

GemTOF: A new and highly versatile method to analyse trace elements and isotopes of gemstones and pearls

Michael. S. Krzemnicki¹, Hao A. O. Wang¹, Walter A. Balmer², Jean-Pierre Chalain¹, Pierre Lefèvre¹, Wei Zhou¹, and Laurent Cartier¹, Henry A. Hänni³

Swiss Gemmological Institute SSEF¹, Chulalongkorn University (Bangkok)², GemExpert (Switzerland)³
michael.krzemnicki@ssef.ch

Introduction

Since decades, the chemical characterisation of gem materials is considered very important as it provides data not only for material identification (e.g. to identify turquoise against its imitations or to identify species within the garnet-group solid solution), but also for detecting synthetics and treatments (e.g. diffusion treatment or inorganic dyes in fissures). 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 for coloured gemstones such as rubies, sapphires, and emeralds, to name a few. This 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.

Since more than a decade, laser ablation inductively coupled mass spectrometry (LAICPMS) has become more and more important for trace element analysis of gem materials with a special emphasis on the chemical characterization of gems from different origins (Guillong & Günther 2001; Rankin et al., 2003; Abduriyim & Kitawaki, 2006). So far, most research was carried out with a so-called quadrupole mass spectrometer system (LA-ICP-Q-MS), by which mass per mass of a pre-defined list of elements (isotopes) (up to about 50 elements per 'sweep') are analysed sequentially, before starting the next circle of mass-hopping with the next 'sweep' of the pre-defined elements.

In the following, the authors will provide insight into a novel and highly versatile and sensitive method to analyse chemical composition (and isotopes) using a Time-Of-Flight mass spectrometer (LA-ICP-TOF-MS) (Wang et al. 2016) and discuss advantages of the so-called GemTOF system (in operation at SSEF since July 2016) compared to quadrupole based systems.

Principle of LA-ICP-TOF-MS and the GemTOF setup at SSEF

Similar to any LA-ICP-MS system, a time-of-flight setup consist of three units: 1) a *laser* for sample ablation, 2) an *ICP unit* for ionisation of the ablated material into (mostly singly) charged ions, and 3) a *mass spectrometer*. Specifically for our GemTOF setup, we use a nanosecond-pulsed deep-ultraviolet laser at 193 nm (NWR193UC ArF excimer laser from ESI, UK), an iCAP Qc from ThermoFisher Scientific, and an icpTOF time-of-flight mass spectrometer from ToFwerk, Switzerland).

The principle of a 'time-of-flight' (TOF) system is based on the fact that the 'flight' duration for a specific ion passing through a fixed flight tube is related to its mass to charge ratio (m/Q). As a consequence, light ions will travel faster through the system than 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 traveling to the detector is so minimal that one may even consider them to arrive almost at 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 simultaneous full mass-spectra from the lightest (${}^7\text{Li}$) to the heaviest isotopes (${}^{238}\text{U}$) at a high speed and high

spectral resolving power. Routinely, it provides limits of detection of about 1 ppm for light elements to ultra-trace levels of less than 10 ppb for heavy elements.

What is the advantage of time-of-flight (TOF-MS) compared to quadrupole mass spectrometry (Q-MS)

The key difference between quadrupole (Q-MS) and time-of-flight (TOF-MS) is their mass-separation scheme. Whereas the Q-MS instrument sequentially measures one isotope/mass after another (i.e. peak hopping) over a period of time (commonly about 0.5-1 seconds for a set of about 50 elements), the TOF-MS simultaneously analyses the full mass spectrum at high speed (about 0.001 sec per full mass analysis). This basic difference has a number of important advantages, greatly boosting its analytical and application capabilities.

In TOF-MS, there is no need to choose/pre-define a list of elements (isotopes) to be analysed. All masses present in the gem material between ${}^7\text{Li}$ and ${}^{238}\text{U}$ are immediately and simultaneously analysed (Figure 1a). Our research has revealed that this offers great advantages, as we are able to detect a number of (exotic) trace elements in gem materials. They have never been documented before with Q-MS, as they were just not included in the list of elements to be analysed. Additionally, with TOF-MS the full spectral data is stored and can be re-evaluated at any time. This allows us to look for hitherto unconsidered mass peaks even at a later time. This is especially important when analysing samples which are only temporarily at the laboratory. With Q-MS, there is no such option, as only the pre-defined list of elements is analysed, and furthermore as the ablated and analysed volume from the sample is gone.

A drawback of sequential acquisition in Q-MS is, that any ions of other masses are lost for analysis, if they enter the quadrupole during the short period when one mass is being analysed, as the Q-MS system can handle only one mass per moment. So consider the Q-MS system is accumulating the iron signal from a sapphire, it will not measure beryllium, which was ablated at the same time from the sapphire and ejected at the same time into the Q-MS system. With the simultaneous full mass-spectral range of the TOF-MS, there are no such drawbacks, which has an impact on quality of the analysis and the limit of detection (LOD), but also allows us to considerably reduce the amount of ablated material required from the sample, thus creating less impact, i.e. a smaller pit on the analysed gemstone (usually between 10-100 μm pit diameter).

The high speed of TOF-MS analysis can capture short transient signal at much greater detail than with the peak-hopping mode of the quadrupole setup. It is thus ideal to analyse small-scale chemical zoning in gems, or tiny inclusions encountered during laser ablation of a gemstone.

And finally, the TOF-MS setup offers a much higher mass-resolving power than Q-MS. It thus reduces misinterpretation (and wrong quantifications) due to peak interferences (Figure 1b). As we have access to all isotopic masses of an element (full mass spectrum), it is even possible to mathematically correct certain isobaric mass interferences, relying on the constant ratio of natural abundance of the isotopes of the involved chemical elements.

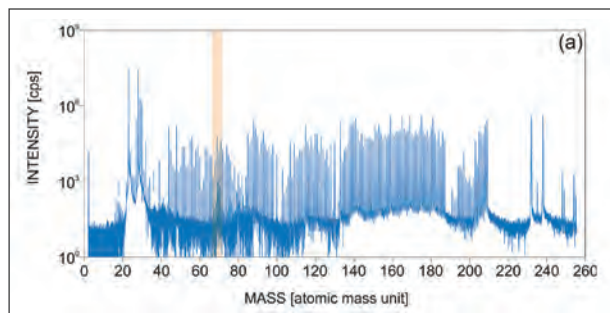


Figure 1a. Full mass spectrum (‘snap picture’) acquired by LA-ICP-TOF-MS (average of 20 s ablation)

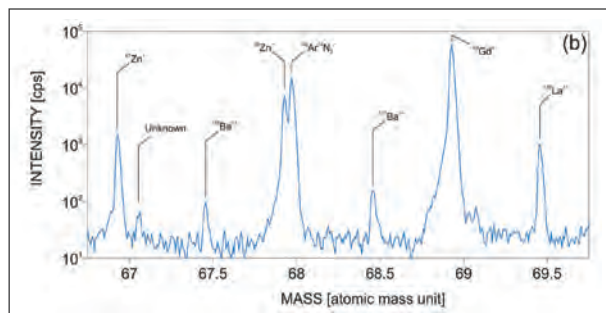


Figure 1b. Mass resolving power of this method exemplified by the ${}^{68}\text{Zn}^+ / {}^{40}\text{Ar}{}^{14}\text{N}_2^+$ interference.

Application of GemTOF analyses on gem materials for research and in daily routine analysis

In the past months, we have analysed with our GemTOF instrument a large number of gem materials from our reference collections (SSEF collection and Henry A. Hänni collection) but also numerous client stones.

At SSEF, a major focus of research is the chemical characterisation of gemstones and their inclusions from different geological settings and geographic origin, given our expertise in this field. The authors will present GemTOF data on a number of gemstones, including sapphires, rubies, spinels, and Paraiba tourmaline, to name a few. We also will present our preliminary age dating results on zircon inclusions in various gemstones based on the widely used U-Pb system (Coenraads et al., 1990; Sutherland et al. 2002; Link 2015).

And finally, we will also discuss analytical limitations due to the GemTOF instrument itself and due to overlapping chemical compositions of gemstones from different geographic origin but similar geological setting.

Conclusions

GemTOF is a new and highly versatile method in mass spectrometry to analyse the full mass-spectrum of gemstones at high speed and high sensitivity. It is based on the 'time-of-flight' principle (TOF-MS) and is characterised by a number of important advantages compared to the more commonly applied quadrupole setup (Q-MS). Although this new method provides a wide range of chemical data, we would like to remind the reader of the fact, that in our opinion any conclusion (e.g. about a probable origin of a gemstone) has to rely on an approach, which combines advanced analytical methods (such as GemTOF, Raman, etc.) with traditional gemmological methods (such as meticulous microscopic observation).

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