted, the sample has to be re-ablated.

Figure 4: ICP-MS can measure most of the elements in the periodic table (shown in solid colours, with the atomic number indicated in the top-left corner for each element). The greyed-out elements are difficult to ionize, have strong interferences and high backgrounds, or are not commonly seen in geological samples.

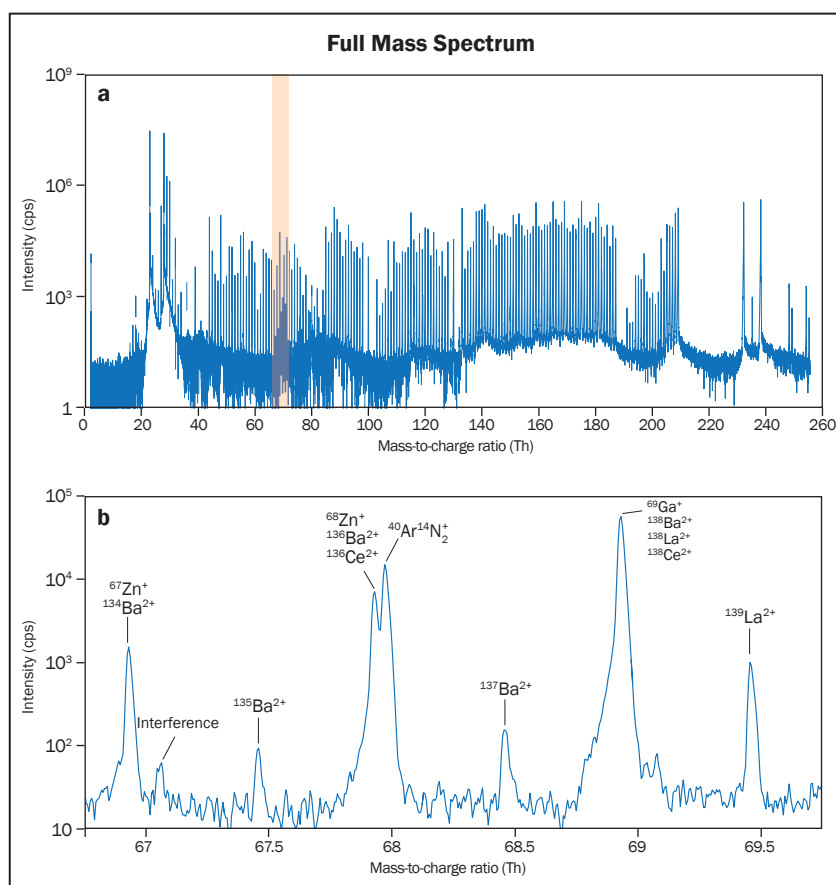
For LA-ICP-Q-MS measurements, only some of the elements (e.g. those with blue outlines) are selected using one of the isotopes from each element. By contrast, LA-ICP-TOF-MS measurements not only analyse all of the (solid coloured) elements simultaneously, but also almost all isotopes of those elements.



By comparison, LA-ICP-TOF-MS ‘snaps pictures’ of the full and continuous mass spectrum without the need to assign isotopes of interest (e.g. an ‘averaged picture’ from a 20 s ablation signal is shown in Figure 5a). Details of the ‘picture’ can be revisited at any time, and the isotopes of interest also can be changed, even after the measurement has been completed. Such a spectrum reveals almost the full elemental composition, reaping the benefits of the robust

plasma source. As a further consequence of this ‘picture snapping’, it is possible to considerably reduce the amount of ablated material required from the sample, thus creating a smaller and shallower crater on the analysed gemstone. In contrast to commonly used quadrupole mass spectrometers, there is no risk of needing to re-ablate the stone due to an incomplete or ‘badly’ chosen predefined list of isotopes, because the full mass spectrum is registered.

Figure 5: (a) An averaged full elemental mass spectrum is shown from a 20 second LA-ICP-TOF-MS measurement of NIST610, a silicate standard reference material. Mass-to-charge ratios (in units of Thomson) through the entire elemental range were acquired simultaneously. (b) Details of the orange region in (a) illustrate the mass resolving power of TOF-MS ($m/\Delta m \approx 3,000$), which is better than quadrupole MS (normally $m/\Delta m \approx 300$) in resolving some interferences.



Due to technical limitations, the ICP-TOF-MS model described in this article cannot measure light isotopes (e.g. ${}^7\text{Li}$, ${}^9\text{Be}$, ${}^{10}\text{B}$, ${}^{11}\text{B}$, etc.) while maintaining a high sensitivity for heavy isotopes (e.g. ${}^{232}\text{Th}$ and ${}^{238}\text{U}$, etc.). In these situations where access to a low m/Q range is required, another set of ion optic voltage settings can be applied. Since the parameters can be pre-set and changed quickly, it is hence feasible to complete the full elemental analysis from Li to U with two measurements (each focused on either low or high m/Q). Taking advantage of simultaneous acquisition, this limitation may not necessarily increase measurement time or have more impact on a sample compared to sequential LA-ICP-Q-MS.

High Mass-Resolving Power

As depicted in Figure 5b, the full mass spectrum ‘picture’ is taken at a high mass-resolving power (i.e. $m/\Delta m \approx 3,000$, where m is the nominal mass of the peak and Δm defines the mass difference between two resolved peaks), and this may help with potential interference problems. For example, when analysing ${}^{68}\text{Zn}^+$, the polyatomic ion ${}^{40}\text{Ar}{}^{14}\text{N}_2^+$ at nominal $m/Q = 68$ as well as doubly charged ions ${}^{135}\text{Ba}^{2+}$ and ${}^{137}\text{Ba}^{2+}$ present at $m/Q = 67.5$ and 68.5 cause interference when using Q-MS (resolving power $m/\Delta m \approx 300$). The higher resolving power of TOF-MS separates ${}^{40}\text{Ar}{}^{14}\text{N}_2^+$ from ${}^{68}\text{Zn}^+$. The doubly-charged species are, however, close in mass to ${}^{68}\text{Zn}^+$, and their separation requires higher resolving power or the application of various mathematical correction models.

High-Speed Mass Spectrum Acquisition

ICP-TOF-MS is capable of ‘snapping’ a full elemental mass spectrum at a maximum speed of 33,000 ‘pictures’ per second, but the data transfer speed from instrument to computer is limited. Therefore, the ‘pictures’ are commonly averaged and downloaded to a computer at a maximum speed of $\sim 1,000$ ‘averaged pictures’ per second. By contrast, Q-MS commonly measures only 2–5 sweeps per second (i.e. complete analysis over the list of predetermined isotopes, analogous to ‘averaged pictures’). The fast ‘frame rate picture snapping’ from TOF-MS can capture more details of a continuous change of sample concentration (e.g. local chemical zoning in gems), and any instantaneous short-signal events (e.g. tiny inclusion, nanoparticle, etc.) also can be resolved.

It is worth mentioning that not all ions from the continuous mass spectrum are eventually detected due to the discrete sampling nature of TOF. The detection efficiency of ICP-TOF-MS is less than 100%, but generally higher than Q-MS (Borovinskaya et al., 2013).

Limit of Detection (LOD)

The LOD is a figure of merit when describing the detection capability of an analytical instrument. During routine LA-ICP-MS analyses, LOD is often given in the unit of parts per million (ppm) or parts per billion (ppb), indicating the lowest concentration of analyte that is sufficient to provide a significant signal above background. There are two major factors for determining LOD: the sensitivity of the instrument and its background signal level. In general, higher sensitivity and lower background noise are necessary for a better LOD. As a result of recent instrumental developments, LA-ICP-TOF-MS has an improved multi-element sensitivity. While benefiting also from lower background noise, it provides better LOD than Q-MS (Borovinskaya et al., 2013).

As summarized in Figure 6, the LOD values of LA-ICP-TOF-MS, calculated using a widely accepted method (Pettke et al., 2012), range from single-digit ppb for heavy elements to low ppm for light elements. Although this is satisfactory for most gemmological studies, a larger laser spot size or a higher laser repetition rate can further boost the sensitivity, thereby further improving LOD values. Specifically for GemTOF at SSEF, it is possible to enlarge the spot size up to $150\ \mu\text{m}$ in diameter and increase the laser repetition rate up to 200 Hz (theoretically giving one to two orders of magnitude better LOD). This will, however, produce a larger and deeper crater on the girdle of the gem. In case both minimized ablation impact and improved LODs are required, then collision/reaction cell technology can be used (e.g. QCell by ThermoFisher Scientific; see ‘k’ in Figure 3). A QCell is an inert or reactive gas-flushed container that is installed on the ICP-TOF-MS. When ions fly through this device, they collide and/or react with gas molecules. In collision mode, polyatomic ions (which may cause interferences) run into inert gas molecules and lose energy more efficiently than the elemental ions of interest; then they can be removed from the beam by using energy filtering. Moreover, less-energetic ions also improve the

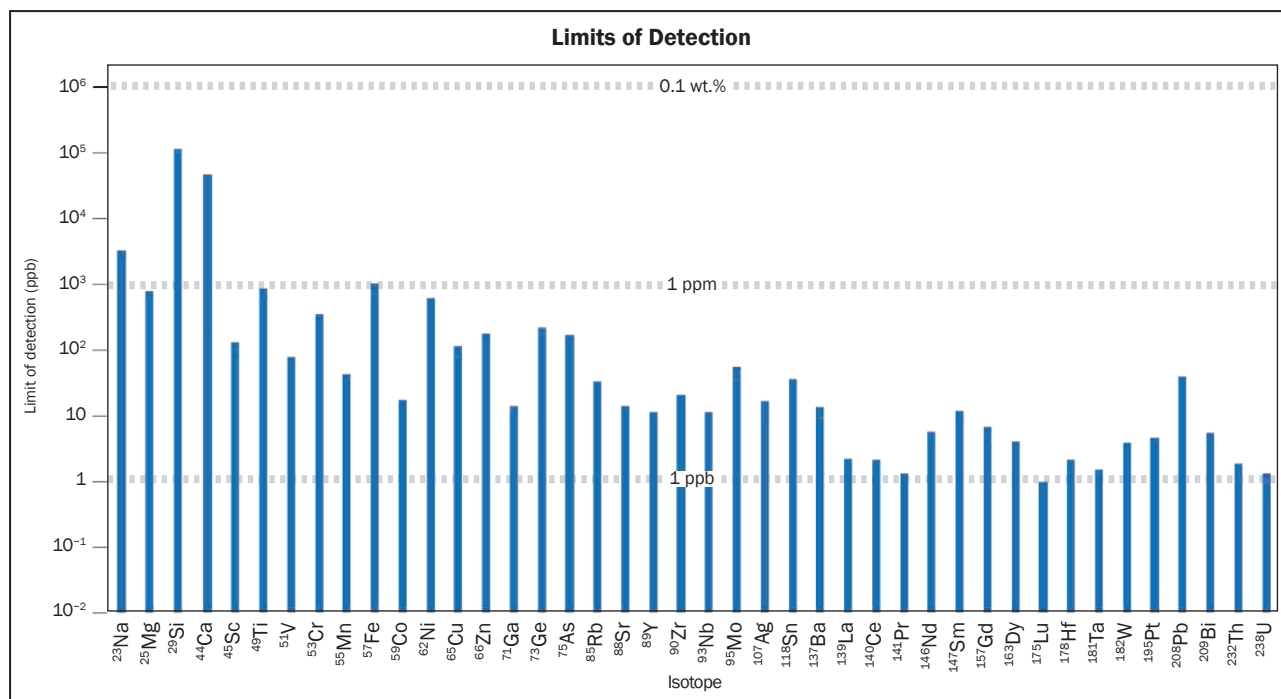


Figure 6: Limits of detection are shown for the LA-ICP-TOF-MS measurement of NIST610 reference material (most elements are ~450 ppm in concentration) in Figure 5 using a 40 μm diameter laser spot size and a 20 Hz laser repetition rate. Only a selected list of isotopes are displayed in the figure.

mass-resolving power of ICP-TOF-MS. Alternatively, interferences may selectively react with gas molecules (e.g. H₂) and disassociate to neutral particles or ions of a different m/Q.

Isotopic Analysis

Isotopes of an element differ in their masses but are naturally present at constant ratios of abundance. Considering fast-varying transient signals, especially from tiny inclusions or from a small area on a gemstone in chemical imaging analysis, it is highly likely that isotope ratios analysed at different sequential time intervals with Q-MS will have high uncertainty. The measurement of isotopic ratios using simultaneous acquisition of TOF-MS is thus expected to be better than that using Q-MS.

Isobaric interferences (isotopes appearing at the same nominal mass) create difficulties for determining the actual contribution of an isotope of interest. Inherently with TOF-MS, all other isotopes of the same elements of interest and interference are collected at the same time. Based on their constant natural abundance, mathematical corrections can be applied in order to improve accuracy of the trace-element quantification.

However, slight differences in isotopic ratios may result from the unique natural formation/production history of gemstones and pearls. This uniqueness could help to answer the question of carbon source for diamonds (e.g. Cartigny, 2005), to determine a gem's origin (e.g. Coenraads et al., 1990) or to separate synthetic from natural gemstones. Again, high-precision isotopic ratio determination is mandatory for such applications.

Methodology

The GemTOF system used at SSEF includes a high-performance 193 nm laser ablation unit (model NWR193UC from ESI, Huntingdon, UK) and an ICP-TOF-MS (model icpTOF from ToFwerk AG, Thun, Switzerland) upgraded from an optimized ICP-Q-MS unit (model iCAP Qc from ThermoFisher Scientific, Reinach/Basel, Switzerland). Due to installation limitations at the instrument demonstration site, it was not possible to test a combined setup of a NWR193UC laser ablation unit and ICP-TOF-MS. The results summarized in this article used a NWR213 LA system (from ESI) operating at 213 nm wavelength and an ICP-TOF-MS (same model as GemTOF). SSEF conducted a separate



Figure 7: These four sapphires (1.40–3.06 ct) were analysed by LA-ICP-TOF-MS. From left to right, their documented origins are Kashmir (LABc_126), Sri Lanka (LABc_899 and LABc_906) and Myanmar (LABc_926). All samples are from the H. A. Hänni collection at SSEF. Photo by Vito Lanzafame, SSEF.

evaluation of the NWR193UC system and found it to be more suitable for gemstone analysis than the NWR213 unit. Given the focus of the current research on the mass spectrometer, the comparison of different laser wavelengths is not included in this article, and related information can be found elsewhere (Guillong et al., 2003). Notably, these two laser-ablation instruments do not change the qualitative picture of the key points highlighted.

For the experiments described in this article, the 213 nm laser was focused into a 40- μm -diameter spot, ablating in single-hole-drilling mode at a repetition rate of 20 Hz. The laser fluence was set to 15 J/cm². Helium was used as the carrier gas, with a flow rate of 1.0 L/min. Before each measurement, five pre-ablation shots were done to clean any surface contamination from the sample. In all measurements, the first 30 s were recorded as background without ablation, and then the sample was ablated for 20 s.

The ICP-TOF-MS unit was operated at a power of 1,400 W. Argon was used as the nebulizer gas at a flow rate of 0.8 L/min. Without losing key information, the TOF detector collected 10,000 spectra and then reported one averaged spectrum (3.3 spectra per second, maximum 1,000 spectra per second). Though demonstrated in ‘slow’ acquisition mode, the importance of being able to acquire full spectra at the highest speed will be discussed below in the ‘Analysis of Inclusions’ and ‘Imaging of Chemical Zoning for Gem Research’ sections.

NIST610 standard reference material was used for external calibration and Al was used as an internal standard for sapphire quantification. Element concentrations and LOD values were calculated using the methods of Longerich et al. (1996) and Pettke et al. (2012), respectively.

The settings described above are comparable with routine LA-ICP-Q-MS measurements.

Applications of LA-ICP-TOF-MS

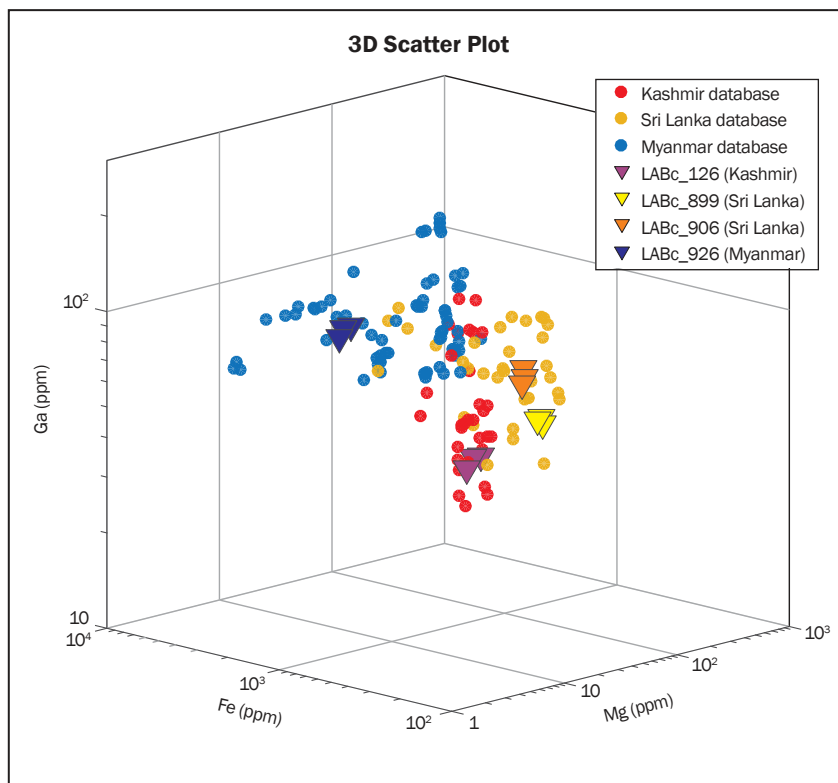
Gemstone Origin Determination: A Preliminary Case Study

The main application of LA-ICP-MS in gemmology is the chemical characterization of gems from various origins according to their major, trace and even ultra-trace elemental composition. The acquired chemical information can be displayed in a binary diagram, ternary plot or 3D plot in order to categorize the data into groups (i.e. geographic origins).

In a preliminary case study using LA-ICP-TOF-MS, we recorded full-mass spectra of four sapphires of documented provenance (Kashmir LABc_126, Sri Lanka LABc_899 and 906, and Myanmar LABc_926; Figure 7) from the H. A. Hänni collection at SSEF. The quantitative results for the trace elements Mg, Fe and Ga were plotted in a three-dimensional scatter plot (Figure 8) together with data from a previous study (Halicki, 2013) that used LA-ICP-Q-MS to analyse sapphires from Kashmir, Sri Lanka and Myanmar in the SSEF reference collection with various colour saturations. The scatter plot reveals that the reference sapphires (circles in Figure 8) plot in separate areas according to their three origins. The four sapphires analysed by TOF-MS (triangles in Figure 8) fit well into the expected plotting areas for the Kashmir, Sri Lanka and Myanmar origins. A drawback of this three-dimensional scatter plot is that only a limited number of trace elements (three in this 3D plot) can be displayed.

By using additional multivariate statistical approaches—such as principle component analysis and linear discrimination analysis—we can in principle take further advantage of the multi-element (multidimensional) information from LA-ICP-TOF-MS and reduce the amount of data to fewer dimensions while maintaining data-set variations in the plot.

Figure 8: This three-dimensional scatter plot shows quantitative LA-ICP-TOF-MS results for the sapphires in Figure 7, together with data for SSEF reference sapphires from Kashmir, Sri Lanka and Myanmar. Trace-element concentrations of Mg, Fe and Ga are displayed using logarithmic scales. Additional plots of this data, seen from different directions, are available in the online data depository on The Journal's website.



Detecting Diffusion Treatments or Coatings

LA-ICP-Q-MS measures a set of preselected elements/isotopes of interest, and ignores all others. This involves choosing the elements/isotopes prior to analysis, and thus one may—by lack of knowledge—omit a crucial element, especially in the case of a previously unknown diffusion treatment or coating. However, LA-ICP-TOF-MS collects all information in the full mass spectrum with no information loss. It is therefore perfectly adapted to detect new and undisclosed chemical treatments. And thus it may help avoid an unprepared situation for gem laboratories such as when Be diffusion-treated corundum entered the market (Emmett et al., 2003).

Analysis of Inclusions

Most gemstones contain various types of inclusions, which may provide key information about the formation conditions of the sample in a minute volume. If the laser is used to analyse a surface-reaching inclusion or to ablate through a shallow surface layer of the host gem to reach an inclusion, such information can be registered by the ICP-MS. The sampling of inclusions by the laser usually lasts for only a very short time (ranging from less than a second to a few seconds of ablation time), as inclusions are commonly very small. The short signal interval often is too

brief for complete sequential acquisition of all isotopes of interest with one sweep using Q-MS. However, since TOF-MS offers simultaneous acquisition at a very high speed, hundreds of full-mass spectra can be collected from a tiny inclusion with only <0.5 s of ablation time. Consequently, TOF-MS provides more accurate concentrations for specific elements and a more reproducible multi-element quantification of the chemical composition of a tiny inclusion in a complex matrix such as a gemstone.

Geological Age Dating

Some elements in nature have constant ratios for their isotopes (only stable isotopes), while others have one or more radiogenic isotopes, which results in a steady change of their isotopic ratios over time due to the radioactive decay from parent to daughter isotopes. The decay process is related to the half-life of the parent radiogenic isotope. By measuring the ratio of the daughter-to-parent isotopes, the elapsed time or age can be calculated using the known half-life constant for the radiogenic pair.

The widely used U-Pb dating system ('geological clock') uses daughter-parent radiogenic pairs of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$. Zircon is by far the most useful mineral for age dating, as it contains U but no Pb when it forms, with limited contami-

nation from host rocks after formation. Age dating of surface or near-surface zircon inclusions in gem corundum (so far mostly sapphires) has been studied (Coenraads et al., 1990; Sutherland et al., 2002, 2008; Graham et al., 2008). More recently, age dating of zircon inclusions analysed by LA-ICP-Q-MS was performed on faceted sapphires from highly relevant origins to the gem trade (e.g. Link, 2015). These studies show that age dating can be used as a valuable tool for origin determination in gemmological testing, reflecting different formation times for sapphires from particular geological contexts. However, to precisely determine geological age, ratios of parent and daughter isotopes need to be measured at a high reproducibility. At the same time, interfering isotopes from the geological background of a given sample must be monitored and used to correct the ratio of radiogenic isotopes. As discussed previously, higher-precision isotopic ratios are expected when possible interfering isotopes are measured simultaneously by LA-ICP-TOF-MS. Therefore, this technique can be quite suitable for age dating, especially when the zircon inclusions are minute.

Besides a sensitive mass spectrometer, precise age dating relies on proper standard reference materials as well as corrections for laser ablation artefacts (e.g. fractionation). This must be addressed regardless of whether TOF-MS or Q-MS is used.

Imaging of Chemical Zoning for Gem Research

The formation of gem materials is a complex process both spatially and temporally. Chemical (and colour) zoning is common, caused by intrinsic (e.g. oscillatory growth zoning) or extrinsic (e.g. change of rock chemistry due to fluid infiltration) factors. Detailed mapping of elemental distribution may provide valuable information about formation kinetics that cannot be readily perceived based on just a few analytical spots. Quantitative imaging of trace-element distribution thus can be a powerful tool, particularly at high spatial resolution, such as from using homogenized 10 μm (or even smaller) laser spots. The amount of ablated material from such a tiny laser spot is minute and provides a brief transient signal. By controlling the ablation process, it is possible to gain two-dimensional or even three-dimensional elemental distribution images (Burger et al., 2015). Hence LA-ICP-TOF-MS is preferred for chemical mapping at high spatial resolution.

Conclusion and Outlook

The Swiss Gemmological Institute SSEF recently installed an LA-ICP-TOF-MS system, named GemTOF. This system is equipped with a 193 nm LA unit and an ICP-TOF-MS instrument.

LA-ICP-TOF-MS is a relatively new and highly sensitive technique for the chemical analysis of gemstones and pearls. This article discusses the advantages, compared to LA-ICP-Q-MS, as well as limitations of this technique. The main advantage is the simultaneous acquisition of full elemental mass spectra with high mass-resolving power and ultra-high acquisition speed. ICP-TOF-MS does not jump from one mass to the next through a series of preselected isotopes, as Q-MS does. Therefore, it is not necessary to preselect isotopes of interest, which requires assumptions about the trace-element composition of a sample and careful consideration of possible peak interferences before the measurement is performed. Since a full mass spectrum is recorded, TOF-MS allows adjustments for the isotope of interest, even after ablation and analysis, in contrast to Q-MS where re-ablation would be needed.

LA-ICP-TOF-MS yields high-quality elemental analyses, produces multidimensional data and feeds the database for statistical analysis. The combination of improved sensitivity and low background noise guarantees a superior limit of detection for heavy elements in single-digit ppb and for light elements in low ppm concentrations. In addition to routine measurements, this new and sophisticated analytical method complements other gemmological testing instruments. This will enhance applications such as trace-element characterization of gemstones and pearls for origin determination and treatment detection, and will open new research opportunities for age dating, inclusion studies and high-spatial-resolution chemical mapping of gems.

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