# Laser-Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS): setting operating conditions and instrumental performance

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Abstract. — The concentration of thirty nine geochemically relevant trace elements, from $^7$Li to $^{238}$U, was determined in standard silicate glasses (NIST610, NIST612, BCR-2) using the Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) instrumentation at the Department of Earth Sciences of the University of Cagliari (Italy). The device is a Quadrupole ICP-MS (Perkin Elmer Elan DRC-e) coupled with a 213 nm Nd:YAG laser probe (New Wave Research). This configuration allows rapid, high quality, *in-situ* trace elements analysis in glasses and minerals. The calibration strategy, achieved using synthetic multi-element glasses (NIST612), with $^{44}$Ca as internal standard, gives an analytical accuracy within 5% error level, providing a precision between 1% and 9%, at 40 μm of crater size for all elements. At a laser spot size of 40 μm, the lower limit of detection (LLD) ranges between 0.001 and 1 ppm for all the elements; it increases by about one order of magnitude, without any significant fractionation among the different elements, for a laser spot size of 15 μm. Quality control of LA-ICP-MS analyses is routinely performed analysing a natural standard glass, the BCR-2, certified by the USGS, considered as unknown sample. Results indicate that the instrumentation capabilities are suitable for the geochemical characterisation of various materials of mineralogical, petrological, geological and environmental interest.

Riassunto. — Le concentrazioni di 39 elementi in tracce, dal $^7$Li al $^{238}$U, sono state determinate in vetri silicatici standard (NIST610, NIST612, BCR-2) usando la strumentazione *Laser Ablation Inductively Coupled Plasma Mass Spectrometry* (LA-ICP-MS) installata presso il Dipartimento di Scienze della Terra dell'Università di Cagliari (Sardegna, Italia). Lo strumento è composto da un ICP-MS del tipo Perkin Elmer Elan DRC-e accoppiato con un sistema laser Nd:YAG, sviluppato dalla New Wave Research, che lavora ad una lunghezza d'onda di 213 nm. Questo insieme consente di determinare rapidamente, e con un'alta qualità, le concentrazioni di tutti gli elementi in tracca in vetri e minerali. La calibrazione è stata ottenuta usando vetri sintetici certificati dall'USGS come materiale di riferimento (NIST612) e il Ca come standard interno, analizzato mediante SEM-EDS. La strategia di calibrazione utilizzata ha permesso di ottenere risultati con una accuratezza intorno al 5%, e con una precisione analitica che varia tra 1% e 9 %, utilizzando un diametro del fascio laser di 40 μm. Per dimensioni del diametro del fascio laser di 40 μm, il minimo limite di rilevabilità varia per tutti gli elementi tra 0,001 and 1 ppm, ed aumenta di circa un ordine di grandezza, senza che si verifichino processi di frazionamento tra i diversi elementi, per diametri di 15 μm. In ogni sessione analitica si effettuano

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almeno due analisi del BCR-2, un vetro silicatico naturale certificato USGS, considerato in questo caso come campione sconosciuto, per monitorare la qualità delle analisi realizzate durante tutta la sessione. I risultati del presente lavoro indicano che la strumentazione LA-ICP-MS installata a Cagliari ha buone potenzialità per quanto riguarda lo studio geochimico di materiali di diversa composizione, e quindi può essere utilizzata a supporto di varie tipologie di ricerche a sfondo sia minero-petrografico che geologico o geologico-ambientali.

## Introduction

In the last 20 years, Earth scientists have developed the Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICP-MS) as an analytical method aimed at investigating the *in-situ* chemical and isotopic variations in geologic materials (Gray, 1985; Arrowsmith, 1987; Hager, 1989; Denoyer, 1991; Denoyer *et al.*, 1991). In 1985, a Laser-Ablation device was associated for the first time with an ICP-MS for the determination of trace element abundances in solids; since then, LA-ICP-MS has been increasing its importance as an analytical tool for the Earth Sciences. The potential of laser radiation to cause ablation and vaporization, when it interacts with solid materials, is exploited as a method of sample introduction for mass spectrometry. The different species produced, including particulates, ground-state atoms, excited atoms, and ions, are utilised for elemental analysis via mass spectrometry (MS). The interaction of laser light with the sample depends upon both the characteristics of the laser beam and the physical properties of the solid. The early commercial laser ablation systems, specifically developed for ICP-MS, utilised a Nd:YAG design, operating at the primary wavelength of 1064 nm in the infrared region. However, in the analyses of pale coloured minerals (i.e. those with low transition metal abundances) or those minerals with a low absorption in the infrared, much of the laser light passes through the sample and is absorbed by the volatile bearing mounting material. This can lead to catastrophic failure of the mineral as chunks are blown from the surface by the expanding bubbles of gas underneath (Jackson *et al.*, 1992). To overcome some of these problems a number of researchers have modified the Nd:YAG laser by multiplying the laser frequency, reducing its wavelength to 532, 266 and 213 nm (Longerich and Diegor, 2001). Nowadays, laser ablation is considered a very reliable sampling technique for ICP-MS, capable of producing very high quality data directly on solid samples and powders. It supports many geological studies such as those involving mineral exploration, isotopic age determinations, geochemical investigations of melting and mass transport in natural and experimental systems, and environmental studies. Many other uses in the field of Earth Sciences are continuously proposed thanks to the increasing presence of LA-ICP-MS devices in Earth Sciences labs.

With respect to other analytical techniques for trace elements, some of the many advantages offered by this technique include: minimal sample preparation, low blanks, high spatial resolution at the sub-mm scale (to 20 μm), elemental mapping across the surface of a sample, high sensitivity and detection limits below the ppm level, rapid analysis times (typically 2 min per point analysis) and minimum matrix effects for a wide variety of target materials, allowing straightforward calibration of the analyses.

In this paper we describe the technical characteristics of the LA-ICP-MS microprobe installed at the Earth Science Department of the University of Cagliari (Italy), and we present some preliminary results obtained on the reference standard materials in order to evaluate sensitivity, detection limits, precision and accuracy of the instrument. The calibration of the instrument and the operating conditions have been derived using standard silicate glasses (NIST610, NIST612, BCR-2). The concentration of 39 trace elements, from $^7$Li to $^{238}$U were determined in NIST612 and BCR-2 sample, considered as unknown, in order to test the instrument on materials with different composition and concentration of trace elements.

## Applications of the LA-ICP-MS

Laser ablation has been applied to the determinations of the trace element concentrations

in a wide range of materials in many different studies, including volcanology, petrology, mineralogy, ore deposits, materials and forensic studies, cultural heritage and environmental sciences. In the environmental science, LA-ICP-MS analyses is applied to a variety of biological structures, such as tree rings, mollusc shells, otoliths, fin ray and fish scales (Veinott, 2006). This is a consequence of two important factors: analyses of solids by laser requires little or no sample preparation; the determination of trace elements content or isotopic composition in almost all types of materials is achieved at high spatial resolution.

## INSTRUMENTATION AND PECULIARITY OF LA-ICP-MS

Experiments were carried out using a Perkin Elmer Elan DRC-e Quadrupole-ICP-MS, coupled with a New Wave Research UP 213 series laser ablation device.

The ICP-MS standard instrument configuration consists of a plasma (luminous volume of partially ionised gas) as ion source (ICP), generated from radio frequency magnetic fields induced by a copper coil, wounded around the top of a partly demountable glass torch, with removable alumina injector. Nickel cones (sampler and skimmer), in vacuum environment represent the interface for extracting ions from the plasma and transferring them in the region of the mass spectrometer (MS). The Perkin Elmer Elan DRC-e offers the possibility of working with the Autolens system, i.e. using a single ion lens, that does not interact with other lenses, providing optimal transmission of ions at every mass in a multielemental analysis. The voltage of the ELAN single ion lens can be readily controlled in step with the quadrupole to provide the optimum ion transmission for each mass. A quadrupole, which progressively select ions with specific mass to charge ratio, is used as mass analyser. Ions are detected by a Channel Electron Multiplier (CEM), at the end of which there is a computer for data collection and processing.

The laser ablation system consists of an Yttrium Aluminium Garnet ($Y_3Al_5O_{15}$) rod doped with approximately 3 wt% $Nd_2O_3$, working at wavelength of 213 nm. This wavelength gives significantly improved ablation characteristics, in particular reducing the damage of the area around the crater (Fig. 1) and yielding constant ablation (measure of mass of ablated material for a mineral relative to ablated mass from external standard), for widely different matrices, suggesting that the absorption of 213 nm radiation is substantially matrix-independent (Jackson, 2001).

The Q-switched laser is characterised by a single large output pulse which releases the energy stored in the cavity as shorter pulse with both higher average and peak power. The output of a Q-switched Nd:YAG laser is a train (typically 1-20 Hz) of high intensity pulses. The laser beam is highly directional, has a very high wavelength purity ($\lambda = 1064$ nm) and strong spatial and temporal coherence, that results in an enhanced ablation efficiency and a representative composition of the material ablated. The pulse repetition rate controls the sample removal rate for a given pulse energy and, consequently, controls peak/background ratios and ablation time available for a given pit size. The maximum repetition rate of the laser can generally be used (typically 10-20 Hz), with lower pulse frequencies being used to ablate very thin samples, to reduce count rates
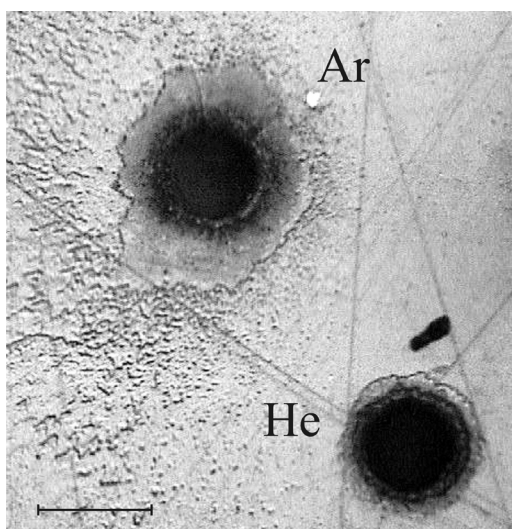


Fig. 1 – Comparing spot area using Argon and Helium as carrier gas. In the first case the area around the crater is damaged and interested by the deposition of a little quantity of ablated material, while using He these problems are avoided. The black bar correspond to 50 μm.

for very concentrated samples or to produce a prolonged stable signal when required e.g. as when optimising the operating conditions of the ICP-MS (Günther *et al.*, 1999).

Helium gas was used as carrier inside the ablation cell and mixed with Argon, the makeup gas, before entering the ICP. In this way, reduction of the observed fractionation magnitude, both at the ablation site and during the transport toward the ICP-MS, is obtained, enhancing the transport efficiency of ablated material (Günther and Heinrich, 1999; Jackson, 2001; Horn and Günther, 2003) (Fig. 1).

Ablation spot diameter ranges between 10 and 100 µm. The selection of the spot size used during ablation is a critical parameter that must be adjusted according to application. **Analyses of** small samples, for example, require a reduction in the size of ablation crater, without changing sensitivity. In last-generation instruments, laser energy can be decreased and laser spot size reduced (consequently reducing the volume of ablated material) without changing the Lower Limit of Detection (LLD), thus offering the potential to generate data from smaller samples. The LA system incorporates a variable or interchangeable aperture in the laser beam path that is imaged onto the sample surface by the laser objective lens. The instrument is characterised also by a "Resonator-flat" beam that yields uniform craters with energy densities that remain constant when changing spot sizes. Moreover, the LA system is equipped with an additional control of the spot size that is achieved using a beam expander.

The pulse energy ranges from 0.2 and 2 mJ and is controlled by an optical attenuator, with the advantage of a linear polarisation of the laser beam. The optical attenuator is placed directly after the IR head, before any harmonic generation crystals, because IR polarizer does not require expensive UV transmitting materials. This also protects subsequent components from high energy photon (UV).

The laser ablation device is equipped with a video camera for the high resolution sample viewing, ensuring an accurate focussing of the sample and an easier identification of the areas to be analysed. The system is remotely controlled using the Elan Version 3.0 Perkin Elmer Sciex package.

## Operating conditions

To achieve maximum intensity across the full range of masses, the ICP-MS parameters, such as the RF power, ion lens voltage and mass calibration, were optimised by continuously aspirating a solution of 10µg/l of Mg, In, Ce, Ba and U in 0.5% $HNO_3$. The nebulised gas flow was adjusted so that CeO/Ce results < 3% and doubly charged ion production as measured by $Ba^{2+}/Ba^+$ was < 3%.

To determine trace element concentrations in the ablated material, data were collected by peak hopping. **Mass resolution, measured as peak width,** was set to 0.7 Atomic Mass Unit (amu) and the peak intensity for each element was obtained by measuring the signal intensity at the centre point in the mass range defined for each element. The dwell times (measurement times on each isotope during one quadrupole sweep) was 10 ms **per amu,** one sweep of the mass range per replicate and 300 replicates per analysis, including 80 replicates on the dry gas to establish the background prior to ablation. Total analysis time was 2 min per spot, including 1 min of backgrounds acquisition (Fig. 2).

Signal detection was performed in dual modes, ion counting and analog, operating simultaneously. Data were collected in time-resolved graphics mode to monitor eventual compositional heterogeneities that might be present in the sample at the scale of the laser sampling and to monitor the inter-element fractionation. The instrument was operated with the Autolens on; data were transmitted to a PC and processed by the GLITTER program (Van Achterbergh *et al.*, 2001). Operating conditions used in this work are summarised in Table 1, both for the ICP-MS and LA devices.

## Reference materials

In this work, the NIST 612 and NIST 610 reference materials, partially certified by the National Institute of Standards and Technology (NIST), were adopted. They represent the reference material used in almost all the LA-ICP-MS labs for the calibration of microbeam analyses.

Both are silicate glasses spiked with a range of trace elements at a nominal concentration of 50 and 500 µg g$^{-1}$ respectively. Pearce *et al.* (1997)
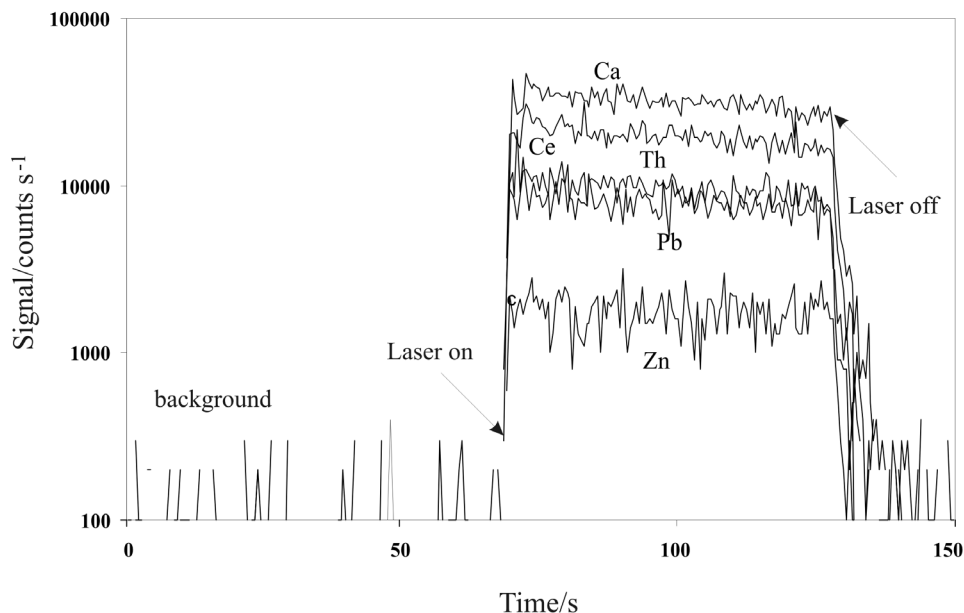
**Fig.2** – Real time window of the signal intensity during time for each element. During the first 60 s of the analysis, the laser is switch off for the background acquisition.

compiled a database of published data for these reference materials more than new analyses from four additional laboratories, to provide an interim working value for a wide range of elements (Table 2). For the quality control of the analyses, BCR-2 glass, a standard prepared from Columbia River basalt by the US Geological Survey, were routinely utilised in accordance with the other LA-ICP-MS labs (Table 2) (Gao *et al.*, 2002).

Disks of glasses NIST610, NIST612 and BCR-2 were included together in a single mount of epoxy resin, and polished with SiC disks until 1 μm with alumina.

### CALIBRATION STRATEGY

Quantitative calibration of the LA-ICP-MS system requires the knowledge of the concentration of one element (internal standard), analysed independently in the sample and in the reference material (Perkins *et al.*, 1997; Pearce at al., 1999). We use $^{44}Ca$, measured during each analysis as an internal standard, and the data are normalised to the CaO content of the sample as determined

TABLE 1
*Instrumental parameters for the ICP-MS and Laser Ablation instruments*

ELAN DRC-e ICP-MS

| | |
|---|---|
| Nebuliser gas flow | 0.86 l min$^{-1}$ |
| Auxiliary gas flow | 1.40 l min$^{-1}$ |
| Plasma gas flow | 15.5 l min$^{-1}$ |
| Lens voltage | 7.50 V |
| ICP RF power | 1200 W |
| Autolens | on |

New Wave Research UP series 213 Laser Ablation

| | |
|---|---|
| He carrier gas Flow | 0.67 l min$^{-1}$ |
| Energy (10 Hz) | 0.028-0.28 mJ |
| Spot size | 20-50 μm |
| Laser frequency | 10 Hz |

TABLE 2

*Trace elements concentrations (µg g-1) of the reference materials. NIST610 and NIST612 are from* Pearce *at al. (1997), and BCR-2 from* Gao *et al. (2002)*

| Elements | NIST610 | NIST612 | BCR-2 | Elements | NIST610 | NIST612 | BCR-2 |
|---|---|---|---|---|---|---|---|
| Li7 | 484.6 | 41.54 | 9 | Ce140 | 447.8 | 38.35 | 53 |
| B11 | 356.4 | 34.73 | | Pr141 | 429.8 | 37.16 | 6.8 |
| Mg25 | 465.3 | 77.44 | 21650 | Nd146 | 430.8 | 35.24 | 28 |
| Sc45 | 441.1 | 41.05 | 33 | Sm149 | 450.5 | 36.72 | 6.7 |
| Ti49 | 434 | 48.11 | 13500 | Eu151 | 461.1 | 34.44 | 2 |
| V51 | 441.7 | 39.22 | 416 | Gd157 | 419.9 | 36.95 | 6.8 |
| Cr53 | 405.2 | 39.88 | 18 | Tb159 | 442.8 | 35.92 | 1.07 |
| Co59 | 405 | 35.26 | 37 | Dy163 | 426.5 | 35.97 | |
| Ni60 | 443.9 | 38.44 | | Ho165 | 449.4 | 37.87 | 1.33 |
| Zn66 | 456.3 | 37.92 | 19 | Er167 | 426 | 37.43 | |
| Rb85 | 431.1 | 31.63 | 48 | Tm169 | 420.1 | 37.55 | 0.54 |
| Sr88 | 497.4 | 76.15 | 346 | Yb173 | 461.5 | 39.95 | 3.5 |
| Y89 | 449.9 | 38.25 | 37 | Lu175 | 434.7 | 37.71 | 0.51 |
| Zr90 | 439.9 | 35.99 | 188 | Hf177 | 417.7 | 34.77 | 4.8 |
| Nb93 | 419.4 | 38.06 | | Ta181 | 376.6 | 39.77 | |
| Cs133 | 360.9 | 41.64 | 1.1 | Pb208 | 413.3 | 38.96 | 11 |
| Ba137 | 424.1 | 37.74 | 683 | Th232 | 450.6 | 37.23 | 6.2 |
| La139 | 457.4 | 35.77 | 25 | U238 | 457.1 | 37.15 | 1.69 |

independently by energy-dispersive X-ray (SEM-EDS) technique, at the Department of Earth Sciences of Pisa. The use of an internal standard accounts for any variation in the amount of ablated material reaching the plasma (the 'ablation yield') between samples and reference material, and any differences in concentration of the internal standard are corrected for the calculation of concentrations (Norman *et al.*, 1998). This also means that the reference material used to produce the calibration should not have necessarily the same matrix composition as the unknown, although a strong difference in matrix composition may introduce further complications (Pearce *et al.*, 2007). Each analytical run consists of a maximum of 20 analyses in which the first and the last are standard materials. The number of 20 analyses represent the best compromise to ensure instrumental stability in the related time interval. The concentration of any unknown element is calculated from the following equation, assuming that the calibration curve is linear and passes through the origin (Perkins and Pearce, 1995):

$$Cel_{unk} = \frac{Cel_{rm}}{(ACPSel/ACPSis)_{rm}} \left( \frac{ACPSel}{ACPSis} \right)_{unk} \left( \frac{Cis_{unk}}{Cis_{rm}} \right)$$

where C = concentration; el = analyte element; is = element selected as internal standard; rm = reference material; unk = in the unknown sample; ACPS = area counts per second (i.e. the integrated counts normalised to the dwell time per peak).

Calibration requires that the background corrected signal from all or part of an ablation spectrum of an unknown sample be referenced to

that of a standard material. Background signals are usually obtained measuring the 'gas blank', i.e. with the laser off for 60 seconds before ablation (Fig. 2) (Günther *et al.*, 1999). The same operating conditions have been maintained for the analysis of both the standard and the unknown to overcome effects of differential element fractionation (Perkins and Pearce, 1995).

## Results

### Sensitivity

The instrument sensitivity (cps/ppm) is an important parameter that needs to be evaluated to ensure optimum instrument conditions, especially at the minimum level of response or limit of detection. Sensitivity depends on several factors including ablation efficiency, ionisation efficiency and ion transmission, essentially controlled by spot size and laser power as well as isotopic abundance (Halter *et al.*, 2002). The response curve was obtained on the NIST 612 glass reference material using a 40 μm spot size, a laser output energy of 0.28 mJ and a repetition rate of 10 Hz. The sensitivity varies as a function of the atomic number of the elements, and five different regions of mass-range were recognized in the intervals between 7-29 amu, 43-66 amu, 85-93 amu, 133-177 amu and 181-238 amu. For the first group (from Li to Si) sensitivity is the lowest, ranging between 22 and 165 cps/ppm, with the lower value for the Li. From the mass range between 43-66 sensitivity abruptly increases in correspondence of the Ca, with value of 300 cps/ppm, regularly decreasing until 166 cps/ppm for the Zn. The same trend is shown from Rb to Nb, with a sensitivity 3 times higher. For amu higher than 95, sensitivity is quite constant for all the elements, ranging between 500-700 cps/ppm, and finally, at very high mass-range, a decrease is observed.

### Detection limits

Lower limits of detection (LLD) was calculated (at 3 standard deviations of the background) from the equation:

$$LLD = 3 \times (2B)^{\frac{1}{2}} \times \frac{C}{I}$$

where LLD= lower limit of detection; B= background intensity for analyte; C= concentration of analyte; I= peak intensity for analyte in reference material. LLD is inversely proportional to (ablation volume)$^{1/3}$; it represents a measure of the signal to background ratio of an analytic instrument, and gives a measure of the instrument response (i.e. counts per second per unit of concentration) (Perkins and Pearce, 1995; Pearce *et al.*, 2007). Average minimum detection limits of the selected elements (Fig. 3), were determined on the reference glass BCR-2 using the acquisition parameters shown in Table 1. In order to constrain the variation of detection limits as a function of spot size, analyses were carried out at 40 and 15 μm spot size with a laser power of 0.15 and 0.028 mJ, respectively. At a spot size of 40 μm, the detection limit ranges between 0.001 and 1 ppm for all the elements, except for Si, Ca, Ti and Cr, due to the stringent relationship between sensitivity and background. The elements with high-abundance isotopes show LLD between 0.001 and 0.01 ppm, while for the other elements LLDs are higher than 0.01 ppm. By decreasing the spot size from 40 to 15 μm, detection limit increases about one order of magnitude without any significant fractionation among the different elements.

### Precision (RSD%) and Accuracy (RD%)

The precision (RSD% = [standard deviation / average value] * 100) of the LA-ICP-MS instrument depends on the acquisition parameters, on the total number of ions of analyte detected, on the analyte concentration and on laser spot size. The accuracy (RD% = [(average value - reference value) / reference value] * 100) corresponds to the relative deviation of the average concentration obtained in this study from the reference values (Pearce *et al.*, 1997). In this work, precision and accuracy of the analyses are calculated from 13 replicates on reference material NIST612 obtained in one day, using a spot size of 40 μm, laser output energy of 0.28 mJ and a repetition rate of 10 Hz. Average and reference values, RSD% and RD% are reported for each considered element in Table 3. RSD% and RD% are also shown in Fig. 4. The
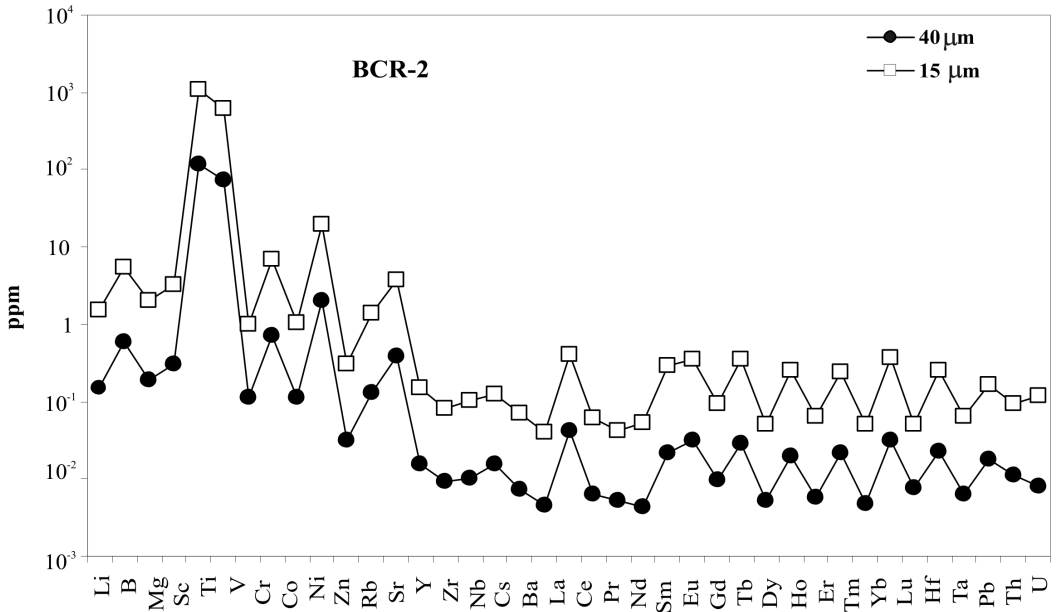
**Fig.3** – Low Limit Detection (LLD) measured on the BCR-2 sample at spot size of 40 μm and 15 μm.
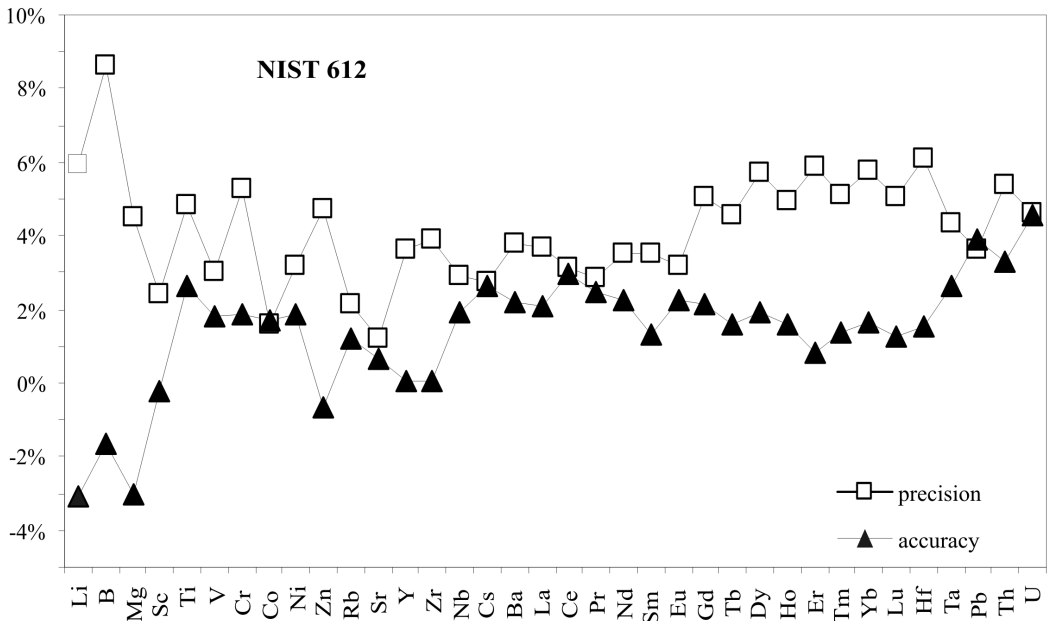


**Fig.4** – Precision (RSD%) and Accuracy (RD%) of the LA-ICP-MS instrument, measured using the reference material NIST612 on 16 replicates in one day.

TABLE 3
*Average and reference values, Precision (RSD%)
and Accuracy (RD%) for each element considered.
The values refers to 13 replicates analyses of NIST
612 in one day*

| Elements | Mean | St.dev. | Ref.value | RSD% | RD% |
|---|---|---|---|---|---|
| Li | 42.82 | 2.56 | 41.54 | 5.95 | -3.09 |
| Ba | 35.16 | 5.31 | 34.73 | 8.61 | -1.66 |
| Mg | 79.60 | 3.70 | 77.44 | 4.48 | -3.05 |
| Sc | 40.88 | 1.13 | 41.05 | 2.41 | -0.21 |
| Ti | 47.37 | 2.35 | 48.11 | 4.83 | 2.63 |
| V | 38.73 | 1.25 | 39.22 | 3.02 | 1.8 |
| Cr | 39.65 | 2.22 | 39.88 | 5.25 | 1.86 |
| Co | 34.91 | 0.81 | 35.26 | 1.62 | 1.73 |
| Ni | 38.11 | 1.46 | 38.44 | 3.18 | 1.87 |
| Zn | 38.31 | 1.81 | 37.92 | 4.72 | -0.66 |
| Rb | 31.41 | 0.83 | 31.63 | 2.14 | 1.21 |
| Sr | 75.71 | 0.88 | 76.15 | 1.21 | 0.67 |
| Y | 37.98 | 1.44 | 38.25 | 3.61 | 0.07 |
| Zr | 35.68 | 1.47 | 35.99 | 3.91 | 0.07 |
| Nb | 37.50 | 1.09 | 38.06 | 2.9 | 1.91 |
| Cs | 40.98 | 1.51 | 41.64 | 2.74 | 2.65 |
| Ba | 37.14 | 1.49 | 37.74 | 3.8 | 2.22 |
| La | 35.17 | 1.30 | 35.77 | 3.68 | 2.07 |
| Ce | 37.61 | 1.41 | 38.35 | 3.12 | 2.95 |
| Pr | 36.56 | 1.29 | 37.16 | 2.87 | 2.45 |
| Nd | 34.69 | 1.39 | 35.24 | 3.54 | 2.26 |
| Sm | 36.50 | 1.61 | 36.72 | 3.51 | 1.34 |
| Eu | 34.02 | 1.59 | 34.44 | 3.2 | 2.27 |
| Gd | 36.37 | 2.13 | 36.95 | 5.06 | 2.12 |
| Tb | 35.47 | 2.18 | 35.92 | 4.54 | 1.62 |
| Dy | 35.54 | 2.55 | 35.97 | 5.69 | 1.95 |
| Ho | 37.49 | 2.58 | 37.87 | 4.97 | 1.57 |
| Er | 37.09 | 2.75 | 37.43 | 5.9 | 0.8 |
| Tm | 37.16 | 2.51 | 37.55 | 5.1 | 1.38 |
| Yb | 39.48 | 3.04 | 39.95 | 5.77 | 1.65 |
| Lu | 37.36 | 2.62 | 37.71 | 5.05 | 1.29 |
| Hf | 34.35 | 2.76 | 34.77 | 6.1 | 1.52 |
| Ta | 39.01 | 2.54 | 39.77 | 4.36 | 2.66 |
| Pb | 37.90 | 1.72 | 38.96 | 3.65 | 3.88 |
| Th | 36.17 | 2.17 | 37.23 | 5.39 | 3.28 |
| U | 36.04 | 2.02 | 37.15 | 4.61 | 4.55 |

precision generally ranges between the 1.2 and 6%, increasing toward the higher mass. Neverthless the maximum value of about 9% is reached for 11B. Accuracy varies between - 5% and 5%. Negative accuracy values are relative to Li, B, Mg and Zn due to an underestimation with respect to the certified material.

CONCLUSIVE REMARKS

Analyses of certified reference materials (NIST610, NIST612, BCR-2) were performed in order to check the instrumental setup and operating conditions. Sensitivity is a function both of the atomic mass number and of the relative abundance of the analysed element; an increase in the signal intensity is observed throughout the mass range, with a minimum response for light elements and a maximum for heavier elements. Low sensitivity values are recorded for major and light elements, such as Si. High sensitivity values are typical of the heavier and geochemical important elements, such as the REE, Pb and U. Analyses of the partially certified natural glass, BCR-2, performed at spot size of 15 µm and 40 µm respectively, indicate that the detection limits of the instrument range between 10 ppb and 20 ppm, with highest values obtained at smaller spot size. A number of 13 replicate analyses of NIST612 carried in one day suggests that precision is increasing toward the higher mass from 1% to 9%, and accuracy is better than 5% for all investigated elements. These preliminary results, obtained on synthetic and natural glass standards, suggest that the LA-ICP-MS instrumentation installed at Department of Earth Sciences of the University of Cagliari is suitable for the *in-situ* analysis of trace elements in geological materials. Technique and methods will be soon applied to characterise natural samples for geological, geochemical and environmental studies.

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