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External calibration strategy for trace element quantification in botanical samples by LA-ICP-MS using filter paper

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HIGHLIGHTS

- Filter paper embedded with reference solution is proposed as solid standard for multielemental analysis by LA-ICP-MS.
- Accuracy of the method was validated by the analysis of different species of botanical CRMs and samples.
- Use of ^{13}C as IS in LA-ICP-MS analysis resulted in improved accuracy and precision.

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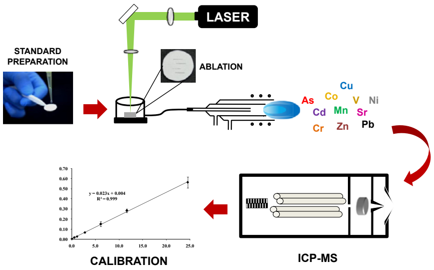
GRAPHICAL ABSTRACT



ABSTRACT

The use of reference solutions dispersed on filter paper discs is proposed for the first time as an external calibration strategy for matrix matching and determination of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn in plants by laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). The procedure is based on the use of filter paper discs as support for aqueous reference solutions, which are further evaporated, resulting in solid standards with concentrations up to 250 $\mu g\ g^{-1}$ of each element. The use of filter paper for calibration is proposed as matrix matched standards due to the similarities of this material with botanical samples, regarding to carbon concentration and its distribution through both matrices. These characteristics allowed the use of ^{13}C as internal standard (IS) during the analysis by LA-ICP-MS. In this way, parameters as analyte signal normalization with ^{13}C, carrier gas flow rate, laser energy, spot size, and calibration range were monitored. The calibration procedure using solution deposition on filter paper discs resulted in precision improvement when ^{13}C was used as IS. The method precision was calculated by the analysis of a certified reference material (CRM) of botanical matrix, considering the RSD obtained for 5 line scans and was lower than 20%. Accuracy of LA-ICP-MS determinations were evaluated by analysis of four CRM pellets of botanical composition, as well as by comparison with results obtained by ICP-MS using solution nebulization after microwave assisted digestion. Plant samples of unknown elemental composition were analyzed by the proposed LA method and good agreement were obtained with results of solution analysis. Limits of detection (LOD) established for LA-ICP-MS were obtained by the ablation of 10 lines on the filter paper disc containing 40 μL of 5% HNO_3 ($v\ v^{-1}$) as calibration blank. Values ranged from 0.05 to 0.81 $\mu g\ g^{-1}$. Overall, the use of filter paper as support for dried aqueous standards showed to be a useful strategy for calibration and plant analysis by LA-ICP-MS.

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1. Introduction

The development of vegetables requires a complex balance of mineral nutrients to grow and reproduce successfully [1]. Besides the uptake of essential macro and micronutrients, metal toxicity is also observed and originates from soil contamination, mining industries and agriculture. Heavy metals, such as Cd, Cu, Pb, Cr and Hg can accumulate in plants being further introduced in the food chain. In this way, the determination of metals content in plants is of nutritional, toxicological and environmental concern [2].

Several analytical methods are available for determination of major, minor and trace elements in plants and most of spectrometric techniques require a previous mineralization step [3–5]. Sample preparation procedures employed for this kind of matrix are usually simple, but acid digestion methods are sometimes related to be time consuming and prone to analyte loss or cross contamination, when compared to direct solid analysis techniques [6–8]. Furthermore, a considerable amount of acid is required, producing laboratory residue. In this sense, atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) have been coupled to sample vaporization/atomization sources, such as electrothermal vaporization (ETV) and laser ablation (LA) [9,10].

Laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS) is a powerful technique that combines the high sensitivity and multielemental capability of ICP-MS with good spatial resolution and direct introduction of solid samples provided by laser radiation [10,11]. The analysis by LA-ICP-MS enables the use of samples in μg level, with sample consumption in the range of pg to fg [12,13].

Obtaining reliable quantitative information from LA-ICP-MS analysis is a challenging task, mainly due to the restrictions regarding to elemental fractionation, matrix properties and transport efficiency of the ablated material, which affect the plasma stability and signal response during the uptake of different sample materials [14–17]. In order to overcome these drawbacks, the development of different quantification strategies have been described for a variety of matrices, such as geological [18], biological [19,20], botanical [21] and others, and the use of solid matrix matched reference materials are mentioned [22,23].

Since the number of solid reference materials from distinct matrices is limited, the development of suitable standards and the establishment of reference elements for standardization are described in literature and consists in preparing in-house matrix matched standards, such as certified reference materials spiked with selected elements [21,24,25] or synthetic standards based on the main sample component [26–28].

Reference elements or internal standards (IS), as they have been denominated, are used either in ICP-MS or LA-ICP-MS analyses in order to promote an improvement in precision and accuracy and the choice of a suitable element to be used for signal normalization should attend some requirements for a satisfactory correction, such as homogeneous distribution in sample and standard; absence of spectral interferences, and correction for any bias during the measurement [29]. Regarding to the analysis of botanical samples by LA-ICP-MS, it has been successfully applied to bark [30], roots [31,32] and leaves [33–35], where the use of ^{13}C is mostly reported as IS due to its considerable concentration and relatively homogeneous distribution, employing the distinct calibration strategies mentioned before.

Besides the use of reference solutions to enrich solid standards, some inert supports have been recently evaluated for deposition and dispersion of aqueous standards, such as PTFE, glass slide and filter paper [36]. Filter paper discs as support for analyte have been recently used for analysis of biological fluids [37–39], tissues [14,40] and liquids [41], but despite the matrix similarity between cellulosic material and botanical structures, filter paper has not yet been evaluated for calibration in LA-ICP-MS for further analysis of plants. In order to compensate differences in the amount of material ablated from standards and samples, in this work ^{13}C was used as internal standard element due to its similar concentration in a pure cellulose material (about 45% m m^{-1}) and the average content in plant tissue (44.5% m m^{-1}) [42].

In this way, we developed a new calibration strategy procedure for quantification of As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Sr, V and Zn in samples of botanical origin by LA-ICP-MS. The quality assurance of results was established by the application of the proposed method to the analysis of botanical certified reference materials and samples. To our knowledge, this is the first work that describes the use of analyte solution on filter paper discs as matrix matched standards for reliable analysis of powder plants.

2. Experimental

2.1. Reagents and standards

Ultrapure water (>18 MΩ cm) was obtained in a Milli-Q system (Millipore Corp., USA) and was used for material cleaning and solutions preparation. Concentrated HNO_3 (65% m m^{-1}, Merck, Germany) was purified in a sub-boilling system (Milestone, Model Duopur, Italy). Multielemental reference solutions containing 10 mg L^{-1} (SCP 33 MS, SCP Science, Canada) and 1000 mg L^{-1} (Certipur® Merck IV, Merck, USA) were used for calibration in ICP-MS and LA-ICP-MS, and dilutions were prepared in 5% HNO_3 (v v^{-1}). Certified reference materials from National Institute of Standards and Technology (NIST 1515 – Apple Leaves and NIST 1575 – Pine Needles, Gaithersburg, USA), and from Community Bureau of Reference (BCR 60 – Trace Elements in Aquatic Plant and BCR 62 – Trace Elements in Olive Leaves, Brussels, Belgium) were used for evaluation of accuracy and precision of the method.

2.2. Samples

Besides the CRMs, two botanical samples with unknown composition were analyzed by the LA-ICP-MS method. Leaves of *Passiflora edulis* (passion fruit) and *Illicium verum* (star anise) were acquired in the local market. Samples were dried for 2 h at 80 °C and milled (analytical mill, IKA A11, Germany) prior to the analysis, in order to obtain a homogeneous particle size distribution.

2.3. Sample and standard preparation for LA-ICP-MS analysis

About 350 mg of each powdered sample or CRM were pressed for 3 min at 10 ton into 13 mm diameter pellets using a manual hydraulic press (Specac, UK).

For calibration by LA-ICP-MS, ash-free filter paper discs (Schleicher & Schüll, Nr. 5891, Germany) of 17 mm diameter were previously decontaminated in 10% HNO_3 (v v^{-1}) and dried at room temperature in a laminar bench (class 100, CSLH-12, Veco, Brazil). Before the addition of reference solution, filter paper discs were weighed in a microbalance with resolution of 0.001 mg (M2P, Sartorius, Germany). A fixed volume of multielemental reference solutions from 0.1 to 10 mg L^{-1} was directly transferred with a micropipette onto the surface of the disc. The paper disc was then dried at 80 °C for 2 min in an infrared apparatus (Spectral Systems, Germany), with the aid of a polytetrafluorethylene tweezers. The dried disc was placed on a glass support and fixed with a double-sided tape and put inside the laser ablation cell.

Correspondent analyte concentration (in μg g^{-1}) on each filter