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A moderate microsampling in Laser Ablation Inductively Coupled Plasma Mass Spectrometry analysis of cultural heritage objects: a review

Barbara Wagner*, Olga Syta, Marek Sawicki

Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, ul. Żwirki i Wigury 101, 02–089 Warsaw, Poland

* Corresponding author: barbog@chem.uw.edu.pl

Abstract

Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is one of modern instrumental methods whose usage in the elemental analysis of cultural heritage objects has recently noticeably increased. The method requires almost no sample preparation and permits the direct analysis of solid samples, availing only minute amount of the material. Although they seem to be microdestructive, ablation processes remain usually within the scale acceptable for art historians, conservators, archaeologists and art curators; therefore, the capability to perform a multi-elemental, ultra trace and isotopic analysis can be introduced to studies of cultural heritage objects. The lack of appropriate matrix-matched certified reference materials or fractionation effects influencing the final quantitative results to a different extent is widely reported among the main limitations of LA-ICP-MS. Despite these constrains, LA-ICP-MS is a method that can be flexibly tuned to collect the desired elemental information and this paper brings together information about the successful application of this method in the analysis of diverse historical materials enabling researchers to build valuable knowledge about cultural heritage objects from all over the world.

Keywords: LA-ICP-MS, cultural heritage, archaeometry, works of art, elemental analysis

1. Introduction

The interest in archaeometric investigations and conservation science is growing every year and guidelines for selecting the optimum instrumental method are discussed in the literature. Van Grieken and Janssens [1] recalled Lahanier et al. [2], who published a list including a few desirable features of the best method of choice for the analysis of cultural heritage objects. The list included the multielemental character of direct measurements, low limits of detection, high sensitivity, versatility, universality, and a relatively short time of the analysis. The non-destructive character of the measurements was also pointed out by Lahanier.

The need to protect cultural heritage objects gives the priority to non-destructive measurements, although many of currently available methods can successfully utilize microscopic mass of samples [1, 3]. Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) is one of modern instrumental methods whose need for sample consumption is reduced to absolute minimum [4–6]. All LA-ICP-MS measurements benefit from very sensitive elemental analysis and low limits of detection (down to $ng \cdot g^{-1}$) [7–10], which allow the successful use of this method during provenance investigations [11–30], material identification [31–35], studies devoted to reconstructions of past technologies [36–42] and conservation research [43–46].

In this paper, we would like to discuss possible research scenarios based on the use of LA-ICP-MS, depending on the size of objects and agreement for sampling as well as a possibility of transportation to the laboratory. The number of papers devoted to the use of LA-ICP-MS for conservation science and archaeometry may be taken as a good indicator for the growing interest in the use of this method for the analysis of cultural heritage objects (Fig. 1).

limits of detection (LOD) to the level of about 10 $ng \cdot g^{-1}$ [47–49]. The later introduction of a commercially available instrumentation gave a new tool for: (i) direct analysis of solid; (ii) microanalysis; (iii) surface mapping and (iv) depth profiling of investigated materials [10, 50]. The method has proven to be applicable for the analysis of literally all solids while elemental or isotopic information is needed.

Over 30 years of experience with laser ablation ICP-MS has resulted in rich literature about fundamentals and applications of the method based on a reliable recognition of its advantages and limitations [4, 50]. The selection of cultural heritage as the research area has not changed the general procedural rules of using LA-ICP-MS; however, various analytical scenarios for using LA-ICP-MS during investigations of valuable objects were proposed.

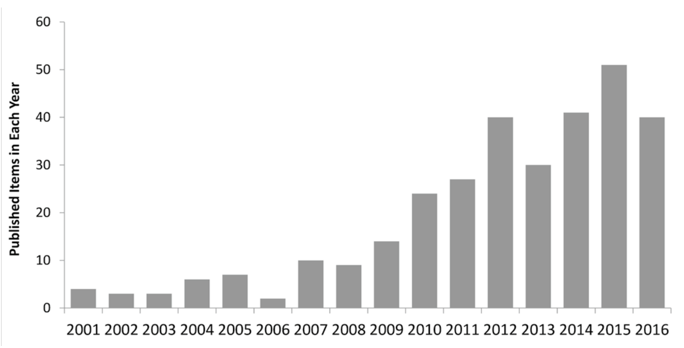

Fig. 1. The number of papers published per each year according to the report generated by Web of Science.

2. Introduction to LA-ICP-MS

LA-ICP-MS was mentioned for the first time in 1985, when Gray described his preliminary study of using laser ablation with ICP-MS during investigation of rock samples [47]. His work extended the previous use of laser ablation combined with ICP-OES lowering

3. LA-ICP-MS setup

Typical LA-ICP-MS systems utilize laser ablation of solids in a neutral gas (argon and/or helium) atmosphere; the possibility to ablate solids in air is reported rarely [51]. While standard set-up is being used, a sample or an object is located in a moveable x-y-z stage and closed in a tightly sealed ablation cell continuously flushed with a carrier gas. A surface of a sample exposed to the laser beam can be observed in the real time with a CCD camera, allowing selection of the investigated area and proper laser beam focusing. The ablated aerosol is then transported by the carrier gas to the plasma and mass spectrometer (Fig. 2), where ions are separated according to their mass to-charge ratio (m/z) [5, 50, 52]. There are no specific technical solutions of LA-ICP-MS setups especially designed for cultural heritage objects investigations; however, some systems facilitating microsampling of precious items were suggested in the literature [53, 54].

Laser ablation is effective practically for all solid materials; nevertheless, the course of the process depends on the number of factors related to chemical and physical properties of the investigated material, as well as parameters of the applied laser set up. Melting and boiling points, or ionization potentials of elements of interest, might also have an influence on ablation processes leading to their different course during the micro-sampling of solids [55–57]. Occurring differences were defined as fractionation, meaning the sum of non-stoichiometric processes changing the analytical response of signals if compared to the real stoichiometry of investigated samples [58]. The reliable quantification is challenging, yet achievable by using shorter lasers wavelengths (Table 1), shorter pulse durations and optimized power densities according to the actual knowledge about LA-ICP-MS measurements [8, 52, 59–66].

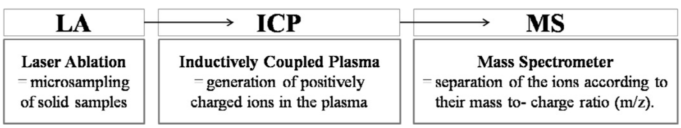

Fig. 2. The scheme of a typical LA-ICP-MS system.

Lasers emitting shorter wavelengths (193 nm) together with shorter pulse durations (fs) can reduce fractionation and would be

Table 1. Selected lasers used in LA-ICP-MS measurements

Wavelength (nm)	Laser type		Pulse duration
1064	Nd:YAG	Solid state	ns
650–1100	Ti:Sapphire	Solid state	fs
694	Ruby	Solid state	ns
532	Nd:YAG	Solid state	ns
355	Nd:YAG	Solid state	ns
308	XeCl	Gas excimer	ns
266*	**Nd:YAG**	**Solid state**	**ns**
248	KrF	Gas excimer	ns
213*	**Nd:YAG**	**Solid state**	**ns**
193	Nd:YAG	Solid state	ns
193*	**ArF**	**Gas excimer**	**ns**
157	F_2	Gas excimer	ns

*) The lasers most commonly used to ablate cultural heritage objects for ICP-MS analysis.

preferably used during quantitative elemental analysis; however, the ablation with the use of Nd:YAG ns lasers emitting either λ=266 nm or λ=213 nm is still popular. Femtosecond lasers are less commonly used [16] for investigations of cultural heritage objects than the nanosecond ones.

To minimize the effects of fractionation Brostoff et al. [16] used fs-LA-ICP-MS in provenance studies of rare ancient gold artifacts. The main groups of the objects were distinguished on the basis of elemental composition and variable content of Ag, Pd, Pt or Sn, Cu and Zn. The multielemental information obtained by means of LA-ICP-MS was important to support historical, technical and stylistic evaluation of the investigated gold objects and was used for matching the fragments by origin of manufacture with a good precision and accuracy.

The appropriate calibration for quantification of multielemental LA-ICP-MS measurements remains a challenging task mainly due to the strong dependence of ablation processes on manifold physicochemical properties of solids. Properly selected reference materials with the known content of elements of interest allow the reliable calibration and accurate determination of the elemental composition of investigated objects (Table 2). Three possible calibration approaches can be used to quantify LA-ICP-MS signals. The most popular calibration approach is based on the use of solid matrix-matched reference materials [61, 67], while dual introduction of standard solutions together with the ablated matter [68–70] or direct ablation of liquid standards [71–73] are less commonly applied.

There are many commercially available and well characterized solid reference materials [43, 74, 112, 113, 134–138] which can be used in LA-ICP-MS investigations (Table 2). Only these of the composition and the structure properly matching analyzed materials can offer accurate quantification by ensuring the consistency of ablation processes for both: the sample and the standard [14]. A careful selection of the matrix-matched standards would provide accurate results of LA-ICP-MS measurements together with internal standardization (IS), which is recommended to reduce matrix effects and correct differences in ablation efficiency of samples [61, 139]. If no adequate standards are available, non-matrix matched calibration approaches could be applied with normalization to 100% procedure [140–143] and allow for collecting information about major, minor and trace elemental composition of investigated objects. In all cases, the results of LA-ICP-MS measurements should be checked according to the quality control protocol.

4. LA-ICP-MS in relation to destructiveness and invasiveness of investigations of cultural heritage objects

Many authors pointed out that LA-ICP-MS causes only those damages that are not visible to the naked eye [32, 54, 76, 93, 113, 144, 145]. A laser beam energy may be focused on an area with diameters of about a few up to several hundred micrometers limiting the post-ablation marks to the selected location. The spot ablation means the micro-sampling of the material from a single point, while rastering or line/multiline ablation allows assessment of elemental/isotopic spatial distribution over a surface of a sample [179]. An opportunity for selective analysis of surface or sub-surface domains is particularly important during investigations of heterogeneous objects, corroded or covered with patina.

Table 2. Reference materials used in LA-ICP-MS quantitative analysis of cultural heritage objects

Sample	Reference materials used
Glass [13, 18, 22, 26, 74–92]	National Institute of Standards and Technology: 610, 612, 614 (trace elements in glass) Corning Museum of Glass: A, B, C, D U.S. Geological Survey: BCR-2G, BHVO-2G, BIR-1G (basalt glasses) Society of Glass Technology: 2, 3, 4, 5, 6, 7, 8, 9
Obsidian [12, 93–98]	National Institute of Standards and Technology: 610, 612 Corning Museum of Glass: B, D U.S. Geological Survey: BCR-2G Natural obsidians from: Glass Butte (USA), Sierra de Pachuca (Mexico), Wekwok (Papua New Guinea)
Ceramic [23, 29, 30, 33, 35, 36, 40, 53, 99–111]	National Institute of Standards and Technology: 679 (brick clay), 1633a (coal fly ash); 610, 612, 614, 1412 (glasses) Corning Museum of Glass: B, D Missouri University Research Reactor Center: New Ohio Red Clay U.S. Geological Survey: BIR1 (basalt); AGV2 (andesite); GSP2 (granodiorite); RGM1 (rhyolite); BCR-2G, BHVO-2G (basalt glasses) National Institute for Metallurgy: NIM-L (lujavrite) Institute for Reference Materials and Measurements: BCR-126A (lead glass) ANRT reference material: FK-N (potash feldspar)
Metal [14, 67, 112–124]	National Institute of Standards and Technology: 500, C1123, C1252, C1257 (copper); 685, 8053, 8054, 8059, 8062, 8063, 8065, 8068, 8074, 8077 (gold); 481 (gold-silver alloy); 610, 612 Federal Institute for Materials Research and Testing: 211, 227, 228, 378 (bronzes) Centre de Developpement des Industries de Mise en Forme des Materiaux: B10, B12 (bronzes) Bureau of Analysed Samples: 50.03–4, 50.04–4, 51.13–4, 71.32–4 (bronzes) MBH Analytical: 32X SN1, 32X SN2, 32X SN3 (bronzes); 31X TB2, 31X TB4 (brasses) Swerea Nordic CRM Working Group: JK 27A (stainless steel), JK 2D (pure iron) U.S. Geological Survey: GSE-1G (lead isotope ratio)
Human fossil [125–128]	National Institute of Standards and Technology: 987 (strontium isotope ratio); 610, 612 New York State Department of Health: RM05–1, RM05–2, RM05–4 (lead-dosed caprine bone pellets) China National Analysis Center: GBW0760 (human hair)
Mortar [129–133]	National Institute of Standards and Technology: 1d (argillaceous limestone); 610, 611, 612, 613 U.S. Geological Survey: BCR-2G

Imaging techniques allow for clear mapping of a distribution of selected elements in forms of 2D [53, 90, 147, 174] or 3D [180] models. Van Elteren with co-workers [180] applied a 3D LA-ICP-MS mapping procedure to the analysis of historic glass to study degradation mechanisms of glass weathering. Previous analytical protocols required cross-sectional fragments of glass for the analysis, which was omitted in this project. LA-ICP-MS measurements are relatively fast; therefore, many analyses were repeated in a reasonable period of time.

Statements indicating a low degree of changes due to LA-ICP-MS analysis include such wording as *quasi-destruction-free* [113], *virtually non-destructive* [19, 32, 54, 76, 93] or *relatively/almost non-destructive* [12, 29, 144–146]. Other papers [35, 77, 125, 147–150] state that LA-ICP-MS as *a micro-destructive method* provides multi-elemental information with *minimal sample damage* and should rather be understood as an attempt to present the method in the best light, not as a precise term describing effects of ablation.

Possible controversies with assigning attributes of *destructiveness* or *invasiveness* to any analytical protocol have been considered in works of Wouters [3, 151], who suggested to use the term *intervention* instead. The **degree of intervention** might be described at three levels: (i) molecular (low change), (ii) microscopic (medium change) and (iii) visual (high change). Wouters nomenclature is rational and useful to clarify the scale of changes provoked by application of instrumental methods to the measurements of cultural heritage objects.

According to Wouters [3, 151], microscopic interventions/medium changes to cultural heritage objects can be expected if the ablation was executed directly from the analyzed item. Ablation is usually performed inside ablation cells; therefore, a size of an object to be analyzed is important [7, 53, 54, 152–157]. Variable constructions of ablation cells were described in the literature, allowing the best selection of analytical approach for particular size and shape of objects.

5. Degree of intervention induced by LA-ICP-MS measurements

The development of methodology for studying cultural heritage objects is paired with specific restrictions in order to keep the analyzed objects possibly intact, to remain them within the molecular or microscopic degrees of intervention. These requirements can be met during the application of LA-ICP-MS; however, depending on the size and uniqueness of investigated objects, different scenarios for conducting laser ablation can be proposed (Fig. 3).

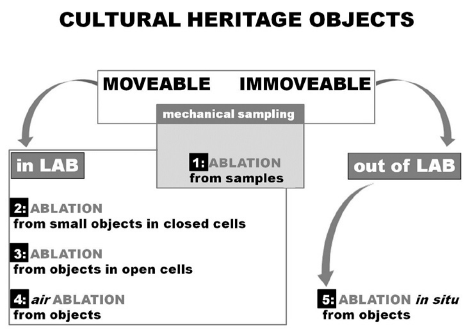

Fig. 3. Various scenarios for using LA-ICP-MS during investigations (the description is given in the text).

5.1. Scenario 1: mechanical sampling followed by laser ablation from the taken fragments

The most common scenario of using LA-ICP-MS for the analysis of cultural heritage objects concerns ablation of samples mechanically taken from artifacts (Fig. 4). Mechanical sampling enables the investigations of the chemical composition of immoveable or large moveable objects which cannot be transported to a laboratory. The step of mechanical sampling takes responsibility of the scale of intervention to the object of interest because the same sam-

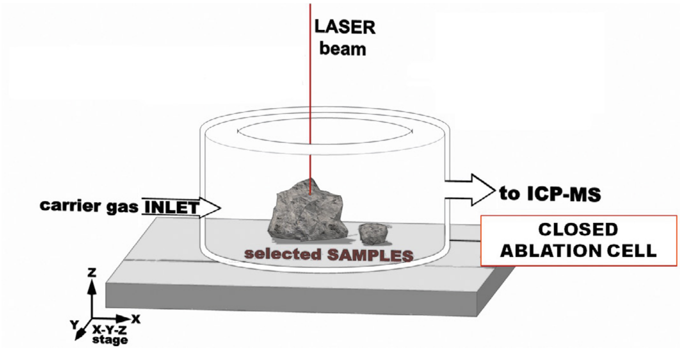

Fig. 4. Scenario 1: ablation executed in closed cell from samples.

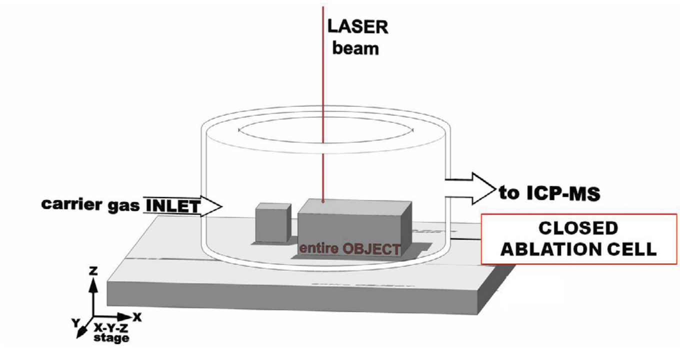

Fig. 5. Scenario 2: ablation executed directly from the object, which fits to a closed ablation cell.

pling, not the process of laser ablation, is the most destructive step in the whole analytical procedure.

Collected fragments can be additionally analyzed by other methods [74, 96, 101, 102, 105, 115, 126, 129, 135, 158–165] to broaden the knowledge about their chemical composition. Small samples are often taken from historical glass to be analyzed by means of SEM-EDX and LA-ICP-MS [38, 74, 79, 84–89, 135, 166–169]. In this case, small fragments are embedded in resin blocks and prepared in accordance to EDX analysis requirements (polishing, carbon coating). They can be analyzed in the same form by means of both methods. The results from SEM-EDX analysis may be used first to select and then to determine the content of the internal standard (CaO or SiO_2). These two methods provide results with a satisfactory correlation for major and minor elements, while LA-ICP-MS additionally allows for determination of trace elements.

The incorporation of LA-ICP-MS into research involves the necessity to sample large objects. The inner volume of the standard closed cell prerequisites the size of an item which can fit it during ablation; therefore, objects of small sizes can be located inside a cell, allowing direct laser ablation from the object (Fig. 5).

5.2. Scenario 2: direct laser ablation from small objects

The size of an item plays an important role in the analytical procedure including LA-ICP-MS investigations when no agreement can be obtained for the mechanical sampling of the object. The commercially available ablation cells are characterized by the defined dimensions and only objects that are small enough to be placed inside the ablation cells can be ablated directly [11, 12, 78, 93, 106, 117, 127, 170–173]. This scenario allows not only to lower the level of intervention to the minimum, but also the most time-consuming step of samples preparation is eliminated and LA-ICP-MS measurements can be performed much faster [18, 19].

The shortening of the analysis time is a beneficial side-effect of the scenario 2 and is helpful for investigations of objects which are found in large quantities, like glass beads from archaeological sites all around the world [76]. Robertshaw et al. [18] analyzed more than 360 glass beads from the southern Africa, while Dussubieux et al. [19] reported the results for 486 items of archaeological glass beads from India, Sri Lanka, Bangladesh, Thailand, Malaysia, Indonesia, Cambodia, Vietnam and Turkey. Thanks to availability to a number of data on a large group of similar objects, it was possible to conduct statistical surveys and extract information about the existence of variable sub-groups representing several glass-making centers. The hypothesis about the existence of a few glass making centers in different locations was supported by the results of LA-ICP-MS investigations of mineral soda-alumina glass and allowed to distinguish the sub-groups on the basis of concentrations of selected elements (Ca, Mg, U, Ba, Sr, Zr and Cs).

5.3. Scenario 3: the use of open ablation cells

Objects that are too large to be placed inside the ablation cell can be analyzed with the use of so called "open" or "moveable" ablation cells (Fig. 6) [53, 54, 152–153, 174]. Small open ablation cells are adhered to the surface of an object, maintaining the degree of intervention of LA-ICP-MS measurements at the microscopic level [53, 54, 175].

The use of open ablation cells allows to avoid mechanical sampling from valuable objects and thus expands the range of applications of LA-ICP-MS. The use of such scenario is more time-consuming than the previously described ones. The object has to be handled with the highest caution to avoid damage caused by mounting at the x-y-z stage for the time of ablation. Open cells are usually characterized by small intrinsic volumes that permit the shortening of the wash-out-time from the cell; therefore, the investigations of elemental distribution with the use of this scenario are facilitated. Various designs of open cells were proposed [53, 54, 152, 153, 175, 176]; however, the optimum construction should allow their use irrespective of the particular size or shape of the object and would be insensitive to the surface irregularity.

Devos, Moor and Lienemann [54] described the successful use of ablation open cell during elemental analysis of silver artifacts. The open cell was used because the objects of interest were too large to fit into a standard ablation cell and the mechanical sampling of them was not allowed. Contents of Ag, Zn, Cd, Sn, Sb, Au, Pb and Bi were determined and allowed to discriminate one forgery among the originals. A crater-to-crater repeatability of the normalized signals was reported below 10% RSD (n=3) for most of the selected elements with detection limits within the sub-ppm to ppm range.

Low limits of detection are the most preferred advantages of LA-ICP-MS measurements. Recently, sampling systems with no ablation cell have been developed for a direct atmospheric ablation [67, 177], according to the scenario 4 (Fig. 7), and also allow to maintain limits of detection at the

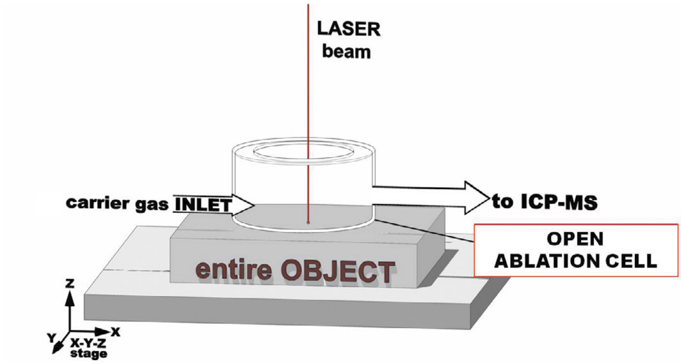

Fig. 6. Scenario 3: ablation executed in an open cell attached to a surface of an object.

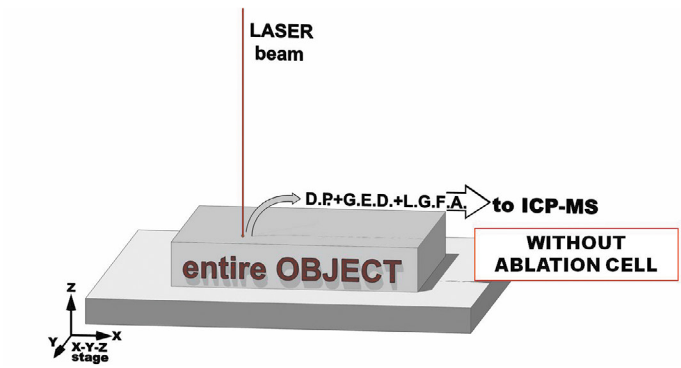

Fig. 7. Scenario 4: air ablation without using any ablation cell. **D.P.** = diaphragm pump; **G.E.D.** = gas exchange device; **L.G.F.A.** = laminar gas flow adapter [177].

low level for most of the elements. This kind of technical solution seems very promising for all cultural heritage objects investigations in the near future, releasing the LA-ICP-MS measurements from having to be run only in a sealed ablation cell.

5.4. Scenario 4: direct laser ablation from cultural heritage objects in ambient air

The innovative direct sampling by laser ablation in ambient air during LA-ICP-MS measurements was described by Kovacs et al. [67] in 2010. The open set-up was used for ablation with no cell at all. The exchange of air to argon by means of a gas exchange device was required together with a diaphragm pump, which then permitted the transportation of the laser-generated aerosol into the ICP-MS. The level of oxides formation was monitored carefully as it was considered a possible limitation of this method. Oxide formation and count rates of the gas blank or potential spectral interferences from polyatomic ions were satisfactory and the accuracy of the obtained results was similar to the one achieved with closed transport systems.

In 2013 Dorta et al. [178] described laser ablation sampling in air under atmospheric pressure coupled with MC-ICP-MS. A lead isotope ratio analysis was performed, using two brass certified reference materials, galena and zircon. The precision and accuracy of the measurements were similar to the obtained by conventional LA-MC-ICP-MS in a sealed cell and helium atmosphere. The direction of development of such systems enabling the ablation in ambient air directly from the surface of unique objects seems very promising. Such instrumentation would cancel most of limitations for dimensions of objects easily analyzed by means of LA-ICP-MS. There is still a need to transport objects to the laboratory; therefore, the simplicity of using LA-ICP-MS method will remain mostly for moveable objects.

5.5. Scenario 5: use of portable laser ablation sampling device

The use of a portable laser sampling device facilitates the analysis of any immoveable cultural heritage objects (Fig. 8). These objects were the last category, which could not be investigated by means of LA-ICP-MS without mechanical sampling until the paper by Glaus et al. [177] reported the use of the portable sampling device applicable to the ablation of any object regardless of its size and location. Ablated particles are collected on special filters. Filters protected from contamination are transported to a laboratory, where they can be examined either by means of LA-ICP-MS with re-ablation or by any other instrumental method.

This approach allows the *in situ* microsampling of all objects (apart from the underwater cultural heritage) in spite of their dimensions and possibility for being transported to a laboratory. The portable LA sampling device has already been successfully applied to the elemental analysis of ancient Chinese ceramics [177] and the determination of lead isotopic composition [196]. Taking into account all demands of the conservation science or archaeometric investigations, the possible use of the portable LA set up has a huge potential to be used in the future analysis of all cultural heritage objects, which cannot be examined by any other technique without invasive sampling.

The portable laser ablation sampling utilizes all advantages of microscopic degree of intervention caused by laser ablation. Some essential problems, such as polyatomic interferences caused by filter material during the subsequent re-ablation in the lab, element-dependent sensitivity enhancement, signal fluctuations and elemental fractionation have been observed [177]; however, these limitations do not diminish the attractiveness of the proposed method for the elemental and isotopic analysis of immoveable cultural heritage objects.

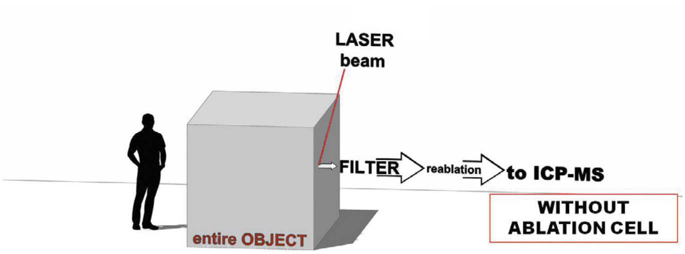

Fig. 8. Scenario 5: air ablation with collection of particulate matter on filters and subsequent re-ablation inside a closed cell.

6. Multi-technique approach incorporating LA-ICP-MS

The results of sensitive LA-ICP-MS elemental/isotopic measurements can be used to support the use of other instrumental methods such as Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry (SEM-EDS) [12, 31, 38, 74, 79, 112, 118, 130, 135, 166, 170, 181, 182], Electron Probe Microanalysis (EPMA) [75, 80, 81, 97, 112, 167, 183–185], X-Ray Fluorescence (XRF) [16, 31, 35, 44, 93, 94, 98, 119, 120], Proton Induced X-Ray Emission [22, 41, 95, 114, 186, 187] or Neutron Activation Analysis (NAA) [23, 36, 99, 100, 107, 108, 114, 146, 188–192]. Leroy et al. [193] reported the first application of confocal Synchrotron Radiation micro X-Ray Fluorescence (SR-m-XRF) with LA-ICP-MS. They examined microscopic slag inclusions in mediaeval armours attributed to a Lombard provenance from stylistic considerations. The potential of coupling SR-m-XRF with LA-ICP-MS during quantification of trace elements in slag inclusions was evaluated with respect to drawbacks and advantages of each method.

LA-ICP-MS was merged with instrumental methods providing molecular information about the determined compounds: Raman spectroscopy (RS) [79, 121, 168, 194], Fourier Transformed Infrared Spectroscopy (FTIR) [131, 194, 195] or Gas Chromatography Mass Spectrometry (GC/MS) [195] during glass, ceramic, bones and wall-paintings investigations.

Di Bella et al. [82], Gallo et al. [83], Walton et al. [169] described the application of X-ray Powder Diffraction (XRPD) together with LA-ICP-MS for the historic glass analysis. The combination of Computed Tomography (CT) and LA-ICP-MS was reported by A. Kreiter et al. [109]. The authors used CT to assess differences in the porosity, number and size of inclusions in three visible distinguishable layers of a ceramic figurine. The LA-ICP-MS analysis was carried out to quantify major, minor and trace elements in the abovementioned figurine layers. The application of these complementary methods led to the answer to a question whether the analyzed object was formed over time using material from the same resource.

7. Conclusions

The interest in the use of laser ablation ICP-MS in archaeometry and restoration/conservation science is constantly increasing; however, the non-destructive character of the measurements pointed out by Lahanier [2] as one of the requirements for instrumental methods most suitable for the analysis of cultural heritage objects cannot be fully attributed to LA-ICP-MS.

The possibility to investigate cultural heritage objects by means of LA-ICP-MS should be always verified according to conservators recommendations, taking into account dimensions of the analyzed objects and the possibility of samples collections, their number and size. The mechanical sampling is one of the suggested solutions, while the other is the possibility to perform the direct laser ablation from cultural heritage objects. The use of open ablation cells or direct air ablation was proposed when the mechanical sampling is impossible or unacceptable. Such direct ablation offers many advantages and expands the usefulness of LA-ICP-MS for the analysis of cultural heritage objects. The real milestone of the development of LA-ICP-MS was the use of mobile LA systems allowing for microsampling independently from a size and the mobility of the analyzed object.

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