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Demonstration

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Demonstrating Rapid Qualitative Elemental Analyses of Participant-Supplied Objects at a Public Outreach Event

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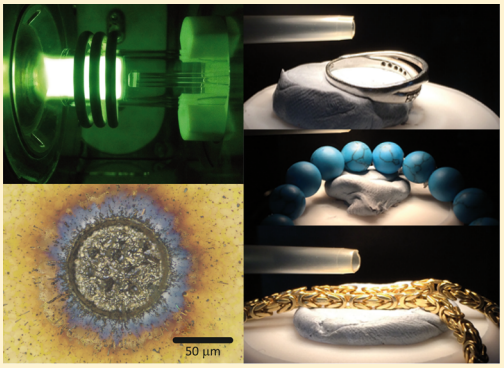
Supporting Information

ABSTRACT: A public demonstration of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) for fast and sensitive qualitative elemental analysis of solid everyday objects is described. This demonstration served as a showcase model for modern instrumentation (and for elemental analysis, in particular) to the public. Several steps were made to adapt conventional laboratory-based ICP-MS instrumentation to bring it to the outreach event and also to improve ease-of-use, which helped facilitate discussion with attendees. Rather than the conventional closed-cell design, this setup consisted of a laser ablation (LA) system that allowed for ablation in ambient conditions which enabled swift sample exchange during the demonstration. A gas exchange device was operated between the LA system and the ICP-MS instrument allowing for the replacement of ambient gases with argon. This particular setup was utilized during an open day event to demonstrate how LA-ICPMS can be used for qualitative analysis of major and trace elemental components in objects. In particular, visitors were encouraged to present objects for elemental analysis. Complete elemental analysis of supplied samples such as keys, coins, rings, and necklaces was demonstrated by recording full mass spectra. Variation of the elemental composition across different regions of objects was shown by scanning the laser beam and acquiring transient elemental signals.



KEYWORDS: *General Public, Demonstrations, Analytical Chemistry, Public Understanding/Outreach, Instrumental Methods, Lasers, Mass Spectrometry, Materials Science, Qualitative Analysis*

INTRODUCTION

Open day events at research institutions are useful opportunities for outreach activities.[1] Researchers have the chance to present their areas of investigation, ongoing research, and results to the general public, as well as to share their enthusiasm for science.[2] Often these events are accompanied by experimental demonstrations[3] or hands-on activities[4] for the audience that help to clarify basic concepts, methods, or implications of their research. Developing suitable and effective demonstrations or activities poses a substantial challenge. Outreach activities should be informative, vivid, appealing, and, if possible, oriented to the demonstrators' specific research area of interest. Showcased exhibitions should also hold up to reasonable scientific rigor, be appropriate for a diverse audience, and be kept short in duration. Interactive components for visitors, which can increase appeal and impact, must be safe for the participants and the presenters.

Scientifica is an open day event for the general public that is organized by the Universität Zürich and the Eidgenössische Technische Hochschule Zürich (ETH Zurich) and held for two consecutive afternoons of a weekend in Zurich, Switzerland. The *Scientifica* event in September 2015 was devoted to the theme "Light" and consisted of 40 short lectures and 60 demonstrations at exhibitions stands. There were 25,000 visitors welcomed during the two day event.[5]

The demonstration presented here was designed to display modern instrumentation for elemental analysis and explore the capabilities of laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS). The goal of this demonstration was to increase visitor interest and create a lasting impression by using LA-ICPMS to perform elemental analysis on visitor-provided objects. Although no sample preparation is needed, the exchange of samples can take up to several minutes. The organizers recommended a general contact time with visitors of not more than 10 min so that visitors had opportunity to visit multiple demonstration stands during the exhibition.

Introduced by Gray in 1985,[6] LA-ICPMS can provide information on almost the complete elemental composition of

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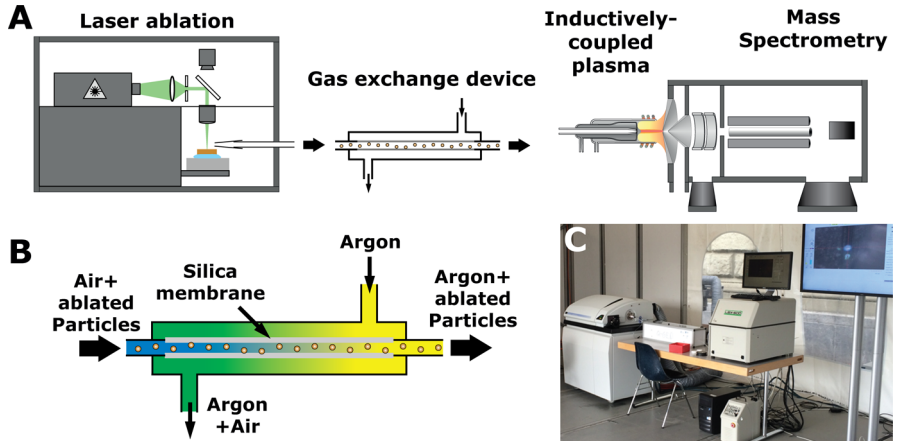

Figure 1. (A) Schematic setup overview, (B) principle of operation of the gas exchange device, (C) setup for the event within a tent.

solid samples. Only elements with a high background in the ambient air or the plasma, e.g. H, C, N, O, or Ar, or those whose positive ion formation is too low in an ICP source (such as F) cannot be determined. This method does not require extensive sample preparation[7] which makes it well-suited for a short experimental demonstration. In LA-ICPMS, a laser beam is focused onto the sample surface, and a small amount of material is ablated and transported via a carrier gas stream into the ICP-MS. Within the argon inductively coupled plasma of several thousand Kelvin, the ablated material is vaporized, dissociated to atoms, and finally ionized. The atomic ions are transferred into the mass spectrometer, where they are separated and detected according to their mass-to-charge ratios (m/z).[7] LA-ICPMS is routinely used for sensitive, spatially resolved elemental analyses in material sciences,[8] geology,[9] archeology,[10] biochemistry,[11] and forensics.[12] It can be considered as quasi-nondestructive because only small amounts of a sample (<10 μg) are ablated in order to obtain qualitative and quantitative information. Moreover, in contrast to methods requiring sample digests, LA-ICPMS largely avoids the generation of chemical waste.

Closed ablation cells are normally used to house the sample, and ablation takes place in an inert gas (He or Ar) atmosphere. Closed cells must therefore be purged with inert gas between samples, which can take several minutes. Ablation is usually carried out in inert gas because it provides effective transport to the plasma and is not detrimental to the argon ICP. To increase the sample throughput for the *Scientifica* event by reducing the time required for sample exchange, a gas exchange device (GED) (originally described for airborne particle analyses via ICP-MS)[13] was utilized. When employed for LA-ICPMS experiments, the GED enabled ablation in ambient air and provided similar performance to conventional closed ablation cells.[14]

MATERIALS AND METHODS

The LA-ICPMS setup (Figure 1) consisted of a commercial LA system (LSX-500, Cetac Technologies, Omaha, Nebraska) and quadrupole ICP-MS instrument (ELAN 6100DRCII, PerkinElmer, Norwalk, CT). The ablated material was aspirated and transported to the ICP-MS via the GED (Q-GED, J-Science Lab Co., Ltd., Kyoto, Japan). In the GED, air was exchanged with argon, but the ablated particles pass quantitatively to the ICP. The entire arrangement was set up in a large tent with a stable floor. Two 55-in. flat screen monitors were set up. One was to display the view of the ablation process, and the other was focused on the ICP-MS results. This allowed better observation visibility for the visitors. In addition to the objects supplied by visitors, a selection of coins, grains of highly alloyed steel, and keys were available to provide example specimens for demonstrations when needed. More details on the setup and parameters can be found in the Supporting Information.

HAZARDS

The instruments used, apart from the GED, are commercially available laboratory equipment and as used for this demonstration posed no hazards to the audience. Instrument interlocks have to be kept in place to avoid any hazards (suffocation, electric shock, or laser radiation related injuries). The need for compressed argon for the operation of the ICP and GED may be seen as the dominant potential hazard. Gas cylinders with compressed gas have to be stored, handled, transported, and secured with care and appropriate equipment. In case of failure or leaking of the supply tubing, argon could potentially accumulate within the exhibition area and cause suffocation. Here, only the low-pressure side (<6 bar) of the gas supply was placed inside the tent, and proper connections of the gas tubings were ensured to prevent this hazard. Extraction of exhaust gases from the ICP has to be provided to ensure stable conditions for the instrument, and the exhaust gas must be vented to outside the tent. Formation of hazardous compounds within the ICP from the surrounding air may include NOx, but the ventilation rate (>4 m^3/min) prevents a notable concentration. Should the exhaust fail, the instrument would shut down and stop any argon from reaching the exhibition area. The laser source is powerful enough to cause damage to skin, eye, and clothes. The intense ICP-emission in the UV spectral region can cause major damage to the eye if exposed; therefore, the instrument has to be kept optically sealed during ablation to prevent injury.

DEMONSTRATION

To begin, visitors were first introduced to the field of elemental analysis and technologies used. For engagement purposes, visitors were asked to provide metal alloy samples. Otherwise, one of the stock samples was used. Samples were placed on the sample holder and fixed using a removable adhesive (Blue-tack, Bostik S.A., La Plaine St Denis, France) if needed.

Laser spot sizes from 25 to 100 μm in diameter and laser repetition rates of 10 or 20 Hz were used for ablation. These

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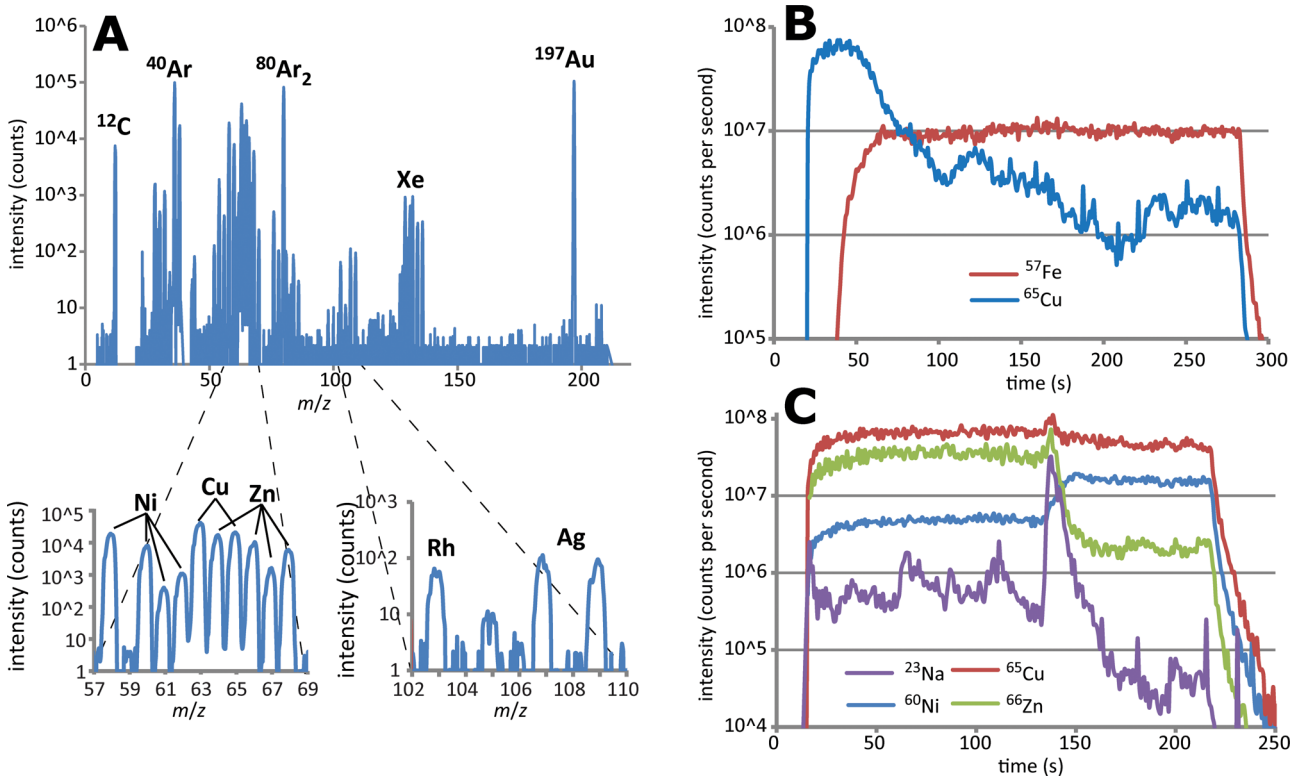

Figure 2. (A) Mass spectra of a gold wedding ring and magnified mass ranges of low-trace (Ni, Cu, Zn) and ultratrace (Rh, Ag) elements. (B) Transient elemental signal profile of the element in the plating (Cu) and core (Fe) of a EURO 0.01 coin during a single hole drilling experiment. (C) Transient elemental signal profile of selected ions from a line scan of a EURO 2 coin from the center to the rim.

conditions provided sufficient signal intensities for the detection of major, minor, and some trace elements during hole drilling in experiments with no lateral movement of the laser spot over the surface. For observation of lateral variations of the elemental composition, line scans were performed by software-controlled movement of the sample holder relative to the laser beam.

Two different approaches for data acquisition were shown. In an overview analysis mode, a mass spectrum of the material was acquired to qualitatively assess the relative abundances of individual elements. Major, trace, and ultratrace elements can be detected within a single analysis which allows for rapid identification of the approximate composition. The concept of isotopes and their relative natural abundances can be easily demonstrated in this mode. The second mode focused on the variability of elements across heterogeneous samples. Here the transient signal evolution of selected isotopes was monitored during the ablation process.

To ease the procedures during the demonstration, the two ICP-MS data acquisition methods were prepared in advance: one for observing transient signal intensities for selected isotopes (see this list in the Supporting Information) and one for a mass spectrum acquisition time within ~90 s. After cleaning the sample surface from ablated and resettled material, the craters of the objects were hardly (if at all) visible to the naked eye and indistinguishable from scratches resulting from daily handling.

During *Scientifica*, a wide variety of samples were provided by the visitors and analyzed: mostly keys, rings, and coins. The modifications to the LA-ICPMS setup for this demonstration proved to be effective for a swift sample exchange within seconds, while maintaining the overall capabilities of the instrumentation for determination of elemental composition. Without an ablation cell, it was also possible to analyze large, irregular objects such as necklaces and bracelets.

RESULTS

Acquisition and display of mass spectra were used to illustrate the multielement capability of LA-ICPMS and helped the scientist presenters explain how materials of unknown composition can be characterized. Display of this data also helped explain new (or forgotten) concepts of elements, isotopes, and isotope patterns. For example, the mass spectrum from the ablation of a white gold ring was recorded (Figure 2A). Apart from the background signals (carbon, from residual carbon within the ion source, argon and traces of xenon from the plasma gas), gold can be detected as the major component. Furthermore, the trace elements of nickel, copper, and zinc, components of the white gold alloy, along with even lower intensities from silver and rhodium (probably from a thin surface layer) were detected.

The setup was also used to effectively show recognition of changes in elemental compositions from different regions on coins. During a hole drilling experiment on a EURO 0.01 coin, signal intensities of copper and iron were monitored (Figure 2B). These two elements originate from the copper covered steel structure of the coin. It can be easily observed how the laser ablation first removes the copper plating (20−45 s) before reaching the iron core, when the copper signal decreases while the iron signal stabilizes.

In another example, the laser ablation position was scanned (line scan) from the outer ring (cupronickel) to the core (nickel-brass) of a EURO 2 coin; the intensity changes in zinc and nickel correspond to the different alloys present (Figure

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2C). The measurement here was started at the inner nickel-brass section (20 s) of the coin and progressed toward the rim at a scan rate of 10 μm/s. The composition of the nickel-brass is reflected by the high intensities of copper and zinc with trace amounts of nickel. Within about 1.5 mm the transition region of the coin was reached, where the groove toward the cupronickel can be identified by the peak in the sodium signal at around 145 s. This is a result of accumulation of salts from fingerprints and other environmental sources. The cupronickel then only mainly contains copper and nickel, which is immediately obvious from the transient signal after 150 s.

CONCLUSION

On the basis of the theme "Light" of this open-day event, it was demonstrated how the destructive effect of light beams can be utilized for chemical analyses. A laser was used to ablate small amounts of material, which were then analyzed by ICP-MS for elemental characterization of a variety of everyday objects without showing any visible damage to the item. By employing a GED, there was no need for an ablation cell, and the sample exchange was sped up drastically.

LA-ICPMS was well-suited for representing state-of-the-art analytical instrumentation by exemplifying several general technological capabilities of elemental analysis, e.g., fast analysis and mapping capabilities. The experiments demonstrated were an effective way to illustrate and elucidate the technology and capabilities of LA-ICPMS. Depending on the questions asked by the visitors, we discussed the technique components, ongoing research projects, method development, and applications in geology, archeology, and elemental imaging. The typical contact time did not exceed 10 min, even though some visitors were absorbed in longer discussions with the presenters.

It should be noted that the demonstration was not intended for quantitative analysis. In fact, for time constraints and clarity, experiments did not include calibration measurements required to perform accurate quantifications.[15] This was brought to the visitors' attention, while referring to the general and quantitative capabilities of the methods within a laboratory environment. Therefore, only qualitative analysis was feasible, which was sufficient for the intended purpose.

While here the instruments were presented outside a laboratorýs environment due to the concept of *Scientifica*, this demonstration could also be kept in a lab. In principle, this demonstration could be adapted to an ICP optical emission spectrometry (OES) system with reduced sensitivity and (relative) simplicity of spectra.

Overall, about 200 visitors attended this demonstration during *Scientifica*, and visitor interest was high. Coins and any form of jewelry were found to be very exciting samples for this demonstration. Using visitors' objects as samples without noticeable damage was a reasonable strategy to increase interest and impact of the demonstration. Usually three or four staff members were present for the event at a given time to perform the demonstration and interact with the visitors, rotating between the different aspects of introduction, demonstration, and subsequent discussions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00391.

Information on experimental details (PDF, DOCX)

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Notes

The authors declare no competing financial interest.

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