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Current approaches to calibration in LA-ICP-MS analysis

Natalia Miliszkiewicz, Stanisław Walas[1], Anna Tobiasz

Department of Analytical Chemistry, Faculty of Chemistry,
Jagiellonian University in Krakow

Abstract

For solid sample quantitative analyses by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), the main analytical problem is the calibration step: evaluation of the function (equation) that correlates the signal with the concentration of analyte in the sample. Except for basic standards preparation, problems result from non-stoichiometric effects during vaporization, transport of ablated aerosol, atomization, and ionization in the plasma. These effects, called elemental fractionation, are mainly sample matrix dependent and thus suggests that standards used for calibration should accurately match the sample matrix. Preparation of such standards is a difficult and time-consuming process, so since the beginning of LA-ICP-MS applications for quantification of solid sample composition, different approaches are being developed to solve the problem, primarily complete matrix matching. Because the calibration of LA-ICP-MS is a key factor for its quantification capabilities, this review summarizes recent calibration approaches and related standard preparation techniques for the analysis of various solid materials by LA-ICP-MS. Selected papers concern the application of reference glasses; solution based standards; synthetic standards based on the main sample matrix component or powdered matrix certified reference materials; matrix-matched standards based on spiked sample material; and non-matrix-matched standards, for calibration. Isotope dilution methods and signal normalization protocols used in order to improve precision are also considered.

Key words: laser ablation; inductively coupled plasma mass spectrometry; calibration

[1] Corresponding author: e-mail: walas@chemia.uj.edu.pl, phone: 4812 6632233

Contents

1. Introduction

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) offers the capability of direct solid sample analysis and generally provides full elemental coverage with minimal sample preparation. LA is a technique that avoids contamination or loss of analytes during preparation procedures (e.g. digestion or dissolution) [1; 2; 3; 4; 5; 6; 7]. Moreover introduction of a sample without typical solution components (dry plasma) into ICP improves atomization and reduces some matrix effects. Nevertheless, it requires a specific approach to calibration. Regardless of indisputable progress in laser technology as well as improvement in quantification procedures in the last decade [8], it still suffers from limited availability of commercial calibration standards [4; 5; 9]. The matrix dependence of the signal is the Achilles' heel of laser ablation sampling, especially for ablation of metals and semi-metals using ns-lasers.

For calibration of LA-ICP-MS analyses various strategies have been proposed. Among these strategies the application of solid matrix-matched standards is often recommended [10]. Unfortunately, reference materials usually used to prepare such standards are expensive and do not cover either the type of matrix or range of concentration of analytes in the sample. On necessity, some laboratories prepare their own matrix-matched standards by mixing sample, or adequate to sample matrix material, with elemental standards to adequately adjust the concentration ranges of analytes in the prepared standard. Apart from being time-consuming to prepare, these standards generally have unknown homogeneity which could reduce precision of analysis. To ensure spatial resolution fit for purpose, micro-homogeneity of such standard material has to be verified and optimized [5].

Except for the problem with precision, crucial drawback of LA-ICP-MS analysis influencing accuracy is caused by still non-recognized matrix interferences, especially when standards of unmatched matrix are used [4; 8; 9]. Nevertheless, calibration procedures based on exploitation of non matrix-matched standards are also in a great focus of interest.

This review article is focused on the general aspects related to calibration and standards preparation for LA-ICP-MS applications. A brief summary of different approaches is presented in the following paragraphs.

2. Parameters influencing analytical signals in LA sampling

A few facts must be taken into account if a laser is used for solid material sampling, including the aim of analysis, samples and standards homogeneity, differences in physical properties and thus evaporated mass or method of signals variation compensation [4]. Some non-stoichiometric effects influencing sampled masses are defined as fractionation. They include laser-induced preferential evaporation of volatile elements, particle size dependent elemental differentiation, and isotopic specific fractionation [2; 11]. Summarizing numerous paper on elemental fractionation, it can be concluded that the laser ablation efficiency is affected by the laser irradiance; fluency; pulse length and wavelength; the depth-to-diameter ratio of the crater formed; mineralogical factors; the composition of the matrix; and the ablation mode [1; 12]. The strict source of fractionation is still uncertain, but there is a suggestion that such factor as crater diameter to depth ratio plays much more vital role than laser wavelength [8]. Fractionation may be minimized by the creation of well-defined craters; assuring high absorption (low penetration depth) of laser light in the material, short laser wavelengths application; careful adjustment of gas flow; avoiding particle re-deposition over the sample surface; and exploitation of a rapid-pulse laser.

The ideal conditions for analyzing solid samples by LA-ICP-MS could be suggested on the base of a few papers [2; 9; 13]:

- No sample constituents should evaporate from the crater region, e.g. from the melt metallic sample – this is usually not fulfilled in the ns-lasers.
- Stoichiometric composition of ablated aerosol should be the same as in the solid sample.
- Only particles of uniform sizes should be formed during the ablation process and transported without losses to the ICP torch.
- The particles should be small enough to be completely atomized in plasma without any fractionation effects.

Due to the interaction of sample material, laser wavelength, and ablation parameters on the resulting particle size distribution, the ICP operating conditions need to be optimized specifically to eliminate fractionation effects. “Robust’’ plasma operating conditions should be adjusted by minimizing the abundance of temperature sensitive species (e.g. oxide ions) in the mass spectrum [5].

3. Signals normalization protocols

In many cases the precision and accuracy of LA-ICP-MS are worse than those of conventional nebulization ICP-MS. To improve precision of LA-ICP-MS several methods have been proposed including application of internal standardization; shot to shot normalization; monitoring acoustic waves produced during laser ablation; monitoring signals emitted from laser-induced plasma (LIP) or scattered light during sample transport [10; 14; 15; 16]. In the same manner that internal standards are used routinely to improve precision and accuracy in solution nebulization ICP-MS, internal standards in LA provides a more precise determinations. Generally, signals for quantitative analysis are normalized using as an internal standard - an isotope of the main matrix element of an invariable concentration across the sample [17]. In some cases, a trace or minor elements could be also exploited. If there is no element of certified concentration or no minor matrix isotope available, sum of main sample components signals or an added standard can be applied [4; 18].

3.1 Internal standardization

There are two facets of the application of internal standard during LA-ICP-MS analysis. On one hand, it compensates signal variations that occur during the interaction of the laser beam with the sample in the ablation cell, transportation of ablated material and reactions in the ICP plasma. On the other hand, the use of internal standard, if optimally adjusted to analyte, could confine matrix interferences. For clarification, internal standardization corrects multiplicative effects (sensitivity drift, differences of mass ablated, some matrix effects), but mostly additive effects cannot be corrected this way [19]. Since the internal standard should behave as the analyte during ablation, choosing the most suitable candidate, especially for multi-element determinations, is more a matter of compromise and, in some cases, requires labour-intensive sample pre-treatment. Generally, there are a few requirements that an internal standards need to face. Those are homogenous distribution, known concentration (that, in this case, has to be determined by other techniques), and, most importantly, the correction of any bias during measurement.

Carbon is one of the most commonly used elements for internal standardization during the analyses of biological samples [20; 21; 22; 23; 24, 25]. Carbon, as well as sulphur, is said to be able to also correct differences in humidity of samples and reference materials [26]. However, given all previously mentioned requirements together, the role of carbon in LA-ICP-MS is still being investigated [27; 28; 29]. The pioneering work where the ablation behaviour of carbon was discussed did not gain much attention [30]. The authors claimed that

up to 80% of carbon may be released as gaseous (CO_2) or ultrafine particulate species that passes membrane filters. This fractionation leads to different ablation, transport, and behaviour of carbon against analyte in the ICP torch. Austin discovered that ^{13}C can be used as internal standard only if the carbon signal accounts for at least 6% of the gross signal [20]. Pro and con arguments for using carbon as an internal standard were summarized by Frick and Günther [31]. Summing, carbon may not be a good candidate for an internal standard because of the diffusion loss during measurement and confinement of main part of analytes only in the carbon-containing particle (CCP) phase.

As it has been already mentioned homogenous distribution of the element used as internal standard is crucial for precise and accurate determination. For that reason usually element naturally occurring and of major concentration in the sample is chosen [32; 33]. For geological and calcium based samples, isotopes of Ca are often selected to play the role of internal standard [34; 35; 36]. Isotope ^{43}Ca shows better signal intensity and signal to blank ratio compared to ^{46}Ca, as well as significantly more stable signal compared to ^{115}In [37; 38]. The latest is widely used as an internal standard during solution analysis because of its mid-mass position, close to 100% abundance, and almost complete ionization [36; 39].

Ohata et al. [40] tried to compensate the variations of analytical signals for the multi-element analysis of low-alloy steel reference materials using two methods of standardization. The authors compared internal standardization using laser-induced plasma (LIP) emission signal of Fe (373.5 nm) and using LA-ICP-MS signals of ^{57}Fe and ^{60}Ni. The best improvement factors (RSD without correction/RSD with correction) were achieved for ^{60}Ni internal standardization (4.1 – 17). The correlation coefficients (r) using Fe and Ni for signals standardization (0.9985 and 0.9996, respectively) were better than those obtained by LIP Fe emission correction (0.9932).

Although laborious, introduction of selected elements into standards and samples material in order to act as internal standard is sometimes carried on. For that purpose usually elements that are naturally absent in the sample or at the trace level of concentration are chosen. The benefit of mid-range masses and similar to other analytes ionization potential encourage the application of ^{89}Y as internal standards in analyses conducted by different atomic spectrometry techniques [41]. Austin et al. [42] employed ^{89}Y and ^{101}Ru elements for internal standardization in biological soft tissue analyses by LA-ICP-MS along with laboratory made polymer film spiked with Cu and Zn standard solutions. The calibration plots of zinc and copper showed good linearity over the range 0–300 $mg \cdot g^{-1}$ with correlation

coefficients better than 0.999. The authors additionally used ^{13}C for normalization, but although it improved precision, accuracy was better when using ^{89}Y and ^{101}Ru.

Bonta et al. [43] used gold thin layers as internal standard for improving LA-ICP-MS imaging experiments of printed Cu-based patterns, obtaining better quality of images and RSD lowered to less than 5%.

3.2 Summed spectrum normalization

Signal sum normalization techniques require the simultaneous acquisition of all signals from sample components and assumption that the sum of those signals reflects the ablated mass. Considering them as independent techniques for direct measurements of ablated mass allows only to obtain semi-quantitative information, but using entire sample matrix just like single internal standard can correct for signal variations and improve precision of LA-ICP-MS analyses.

Considering individual elemental signals as a function of the summed signals of all sample components has been proved to be a technique immune to matrix effects [14] enabling fast determination of major, minor and trace elements with satisfactory precision and accuracy [44; 45; 46]. Such normalization strategy along with external calibration using reference silicate glasses was applied by Chen et al. [47] to determinate fifty four major and trace elements in carbonate. The MRM-NoIS procedure (calibrated against multiple silicate reference materials without using an internal standard) corrects matrix-dependent amounts of material ablated during each run. Results of carbonate standard MACS-3 analysis was in agreement with the recommended value within 10%. In order to transfer the signal intensity data from the LA-ICP-MS to concentration plots and compare the results to quantitative line scans from the EPMA measurements, Latkoczy et al. [48] used simple sum normalization strategy in the analysis of magnesium based alloys. The results for Mg obtained by both techniques were in good agreement (2.2%).

Analysing the protocol of normalization with the using of summed across sample signals, it can be seen that main sample components play in this method decisive role.

4. Calibration procedures and preparation of standards

Generally, to take full advantage of dry plasma, for LA-ICP-MS calibration solid standards are recommended. Solid standards, except for glass, are inhomogeneous to some extent and effort is required to control the parameter and to adjust it to the analytical requirements. Additionally, the number of readymade, commercially-available solid reference materials or standards is strongly limited. In contrast, liquid standards are easily available and

there are no problems handling with them – mixing, diluting, or doping with missing elements. Therefore procedures using liquid standards are also recommended for different solutions, including their on-line desolvation. In parallel to methods of calibration based on external standards, protocols for signal normalization are also being tested. In the table 1 selection of different calibration approaches, standard materials and related internal standards for LA-ICP-MS application is presented. Some of them will be discussed in more detail later in this article.

Table 1 Calibration methods applied for LA-ICP-MS analyses.

Type of sample	Method of calibration	Internal standard	Reference
geological samples	External calibration using NIST SRMs 610 and 612 (glass).	Li, Ca and Si	[35]
geological samples (basalt, andesite, ash)	Solution calibration conducted by coupling ultrasonic nebulizer to laser ablation cell.		[95]
pyrite	Matrix-matched calibration with “in house” prepared artificial sulphide crystals.		[70]
quartz crystals	Calibration based in direct ablation of aqueous standard solutions and NIST SRM 612 glass analysis.		[112]
Ti-rich minerals	Calibration using synthetic laboratory standards made from $FeTiO_3$ and TiO_2 spiked with minor and trace elements.	Ti	[63]
sediments, soils, ashes	Multi-point calibration based on pellet standards prepared by mixing powdered CRMs with zinc oxide (a binder) and solidified by 2-methoxy-4- (2-propenyl)phenol.		[58]
ambient particulate matter (PM)	Calibration based on the three materials: cellulose ester filters spiked with multi-element solutions, pellets made from ambient PM certified reference material and the same CRM, adhered to a surface (metal disc).	In	[39]
carbonate	Internal standard-independent calibration strategy against multiple silicate reference materials with the normalization of bulk components as 100%.		[47]
calcium carbonate rich materials	Calibration with several reference materials: glass, calcium carbonate powder spiked with analytes of interest and natural geological reference material.	Ca and In	[37]
mussel shells	Calibration with matrix-matched standards made by co-precipitation of twelve elements into $CaCO_3$ matrix.	In, Tl, Sr, Ca	[36]
brass, aluminium and silicate glass	Calibration with non-matrix-matched standard - NIST 610 glass reference material.		[13]
brass, platinum, gold	Solution based calibration with standard addition method.	Cu	[94]
gold	Solution calibration performed by transferring Ag into chloro-complex and diluting it with multi-element solutions.		[97]
lead fire assay buttons	Combination of three calibration strategies – isotope dilution method, single standard addition and internal standardization.	Au, Rh	[73]
ferromanganese nodules	Calibration based on dilution method with MnO_2.	Mg	[33]
feldspar, sulphide	Calibration using silicate glasses.		[87]
silicates	Matrix-independent liquid calibration with standard solutions introduced into ICP by an Aridus liquid sample introduction system with aerosol desolvation.		[46]
steel disks	Comparison of three compensation methods, all based on internal standardization – with use of laser induce plasma (LIP) Fe emission, Ni^+ and Fe^+ signals.	Fe, Ni	[40]
glass (NIST 613) and low density polyethylene	Calibration using aqueous standards with modified absorption coefficients.	Co	[98]

CRMs (sediment, soil, powdered milk)	External calibration against CRMs pressed powders with modified (by organic binders) absorption coefficient.		[59]
glass, apple leaves	On-line isotope dilution method using standard solution with isotope enriched tracer nebulised to the laser-ablated sample material.		[102]
rat brain tissue	Calibration with matrix-matched laboratory standards.		[79]
snail longitudinal tissue	Two strategies applied: one point calibration using CRM and use of matrix-matched laboratory standards (made from spiked CRM or sample material).		[76]
tissues samples (chicken breast)	External calibration with laboratory made standards – PMMA films mounted on the quartz slides and spiked with a.i. metallo-organic standards of Zn and Cu.	Ru and Y	[42]
animal bone	External calibration against reference materials (NYS RMs and NIST SRMs - 1486 Bone Meal and 1400 Bone Ash).	Ca	[38]
teeth	Calibration with matrix-matched laboratory standards - powdered teeth spiked with standard solutions.	Ca	[34]
hair	SRM free, on-line solution based calibration.		[96]
plant tissue (tobacco)	Calibration employing matrix-matched standards from powdered tobacco leaves spiked with standard solutions of selected elements.	^{13}C	[26]
plant tissue (orchard and tomato leaves)	External calibration using Bowen's kale reference material.	Fe and ^{13}C	[113]
green leaves of desert plants	External calibration based on several pressed reference materials.	^{13}C	[53]
cell cultures	Calibration with thin agarose reference film spiked with elements of interest.		[85]
water	Two methods of calibration: external calibration with aqueous standard solutions pipetted onto the PTFE filters, and standard addition method.		[99]

4.1 Calibration based on matrix-matched standards

Since fractionation is a very complex process, still not entirely understand, taking place during aerosol formation in the ablation chamber, transport of the aerosol into the ICP and during all reactions in the ICP plasma, ensuring that standards and samples behave in the same way during ablation can significantly improve analytical capabilities LA-ICP-MS towards quantitative analyses [49]. External calibration using matrix-matched standards, based either on available certified reference material or laboratory prepared "home-made" standards, is still commonly accepted method for LA-ICP-MS calibration. If there is no suitable CRM, matrix matching can be obtained by the addition of selected elements into a powdered matrix, based on either available CRM or the main sample matrix component or by preparing standards with a use of sample material, spiked with elements of interest.

4.1.1 Standards based on powdered matrix reference materials

Certified reference materials (CRMs) are mainly applied to validate the analytical procedure developed for routine analyses. In many cases, the use of commercially available certified reference materials (CRMs) for standards preparation seems to be a reasonable approach. If a suitable reference material, matched to sample matrix, is available, it can be

directly used as external standard or spiked with selected elements chose for internal standardization, and/or mixed with a binder, e.g. polyethylene powder [38; 50; 51; 52; 53; 54; 55; 56; 57]. Such preparation procedure was applied by Pakieła et al. [58] for analysis of soils, sediments and ashes samples. The standards were prepared by mixing powdered solids reference materials with two binders - zinc oxide and 2-methoxy-4-(2-propenyl)phenol. Zinc 2-methoxy-4-(2-propenyl)phenol complex immobilized the powdered materials and improved homogeneity of the pellets. The determination coefficients of calibration lines obtained this way were at the level of 0.99. Average recovery for Mn, Co and Pb determined in BCR 143R soil versus RM8704 river sediment was 100 ± 2%.

Standards prepared on the base of CRM can be modified in order to improve signal sensitivity. O'Connor et al. [59] prepared mechanically stable discs made from pressed powdered CRMs with modified absorption coefficients. To change the absorption, three powdered organic binders - vanillic acid, pyrazinoic acid, and nicotinic acid, all with high optical absorption at the wavelength of laser energy (213 nm), were tested and each one was admixed to the CRMs according to two methods – simple grinding in a mortar and with a use of a MM200 mixer mill. Results showed that samples with vanillic acid had the highest absorbance and thus LA-ICP-MS sensitivity (three-fold gain). The vanillic acid binder yielded a considerable improvement of precision (more than triple lower RSD) when analyzing sample and standard that differs greatly in terms of matrix composition (soil or sediment and milk powder).

Garbe-Schönberga et al. [60] recently proposed a new method for producing nano-particulate pressed powder pellets towards LA-ICP-MS applications. Natural rock powder reference material was milled according to the optimized wet-milling protocol in aqueous suspension with a use of high power planetary ball mill and agate tools, resulting in an average grain size d_{50}<1.5μm, which provide satisfactory cohesion and homogeneity. Such prepared material was pressed into pellets. Precision of analysis of natural rock CRMs with nano-particulate powder pellets, used for calibration, was in the range of 2-5% RSD.

If concentration of analytes in the certified reference materials differs from this expected in the sample, analytes of interest can be added to cover desired concentration range [37; 61, 62]. Such method was examined by Brown et al. [39] for the analysis of ambient particulate matter by LA-ICP-MS. The authors compared three calibration approaches including the use of cellulose ester filters spiked with multi-element calibration solution; pellets of ambient particulate matter CRM pressed with mixture of graphite powder and Mowiol solution (polyvinyl alcohol) as a binder; and the same powdered CRM adhered to the

surface of a metal disc. It was found out that spiked filters used as standards gave more reproducible results than those based on powdered CRM and thus could be used in LA-ICP-MS for correcting drifts or as an indirect calibration material.

Comparison of Ti minerals analysis calibration based on natural reference materials and synthetic standards was presented by Ødegård et al. [63]. Ilmenite, rutile, and a Ti-rich magnetite CRMs were exploited as natural Ti-containing minerals, but synthetic standards consisted of $FeTiO_3$ and TiO_2 matrixes spiked with minor and trace elements. Standards were prepared by direct fusion in graphite electrodes and used for calibration in LA-ICP-MS measurements. Synthetic materials based on TiO_2 matrixes turned out to be homogeneous and compact. For natural materials, segregation and separate phases formation were observed.

Traub et al. [64] prepared synthetic matrix-matched standards by spiking CRM powders of Cu and Zn with a multi-element standard solution, drying with IR-radiation, homogenizing and finally pressing into pellets. Analysing different Cu or Zn based materials, depending on analyte, relative result deviations below 10% were obtained. This calibration method was compared to a dual flow system, where standard solutions of copper and zinc were aspirated by a concentric 100 μL/min microflow nebuliser and admixed to an ablated aerosol in front of the ICP-MS. This resulted in up to 50% relative deviations, depending on the plasma conditions.

Method for fabrication of solid calibration standards by a sol-gel process towards Se and S determination was described by Fitzpatrick et al. [65]. Xerogel standards were analysed by LA-ICP-MS against several reference materials including sulphide minerals, synthetic sulphide, SRM 610 and 612. Heterogeneity of Se in the xerogel was found similar to that in NIST SRM 610, but variation in S local concentration was greater than in SRM 610. Established S content in NIST 612 analysis using xerogel standards was incomparable with its certified values. Xerogels used as standards for S and Se determinations in materials like sulphides do not produce accurate results, but can be applied for analyses calibration of glasses and samples of silicate matrix with low concentrations of analytes. Similar technique of calibration, exploiting xerogel based standards for trace elements analyses of solid samples by LA-ICP-MS was presented by Viger et al. [66]. The authors checked xerogel standards analysing Pb in NIST 1632c Bituminous Coal and obtained precision in the range of 5-8% RSD.

Another method of standard preparation was proposed by Hirata et al. [67]. To obtain standards of different Mn concentration authors diluted geological ferromanganese reference material JMn1 with MnO_2 powder. These standard components were mixed in a few JMn1 to

MnO_2 weight ratios, homogenized in an agate mortar and pressed by a hand-press into pellets. The correlation coefficients of obtained calibration curves for 15 isotopes were mostly better than 0.99. The authors concluded that this simple dilution method can be applicable to the high-spatial-resolution analyses of ferromanganese nodules.

4.1.2 Synthetic standards based on the main sample matrix component

To assure sample and standard matching often the main sample components are used as a base for the standard preparation [68].

Bellotto and Miekeley [36] prepared solid multi-element standards by co-precipitation of twelve elements with a $CaCO_3$ matrix for the trace elements determination in mussel shells or carbonate-based materials. Such spiked powders were pressed into a mechanically stable standard discs without addition of a binder. The authors discovered that co-precipitation of elements with the matrix appeared to be a better method for preparation of homogenous calibration standards than mixing them (in carbonate or oxide form) with the matrix ($CaCO_3$) or adding the standard solutions to a carbonate powder base. The correlation coefficients for all determined elements were better than 0.997. A similar preparation technique of matrix-matching standards based on hydroxyapatite for analysis of dorsal fish spine was used by Ugarte et al. [69]. The hydroxyapatite enriched standards were found to be homogeneous and provided a linear calibration curve with average coefficient better than 0,99. The reproducibility of results obtained for hydroxyapatite pellets and NIST 612 was below 20% RSD.

Dewaele et al. [70] investigated a modified welding technique for the production of artificial sulphide crystals as a matrix-matched external standard for quantitative determination of the trace elements in natural hydrothermal pyrite by LA-ICP-MS. Standards were prepared by resistance heating of pyrite powder, cleaned with isopropanol, and spiked with approximately 0.01g of pure elements (also in the form of powder) in graphite electrodes. For most elements of interest sufficient homogeneity was obtained with RSD below 15%. Similar methods can be used to produce matrix-matched sulphide standards for the LA-ICP-MS analysis of sulphides.

For hair analysis calibration Cheajesadagul et al. [71], to simulate hair matrix, extracted keratin proteins, prepared a keratin films and doped them with Pb standard solution. Such obtained standards were used for calibration parallel with Pb-enriched hair strand standards, prepared by soaking of hair wisp in Pb standard solution of various concentrations. The correlation coefficients of calibration curves were 0.9998 and 0.9851 for Pb doped keratin

films standards and Pb-enriched hair strand standards, respectively. Although both materials seemed to be a good matrix-matched standard for Pb determination in hair, low homogeneity was found in the case of Pb-enriched hair strand standards, with RSD higher than 20%. The method has a potential to become useful for other, than Pb, elements determination.

4.1.3 Matrix-matched standards based on spiked sample material

Matrix-matched calibration enables accurate quantification without the need to correct bias errors caused by matrix effects. This means that signal intensity is no longer dependent on the mass sampled by the laser radiation. General preparation procedure of matrix-matched standards with a use of solid sample material includes milling of a sample material, spiking it with suitable elements, drying, if necessary, and pressing into a pellet [72, 73].

Such method was applied by Hanć et al. [34] for the analysis of element migration in human teeth. Portions of the milled tooth material were spiked with multi-element standard solution, dried, and pressed into a pellet. Measurement precisions, established using the standard material, were as follow: 4.2% for Al, 2.7% for Ba, 2.1% for La, and 2.8% for Sr. This study demonstrated the ability of LA-ICP-MS in trace element profiling to achieve a good analytical precision and accuracy of quantitative determination of selected elements.

LA-ICP-MS except for described above analyses has been also exploited for elemental mapping especially of human or animal tissues. In this case, matrix-matched standards are generally prepared with the use of portions or slices of original or very similar tissue, spiked with elements of interest [29; 74; 75; 76; 77; 78; 79; 80].

Such procedure was applied by Jurowski et al. [81; 82] for selected elements mapping in a rat brain tissue. In this research, brains were collected from male rats, that were bred under standard laboratory conditions of lighting, temperature, and feeding (Standard RM1A (P), Merazet; Poznan, Poland). Whole rat brains were homogenized in an agate mortar and spiked with multi-element standard solution to provide assumed concentrations of selected elements. After freezing at -14 ^{o}C, standards were cryo-cutted into slices of 20 μm. The resulting slices were shifted from the cryostat with a brush, placed on a microscope slides and stored in a refrigerator until the day of analysis at −14 ^{o}C. The correlation coefficients obtained for all determined elements were better than 0.99. The authors presented a series of conclusions concerning standard sample preparation procedure and the extrapolative method that was applied in the study. Slightly different procedure was presented by Sela et al. [83]. In this case, rat brains were ground, spiked with aqueous standard solutions of selected elements, and finally encapsulated in silica gel using a sol–gel method with tetraethyl orthosilicate

(TEOS). The objective of the production process was to obtain homogeneous and stable standards with a long shelf life. The correlation coefficients of the calibration curves for all elements were better than 0.97. Brain tissue was also analysed by Reilly et al. [84]. However, the authors proposed a novel preparation procedure, described below, for matrix-matched standards. Slices of sheep brain, mounted on glass slides, were prepared by horizontal immersion in standard methanol solution containing different amounts of Fe and Rh, used as internal standard, for 30 minutes. Prepared standards were stored at room temperature until analysis. Relative standard deviations of 8.3% and 4.7% were obtained for ^{56}Fe and ^{103}Rh, which suggests that both elements are distributed homogenously in the matrix-matched standards. Influence of storing conditions were examined and the lowest RSDs (10% for 5 mg·kg^{-1} Fe and 3% for 20 mg·kg^{-1} Fe) were obtained for standards stored at room temperature. For real samples analyses, the precision of the Fe imaging data (0.1–13%) obtained with normalisation to ^{103}Rh was much better than that obtained without internal standard correction (1–49%).

For the determination of zinc (^{66}Zn) and copper (^{63}Cu) in biological soft tissues (chicken breast), Austin at al. [42] proposed a method of calibration based on standards prepared in the form of a polymer film of polymethylmethacrylate (PMMA) formed onto quartz substrate spiked with standard solutions of the analytes. Calibration curves yielded correlation coefficients better than 0.999 for both elements. Spiked homogenised chicken breast slices were analyzed by LA-ICP-MS against the described film standards. The results were in good agreement (below 2σ) with the values obtained from solution nebulization ICP-MS.

Becker at al. [26] used LA-ICP-MS to quantitatively image metals distribution in plant tissues. For calibration of two-dimensional imagining of Mg, Fe, Mn, Zn, Cu, Cd, Rh, Pt and Pb in tobacco parts, the authors applied standards prepared on the base of dried powdered tobacco leaves of known amount of water. The portions of the dried tobacco leaves were spiked with increasing amounts of the analytes, producing standards of concentrations from 5.3 to 106 μg·g^{-1}, then fixed on glass slides using glutaraldehyde and analyzed. The authors observed that standards deposited on the glass slides cracked and pulverized during the ablation process if the water content was 40% or lower. The linear correlation coefficients of the calibration curves ranged from 0.985 (for 63Cu) to 0.999 (for Pt).

Stärk and Wennrich [85] proposed standards made of agarose gels spiked with multi-element standard solution, prepared in the form of a thin film on the glass microscope slide for calibration LA-ICP-MS analysis of cell cultures. The distribution of analytes in the gel was quite homogenous with 7.5% RSD of the intensities. The detection limit estimated on the

base of calibration curve was 5pg·mm^{-2}. Recovery for most of the elements after acid digestion of the gel was near 100%.

4.2 Calibration without matrix-matched standards

Matrix-matched standards are hugely recommended for calibration in the case of laser ablation sampling, as it was presented earlier in this paper, but their preparation is laborious and add unnecessary complexity for fast and rather simple analyses. Although the sample preparation step is significantly limited, quantification becomes the most time-consuming stage of the LA-ICP-MS technique [86].

Omitting different ablation behaviour between samples and standards, rather simple calibration strategy based on commercially available reference materials, usually NIST reference glasses, can be applied to analyses of different solid samples [35]. Souders and Sylvester [87] demonstrated that precise and accurate data about lead isotopes ratios can be obtained by LA-MC-ICP-MS analyses for feldspar and sulphide containing little to no mercury using just silicate glasses as an external calibration standard, even though these matrices behave differently during the ablation process. The results of LA-MC-ICP-MS measurements were in good agreement, within 0.40%, with those obtained by TIMS (thermal ionisation mass spectrometry) and precision was better than 0.60% RSD. Because for some samples, like mussel shells, matrix-matching can be difficult, Phung et al. [88] decided to use several solid reference materials (NIST SRMs glass and MACS-1 carbonate standards) for calibration, on the assumption that fractionation effects occurring when ArF excimer laser is used does not affect the final results. Obtained accuracy and precision of the ultra-trace determination results were, according to the authors, insufficient.

Since rapid laser pulses were proved to limit fractionation effects, the potential of femtosecond laser ablation for direct solid sample analyses with no matrix-matched calibration was reviewed by many authors [13; 89; 90; 91]. Fernández et al. [11] summarized a variety of examples for elemental and depth-profiling analyses of solid samples by fs LA-ICP-MS in biological, geological, and materials applications. The authors stated that application of femtosecond pulses leads to higher ablation efficiency, excellent lateral and in-depth resolution, narrow particle size distribution, and finally improvement of precision and sensitivity.

4.2.1 Solution based calibration of LA analyses

The lack of suitable CRMs, time-consuming preparation of ‘laboratory made’ standards and their limited homogeneity lead to increase work on application of aqueous standard

solutions for LA-ICP-MS analyses calibration. Despite typical drawbacks, wide availability and simply handling keep standard solutions in a focus of attention for laser ablation applications. Generally three strategies can be applied for solution-based calibration: external calibration - if a matrix-matched blank is available; the analyte addition technique - if no blank sample exists; and the isotope dilution technique for small sample amounts. Excessive mass loading based on simultaneous liquid aspiration (wet plasma) can help to perform more reliable analyses of laser-produced aerosols.

Calibration with an aid of standard solutions is conducted according to two main methods – with a single and dual gas flow systems. In the first approach, ultrasonic or microconcetric nebulizer is coupled to the laser ablation chamber, or even mounted inside it, which results in mixing of ablated sample and desolvated standard solution [92; 93; 94]. The main advantage of this arrangement is a better possibility of optimizing both gas flow rates separately.

The example of application of single flow gas system was presented by Pickhardt et al. [95] for multi-elemental determination in geological samples. For this aim, an ultrasonic nebulizer (USN) was coupled with a laser chamber and then with an ICP torch inlet. In order to arrange matrix matching, the standard solutions were nebulized and mixed simultaneously with an aerosol of a blank target, such as lithium borate, ablated by a focused laser beam. Homogeneous samples were prepared from geological material by powdering, homogenizing, and fusing with a lithium borate mixture in a muffle furnace at 1050 °C. LA-ICP-MS with solution-based calibration provided analytical results with deviations of 1–13% from the reference values for most of the elements. Correlation coefficients of calibration curves were better than 0.998 for U, Ba and Sr.

In the second approach, standard solution after nebulization and laser-ablated sample material are transported separately and mixed in a y-piece junction before they are introduced into the ICP [46].

Such method was applied by Dressler et al. [96] for monitoring of essential and toxic metals in single hair. The authors applied a dual argon flow of the carrier and nebulizer gas to carry a dry aerosol produced by laser ablation of hair sample and a desolvated aerosol of standard solution generated by pneumatic nebulizer. Human hair strands were ablated simultaneously with a nebulization of liquid standards. The linear correlation coefficients of calibration curves for all analytes were between 0.970 and 0.999. The limits of detection for most of the elements were in the range of 0.001–0.900 $\mu g \cdot g^{-1}$.

Kovacs et al. [97] used solution standards and solid standards based calibration for the characterization of two solid gold calibration materials (NA1 and NA2) by fs and ns LA-ICP-MS for fingerprint studies of Peruvian gold objects. Standard solutions were prepared by transferring Ag into a chloro-complex, mixed with standard solutions of elements of interest, and diluted with hydrochloric acid. The aerosol from a self-aspirating concentric PFA microflow nebulizer, and the aerosol from ablation by a femtosecond laser transported in He were mixed in a glass Y-piece injector in front of the ICP. The solution calibration provided precise (<5%) and accurate (<8%) concentrations for most of the elements in NIST solid gold CRMs.

The most straightforward approach would be to perform a simple external solution calibration without the use of additional nebulizers. Few authors made an attempt to analyze liquid samples just with laser ablation method of sampling and with a use of standard solutions for calibration, but the number of papers concerning solid samples analyses this way is very scarce. An example of such work was presented by Boué-Bigne et al. [98]. Since application of standard solutions for LA-ICP-MS calibration is also limited by differences in solid and liquid material laser beam absorption - aqueous standards exhibit lower laser beam absorption than solids – the authors tried to minimize this effect by using aqueous standards with modified absorption coefficients that could improve ablation yielding. To evaluate the conditions of producing dry plasma, the authors ablated a solution containing 9.2 $g \cdot L^{-1}$ of poly-(sodium 4-styrenesulfonate) and estimated the amount of water being transported to the plasma. This solution concentration was chosen as producing beam absorption similar to that of NIST SRM 613 glass. In order to obtain a stable ablation yield, the selected chromophore should present a relatively flat absorption at the laser wavelength, otherwise, it needs to be stabilized by the use of quenchers. For the 266 nm wavelength authors recommend 2-thiobarbituric acid with an absorption coefficient ε_{266}=80 $L \cdot g^{-1} \cdot cm^{-1}$ and maximum solubility in acid solution equal to 4 $g \cdot L^{-1}$. Calibration curves produced using the aqueous standards were linear and reproducible, with correlation coefficients better than 0.993. NIST SRM 613 Trace Elements in Glass and low density polyethylene were analyzed as real samples. Precision of obtained data for polyethylene samples were below 8% RSD for Mg, Cr and Pb, and 17,6%, 61,2% for Zn and Sb, respectively. High RSD value for Sb indicates inhomogeneous distribution of this element in the samples. The results for NIST 613 glass material were in good agreement, approximately $\pm 1\sigma$, with certified values.

For liquid samples analyses, concretely water and blood, a method was recently presented by Hsieh et al. [99; 100]. Procedure of standards preparation was based on placing

droplets of standards and samples onto the filter, drying them and ablating thin dry spots by laser. The correlation coefficients of calibration curves, obtained for several elements determined in water, ranged from 0.9920 to 0.9998. The precision of results obtained for blood analysis was less than 5.7% RSD for all elements, except for Be and Mn (8.6% and 11.1%, respectively).

4.2.1.1 Application of the isotope dilution technique

Laser ablation method of sampling coupled with isotope dilution quantification in mass spectrometry, ignoring the cost of spikes, has the capability to become a very effective technique for accurate and precise quantitative determination of many trace elements. If analyte and its enriched isotope in standard are similarly distributed in the spiked sample, the application of the isotope dilution can significantly limit some fractionation effects [9].

The isotope dilution was recently applied by Yang et al. [101] who used a dual flow gas system and solution standard to determine the boron content in silicon wafers. On-line laser-ablated sample aerosol was mixed with a boron aerosol produced by a conventional nebulization of an enriched (^{10}B) standard solution (SRM 952, NIST) in front of the ICP. This system accurately quantified boron in silicon wafers without the need for an internal or external solid reference material. The relative standard deviations of all of the individual determinations were less than 14%.

Single flow systems and isotope dilution technique were exploited by Pickhardt et al. [102] and Becker et al. [86]. In the first paper, the authors proposed an easy and rapid quantification procedure based on a new arrangement with a microflow nebulizer inserted in the laser ablation chamber. This design allowed quantification with the use of an isotope enriched standard solution (^{235}U/^{238}U: 0.5465) nebulized to the laser-ablated sample material. The arrangement was tested on two types of sample material (NIST SRM 612 glass and 1515 apple leaves reference materials). The precision of measured isotope ratios was about 1.90% and 1.41% RSD for glass and apple leaves, respectively. In the second study, an isotope-enriched (^{204}Pb) solution was nebulized using the microconcentric nebulizer with Aridus desolvator along with ablation of NIST SRM 681 platinum material. By means of LA-ICP-MS using solution calibration with the isotope dilution technique, a value of 13.1±1.1 mg·g^{-1} was determined for Pb in NIST 681 (certified value: 12±2 mg·g^{-1}).

4.2.2 Application of standard reference glasses

Reference glasses are often regarded as nearly ideal reference material for LA-ICP-MS calibration, especially in the field of geological studies. They can be relatively easily prepared

in the laboratory, containing all of the necessary elements homogenously distributed, with the suitable concentration range [95]. Commercially available and well characterized NIST reference glasses (SRM 610 – 617) are widely exploited for external calibration towards LA-ICP-MS application [51; 87, 88; 103; 104; 105; 106; 107; 108; 109].

Method for multi-element analyses of geological samples fused with lithium-tetraborate and calibrated against NIST SRM glass standards were proposed by Günther et al. [35]. Sample fused with $Li_2B_4O_7$ creates glassy discs with a high degree of reproducibility suitable for a quantitative LA-ICP-MS analysis of major and trace elements. The obtained values for the analysis of geological reference materials were compared with consensus literature values and satisfactory agreement was found. The reproducibility of the method was better than 10% for concentrations above 1 mg/g and better than 15% for the lower concentrations. The use of Li as the internal standard offers the possibility of multi-element determinations in unknown geological samples, but the authors found that application of the lithium-tetraborate stoichiometry for the calculation of the Li concentration leads to a constant deviation from the recommended values. Determining of the Li concentration in each sample batch using at least one lithium tetraborate fused geological reference material is necessary.

Yuan et al. [110] established a new procedure for sulphide minerals analysis by LA-ICP-MS using glass reference materials as distinct from Dewaele et al. [70]. Analyzed materials included different NIST reference glasses and synthetic sulphide reference minerals. In addition, internal standardization and matrix normalization method were applied. Relative errors of concentration of major elements were less than 20%. Values of concentration for major, and most trace elements in 12 sulphide minerals determined with NIST SRM 610 used for external calibration, were in a good agreement with certified values and EMPA results.

Although NIST glass standards are very popular, especially for the analyses of geological materials, in some cases they do not cover all of the requirements of the actual matrix or range of analyte concentrations. For that reason, new ‘home-made’ glass standards are still being produced. Different techniques for the preparation of homogeneous targets based on the use of glass standards e.g. direct fusion of rocks, have been described in a review paper by Pickhardt [95]. Detailed procedure of production of a new series of glass standards, containing 45 elements, and their evaluation by comparing with NIST SRM 612 glass was presented by Raith et al. [18].

5. Conclusion

The main purpose of this article is to present a comprehensive but also up to date review of the most useful calibration approaches for the laser ablation technique. The second purpose is to present the virtues and disadvantages connected with the application of laser ablation sampling.

Fifteen years ago Longrich et al. [111] wrote that "the major challenge to the use of laser ablation sample introduction, combined with inductively coupled plasma mass spectrometry, is the problem of calibration". Since then significant progress has been made towards understanding of the ablation process, nevertheless for quantitative analysis the conclusion is still valid to some extent. External calibration with certified reference materials can match a sample matrix, but this is limited by the type of the sample and the range of element concentrations. Also there is a concern about the differences in ablation behaviour between the sample and standard. Laboratory prepared "in-house" or "home-made" standards seem to be the most suitable option. Since they are made from the sample material and spiked with either a standard solution of elements of interest or solid reference material, it is more probable that during interaction with a laser beam and later in the ICP-MS they will act similarly to the real sample. However their homogeneity is for many cases questionable.

In this paper, the authors put an effort in systematize methods of calibration and related standards preparation used for LA-ICP-MS analysis. The usefulness and limitations of the techniques were discussed based on examples of applications. Methodologies were considered that were not strictly dependent on the type and class of instrument (both, laser or mass spectrometer).

Looking on the variety of calibration protocols, standards preparation techniques (matching matrix or not) and scope of applications, it is difficult to rate particular solution. Generally, all propositions fitted for purpose and authors obtained satisfactory results. It shows that for individual research different achievements are sufficient and different labour-consumption is acceptable. Moreover, no one shall judge the methods by comparing selected parameters with those obtained by wet analyses with isolated analyte or adjusted matrix, at least towards the main interferent.

There are still specific issues of LA-ICP-MS that need further investigation and improvements, especially calibration procedures. Nevertheless, the great potential of laser ablation technique will surely provide more established applications for solid sample analyses in the immediate future.

6. References

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