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Quantitative analysis of trace elements in environmental powders with laser ablation inductively coupled mass spectrometry using non-sample-corresponding reference materials for signal evaluation

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ABSTRACT

Laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) is an attractive alternative to traditional procedures for the analysis of environmental samples (i.e., conventional liquid measurement after sample digestion). However, for accurate quantification, certified reference materials (CRM) are necessary which match the composition of the sample and include all elements of interest at the required concentration levels. The limited availability of appropriate CRMs hampers therefore substantial application. In this work, an LA-ICP-MS procedure allowing for accurate determination of trace element contents in powdered environmental samples is presented. For LA-ICP-MS analysis, the samples are mixed with an internal standard (silver oxide) and a binder (sodium tetra borate) and subsequently pressed to pellets. Quantification is accomplished using a calibration function determined using CRMs with varying matrix composition and analyte content, pre-treated and measured in the same way as the samples. With this approach, matrix-induced ablation differences resulting from varying physical/chemical properties of the individual CRMs could be compensated. Furthermore, ICP-related matrix-effects could be minimized using collision/reaction cell technology. Applicability of the procedure has been demonstrated by assessment of Cd, Cu, Ni, and Zn in four different environmental CRMs (NIST SRM1648a (urban particulate matter), NIST SRM2709 (San Joaquin Soil), BCR144 (sewage sludge), and BCR723 (road dust)). Signal evaluation was performed by alternative use of three CRMs for calculation of the calibration function whereas the remaining fourth CRM acted as unknown sample, resulting in a good agreement between measured and certified values for all elements and reference materials.

1. Introduction

Laser ablation mass spectrometry with inductively coupled plasma (LA-ICP-MS) has become a very powerful technique for direct analysis of trace metals in solid samples [1–3]. The main advantages of this technique are the combination of easy access to solid samples without extensive preparation steps and the high sensitivity of ICP-MS necessary for trace element analysis. By direct measurement of the solid sample, disadvantages related to conventional liquid ICP-MS analysis can be avoided. Namely, complex and often time-consuming sample digestions, as well as related problems like analyte losses or sample contamination during pre-treatment are circumvented when using solid sampling techniques. Another major benefit of LA-ICP-MS using “dry plasma” conditions is a considerable decrease of solvent-related interferences [4–8]. However, for analysis of powdered samples such as ash, dust, or soil, the sample has to be transferred into a suitable form for LA. This can be done by fusing [9], pelletizing [10–12], or embedding [13–16] the powder in an appropriate matrix. All of these techniques can be applied to meet the analytical needs.

Although LA is without doubt an attractive technique for direct solid sampling with ICP, accurate sample quantification remains a challenging task. Matrix composition greatly influences the interaction between laser beam and sample affecting the quantity/size of generated particles/aerosol. Furthermore, quantification is not easily achieved due to differences during sample ablation (nonstoichiometric generation of vapor species), variations in transfer efficiency (sedimentation and/or recombination of aerosol), and differences in ionization efficiency in the plasma (aerosol composition/cooling effects, particle size/fragmentary atomization, plasma load) [4–7]. Although some effects can be minimized with the use of femtosecond lasers instead of nanosecond lasers [2,17], certified reference materials (CRMs) with a matrix matching the composition of the samples are often required for reliable quantification.

Although many CRMs are available, the differences in sample composition prove to be a limiting challenge [18]. O'Connor et al. [8,10] emphasized that if the standard composition differs even slightly from the sample, no reliable information can be achieved. Even if there is a CRM with matching matrix composition available, also analyte concentration needs to be in the same order of magnitude. When the analyte

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concentration in the standard varies too much from the sample, quantification is possible although accuracy will be limited. In the analysis of environmental samples (e.g. airborne particulate matter), this problematic is of special importance, since contents of the investigated target analytes may vary over some orders of magnitude while available CRMs cover only limited concentration ranges. A further crucial aspect of CRMs is the limited number of elements with certified concentrations. Thus, besides sample type, also the elements of interest and their respective concentration levels have to be considered. To overcome differences in matrix and analyte composition of CRM and sample, several approaches have been reported. Some effects can be compensated using an internal standard if a feasible matrix element is available or can be added during sample preparation [9,19,20]. Another possibility is to introduce nebulized liquid standards or aerosols mixed with the ablated aerosol into the ICP [21]. Other strategies focus on preparing matrix-matched standards by pelletization [22–25] or fusion [26]. Also approaches based on mathematical ratio calculation can be used as is common for geological samples [27]. However, not all of the before-mentioned aspects can be tackled using most of these quantification methods. A detailed discussion of advantages and drawbacks of frequently applied quantification strategies in LA-ICP-MS analysis of powdered samples has been presented recently [28]. Nevertheless, for the successful application of the mentioned approaches, a CRM is required which matches sample composition and analyte contents closely, a prerequisite which is not fulfilled for all sample types in the field of environmental sciences.

In this work, we present a method for signal quantification in LA-ICP-MS analysis of trace elements in powdered environmental samples using initially non-matrix matched CRMs. Preparation of pellets using a binder material and an internal standard helped to compensate differences in the physical properties of the used calibration standards leading to reduced variations in ablation and transport efficiency. Moreover, matrix-induced spectral interferences such as polyatomic ions were overcome by using collision/reaction cell technology for q-ICP-MS analysis. With this combination, the establishment of a cross matrix calibration with CRMs of different origin was possible. The developed procedure allowed accurate quantification of Cd, Cu, Ni, and Zn in different environmental CRMs (fly ash, soil, dust, urban particulate matter).

2. Experimental

2.1. Chemicals and consumables

All chemicals applied for pellet preparation (sodium tetra borate, caffeic acid, silver oxide) were purchased from VWR, Germany, or Sigma–Aldrich, USA, with highest available grade. NIST SRM1648a (urban particulate matter) and NIST SRM2709 (San Joaquin Soil) as well as EC JRC IRMM certified reference material BCR144 (sewage sludge) and BCR723 (road dust) were used as samples or standards for signal quantification. Powder mixtures were prepared and stored in 50 mL centrifuge vials from Sarstedt, Germany, and in 2 mL micro reactions vials (Eppendorf vials) purchased from VWR, Germany.

2.2. Instrumentation

A standard Nd:YAG nanosecond laser ablation system (NWR 213, ESI, USA), equipped with a fast-washout-cell, was used to ablate the samples. For analysis, the sample aerosol was transferred via 60 cm PTFE tubing to an iCAP Q, a quadrupole ICP-MS with collision/reaction cell capabilities from ThermoFisher Scientific, Bremen, Germany. Helium was used as carrier gas and mixed with Argon after the ablation cell using a Y piece.

Initial mixing of samples and additives was done using a shaker, Vortex Genie 2 from Scientific Industries, USA. Subsequent homogenization was performed using a ball mill (MM 400, Retsch, Germany) to achieve sufficient homogeneity. A conventional laboratory press with 13 mm diameter press molds (Perkin–Elmer, Bodenseewerk, Germany) was used for preparation of sample or standard pellets.

2.3. Pellet preparation

Prior to pellet preparation, the CRMs were dried to constant weight according to the procedures given in the reference data sheets and stored under dry conditions in an exsiccator. Since analyte losses by harsh pre-treatment conditions need to be considered, no milling or grinding steps were performed prior to pellet preparation in order to avoid any changes in the CRM composition. Sodium tetra borate, d(0.9) < 100 μm, was chosen as binder material. The binder was previously homogenized/grinded in the ball mill for 60 min using a pulsing rate of 15 pulses per second. Silver oxide, d(0.9) < 80 μm, was used as internal standard. For facilitated handling, silver oxide has been diluted with the binder component in a 1-to-10 ratio. As optical absorbent at the laser wavelength of 213 nm caffeic acid (CA), d(0.9) < 60 μm, was introduced without any pre-treatment.

For pellet preparation, 50 mg of CRM which acted either as sample or standard, 50 mg of the diluted internal standard (IS) mixture, and 400 mg of the binder component were mixed for 30 min with a pulsing rate of 15 pulses s^{-1}. When adding caffeic acid, 200 mg of binder was replaced by that component. Blank pellets were prepared without sample addition to evaluate background levels and possible contaminations. Thus, all pellets consisted of 1% internal standard, 0 or 10% sample, and 0 or 40% optical absorbant, with 49–99% binder. The homogenized powder was filled into the press mold and pressed into a pellet (13 mm diameter, 10 MPa for 30 s). The thickness of the obtained pellets was 2.0 mm. The pellets were stored in Petri dishes under dry conditions until used for analysis. Neither surface polishing nor pre-ablation processes were used prior to analysis.

2.4. LA-ICP-MS analysis

After inserting the samples, the ablation chamber was purged for 30 min with He at a flow rate of 750 mL min^{-1}. Sample ablation was performed using different parameters. The spot diameter was adjusted to either 100 or 200 μm. The laser output was varied between 30% and 70% with a frequency of 10 Hz corresponding to a fluence ranging between 0.65 J cm^{-2} to 15 J cm^{-2}. The scan speed was varied between 50 and 300 μm s^{-1}. After sample ablation, the aerosol containing He flow was diluted with an Ar gas flow of 0.4 L min^{-1} and introduced into the ICP-MS.

A daily performance check of the ICP-MS was conducted by tuning for maximum signal intensity (^{115}In) while ablating NIST SRM 612. Experiments were done either under standard conditions or by using collision/reaction cell technology (CR-mode). For CR-mode, a collision gas (He with 7% H_2 purchased from Linde, Austria) was introduced at a flow rate of 4 mL min^{-1} into the flatpole of the instrument. The kinetic energy barrier was set to 3 V. Detailed instrumental parameters are shown in Table 1. Signals were recorded in transient signal mode (trquant) with Qtegra software (version 1.5.1189.31) provided by Thermo Scientific. Transient signals consist of the signals of the gas blank, a block-shaped plateau of stable elevated signal during sample ablation and again the gas blank signal after the laser is turned off. Each plateau was divided into 6 regions of 10 s each. Also, a 10 s region was taken from the gas blank as background correction and automatically subtracted. For each pattern, average and relative standard deviations (RSDs) of these 6 (corrected) regions were calculated and used as numeric basis for all further investigations.

At least 6 different areas were analyzed on each sample and/or sample depth. For this purpose, each pellet was (fictively) divided into six sections of equal surface area and a 600 × 600 μm area was ablated in an “S-shaped” pattern in one sweep on each section. To determine not only the lateral pellet composition but also surface vs. bulk composition, the same spots were ablated 4 times in succession. These