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DISSERTATION

Solid sampling approaches for quantitative analysis of trace elements in powdered environmental samples using ICP-based measurement techniques

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ABSTRACT (ENGLISH)

Accurate quantification of trace elements in environmental samples such as fly ash, sewage sludge, road dust or airborne particulate matter is important for assessment of health effects but also to estimate their potential for recycling. To obtain such information in a routinely way ICP-OES or ICP-MS is applied for analysis. When using these techniques in their regular configuration, conversion of the solid material into a liquid solution is necessary. For this purpose, well established procedures such as acid digestion, fusion or dry ashing are reported in literature. However, application of these approaches is limited by the enhanced risk for sample contamination and/or analyte losses, as well as the increased time demand for sample preparation. Therefore, the direct analysis of the mentioned solid samples is considered to be advantageous.

Solid-sampling techniques which are frequently applied in combination with ICP-OES or ICP-MS detection are electro-thermal-vaporization (ETV) and laser-ablation (LA). However, the need of appropriate matrix matched standards or certified reference materials (CRM) for quantitative determinations limits the applicability of the abovementioned techniques. In this work, different approaches for the direct analysis of environmental powders have been developed, which require no or only little sample preparation. The proposed LA-ICP-MS and ETV-ICP-OES procedures were carefully optimized to overcome frequently observed limitations and validated for future routine means. Environmental powders like fly-ash and sewage sludge were chosen as sample material for method development but also for demonstration of applicability.

In the first part of the work improved procedures for analysis of powdered samples were presented, which allow the determination of minor and major sample constituents without the need of certified reference materials closely matching the samples matrix composition. In case of LA-ICP-MS this goal could be achieved with the use of in-house standard materials prepared by pelletizing mixtures of available non-matrix-matched reference materials with binder compounds in the presence of an internal standard. Fast and reliable ETV-ICP-OES analysis of overall bulk concentrations has been enabled using a slurry approach, where the powdered sample is dispersed in a liquid without dissolving them, offering the possibility of external calibration with aqueous standard solutions. The second part of this thesis was focused on the spatially resolved LA-ICP-MS analysis of isolated fly ash particles. Thereby, information about the lateral distribution of various elements present in fly ash particles could be obtained, enabling a more detailed characterization of the particles. For example, elements enriched on the particles surface could be more easily mobilized into the

environment than elements predominantly occurring in the particles core. The recycling of precious metals from environmental powders is also favored in case of surface enriched elements as well as the potential release of toxic elements into the environment.

KURZFASSUNG (DEUTSCH)

In Umweltproben wie Flugasche, Schlacke oder Feinstaub sind verschiedene chemische Spurenelemente enthalten. Die genaue Bestimmung der Konzentration (Quantifizierung) ist einerseits wichtig für eine Beurteilung des Gefahrenpotentials für Gesundheit und Umwelt und andererseits interessant für die Bestimmung eines etwaigen Recyclingpotentials. Routinemäßig werden diese Informationen durch die Analyse mit ICP-OES oder ICP-MS erhalten. Normalerweise müssen die Proben zur Anwendung dieser Techniken vom Feststoff in eine flüssige Form überführt werden. Für diesen Vorgang gibt es gut etablierte und in der Literatur dokumentierte Verfahren wie den Aufschluss mit Säure, den Aufschluss mit Schmelze oder das Veraschen. Diese Methoden sind durch einen hohen Arbeitsaufwand gekennzeichnet, wodurch ein höheres Risiko für den Eintrag von Verunreinigungen und/oder den Verlust von Analyten besteht. Darauf begründend wird die direkte Analyse des festen Materials als vorteilhaft betrachtet.

Oft genutzte Ansätze für die direkte Analyse von Feststoffen mit ICP-OES oder ICP-MS sind Elektrothermische Verdampfung (ETV) und die Ablation mittels Laser (LA). Das Problem dieser Techniken ist, dass für eine Quantifizierung passende Standards oder Standard-Referenz-Materialien mit übereinstimmender Matrix benötigt werden, die nicht immer verfügbar sind. In dieser Arbeit wurden verschiedene Ansätze für die direkte Untersuchung von gepulverten Umweltproben entwickelt, die ohne, oder nur mit wenig Probenvorbereitung auskommen. Die vorgestellten LA-ICP-MS und ETC-ICP-MS Techniken wurden sorgfältig optimiert um die gängigen Einschränkungen zu bewältigen und validiert um eine spätere Routineanwendung zu ermöglichen. Für die Methodenentwicklung und zur Demonstration der Anwendbarkeit der Methoden wurden Umweltproben wie Flugasche und Klärschlamm verwendet.

Im ersten Teil der Arbeit werden verbesserte Methoden präsentiert, mit denen man die Gesamtkonzentration bestimmen kann, ohne auf Standard-Referenz-Materialen mit übereinstimmender Matrix angewiesen zu sein. Bei LA-ICP-MS kann das durch die Anwendung von Standards erzielt werden, die im eigenen Labor hergestellt werden können. Dabei werden die Standard-Referenz-Materialien in Pulverform zusammen mit einem Binder und einem internen Standard zu einem Pellet verpresst. Eine schnelle und zuverlässige ETV-ICP-OES Analyse kann mit dem Slurry-Ansatz erreicht werden. Dabei wird das pulvrige Material fein in einer Flüssigkeit verteilt ohne dass es zur Auflösung der Partikel kommt. Dadurch wird eine Kalibration mit wässrigen Standard-Lösungen möglich. Der zweite Teil der Arbeit befasst sich mit der ortsaufgelösten LA-ICP-MS Bestimmung von Spurenmetallen in einzelnen Flugasche-Partikeln. Dabei erhält man Informationen über die Verteilung der metallischen

Haupt- und Nebenbestandteile der Flugasche-Partikel. Dadurch wird eine verbesserte Charakterisierung der Partikel ermöglicht indem man zum Beispiel unterscheiden kann, welche Elemente an der Oberfläche des Partikels präsent sind, und welche nur im Inneren gefunden werden. Die Elemente an der Oberfläche können leichter in die Umwelt abgegeben werden und sind durch einfachere Recycling-Verfahren zugänglich. Wenn es sich um toxische Elemente handelt können diese wiederum einfacher in die Umwelt freigesetzt werden.

1. INTRODUCTION

Both optical emission spectrometry with inductively coupled plasma (ICP-OES) and mass spectrometry with inductively coupled plasma (ICP-MS) have been introduced and consecutively developed since the 1960ies and 1980ies respectively [1-3]. Both techniques share an inductively coupled plasma, usually generated from Argon (Ar) gas with RF power and a copper coil, as source to obtain qualitative and quantitative atomic information. Plasma, temperatures of up to 10 000 K provide sufficient energy output to start the desired transition processes. For ICP-OES the plasma is used to atomize and excite the introduced sample aerosols. The element specific electromagnetic radiation, which is emitted during the decay from excited state to ground state can be used for qualitative (wavelength) and quantitative (relative signal intensity) analysis. For ICP-MS the target processes are atomizing and ionizing the sample aerosol. The resulting ions can subsequently be extracted and separated according to their mass-to-charge ratio. Qualitative information is obtained by different mass-to-charge ratio and quantitative information is again available from the relative signal intensity. Both techniques are very well established for routine analysis of liquid samples in combination with appropriate sample introduction systems. Up-to-date systems even include automatic start-up and shut-down procedures as well as extensive software packages for experiment design, optimization and data evaluation [4]. Still, continuous work is ongoing for further improvements like reduction of Argon consumption, mixed gas systems, increase resolution and sensitivity or compensation matrix effects (collision/reaction cell technology) [5, 6].

For routine multi element analysis of solid particulate samples, the usual approach is sample digestion combined with subsequent analysis of the derived solution with ICP-OES or ICP-MS[7-12]. This method is well established and delivers accurate results for a wide range of analytes and concentration levels. However, sample analysis is time demanding and labor intensive. Often concentrated mineral acids or oxidants as well as high pressure and/or temperatures are required for complete sample dissolution. Also, pre-treatment poses risks of sample contamination and/or analyte losses. Depending on the involved materials (e.g. silicates) in unknown samples the digestion step must be carefully optimized to achieve quantitative analyte recovery. The demand to overcome the described limitations with direct analysis is increasing steadily due to its apparent advantages for routine investigations of solid materials and the availability of suitable commercial systems.

Especially in the field of environmental analysis with a wide range of different solid matrices and particulate samples as well as trace and ultra-trace level analyte concentrations new direct approaches are desirable. The two approaches for direct solid analysis with ICP-based detection, which have been receiving the most attention, are electrothermal vaporization (ETV) and laser ablation (LA) [13-15].

In electrothermal vaporization, a graphite tube containing a graphite boat with the sample is heated using an electric current to vaporize solid particulates or liquid droplets. A temperature program is usually implemented to separate matrix from analytes and the generated aerosol is transported to the ICP-based detector for subsequent analysis. The implementation of electrothermal vaporization in routine analysis has already been done in the past, hyphenated with atomic absorption spectrometry. This technique is specified in most official analysis standards for single element quantification in environmental or food related matrices. However, hyphenation with ICP-OES or ICP-MS are topics of ongoing scientific interest, especially in rare earth element analysis [16, 17], but not widely available in standard routine laboratories.

In laser ablation, a laser is utilized to directly ablate the surface of a solid sample material. Usually a pulsed laser is employed with pulse rates either in the nanosecond or the femtosecond range. Femtosecond lasers are less matrix dependent due to reduced elemental fractionation effects [18, 19] but far more expensive and therefore not as widely available. The generated aerosol is then transported to the ICP-based detector for subsequent analysis. In contrast to liquid introduction or ETV, when using LA not only total bulk information can be obtained, but also spatially resolved information can be gathered. Nowadays spatially resolved analysis is usually referred to as "imaging". This technique is widely used in the fields of archaeometric, bio- and geological sample analysis [20-23].

In this work, two specific challenges related to the analysis and quantification of solid powdered samples are addressed:

- quantification of unknown samples without using matrix matched calibration or certified reference materials and
- achieving information about the elemental distribution within such samples.

A more detailed discussion on these challenges and the approaches used to overcome them is presented in the following chapter.

2. ANALYTICAL CHALLENGES

2.1. SAMPLE PREPARATION OF POWDERED SOLID MATERIALS

In environmental analysis of solid samples, these usually are available as powders, either in the form of (pre-dried) ash, fly-ash, sludge or dust. The introduction of powders presents some challenges for ICP-based techniques.

For ETV, powders can be directly weighed into the graphite boat and introduced into the graphite furnace for further analysis. Because of the high transport efficiency from the ETV chamber to the ICP (over 60 % to up to 100 %) and the sensitive detectors employed in current ICP-instruments, material amounts are in the mg range which often makes a direct weigh-in challenging. To counteract this the "slurry approach" may be applied. Slurry sampling ETV-ICP-analysis is widely reported in literature [15, 24-26]. The sample powder is dispersed in a liquid without means to dissolve the analytes (e.g. water, nitric acid 1% v/v, Triton X), but to create a suspension suitable for a transfer in the graphite boat. The sample intake can be controlled by varying the slurry concentration (ratio of sample powder to liquid volume) or using different volumes of slurry solution in the boat. The slurry solution can be transferred via pipette for better handling and repeatability.

For bulk analysis with LA, powders need to be converted into compact samples or fixated on a substrate prior to analysis. Before the laser can be operated, vacuum needs to be applied to the ablation chamber to remove remaining air and an ablation gas (usually He) introduced consecutively. The powder particle fixation is crucial to withstand laser impact and not get carried away as a whole during laser pattern application. The usual approaches for powder introduction to LA are: pelletization, fusion, embedding or adhesion to a sticky medium.

Pelletization is a very well-established process for the transfer of powdered samples to compact pellets. Usually the sample material is mixed with a binder, an internal standard and/or other additives. Several binder materials have already been investigated which may positively affect laser energy absorption, reducing thermal effects and are thereby favorable for LA analysis [27-32]. All components may be milled or grinded to improve homogeneity, achieve better mixture and/or reduce particle size. Gentle conditions need to be applied if volatile analytes are involved.

In fusion, the sample material as well as some additives are molten together in a crucible at temperatures around 1000 °C to create more homogeneous fusion pellets compared to standard pelletization. However, depending on the conditions, volatile analytes may not be accessible with this technique [33-35].

Embedding is often utilized in the field of material testing as well as preparation for microscopy, electron microscopy or x-ray-techniques [36, 37]. The sample is added to a multi-component mix of resin which hardens over some time, usually minutes, when combined. The hardened blocks are then directly analyzed or cut, if the sample was totally submerged, with subsequent analyzing of the cross section.

Finally, the powder can be dispersed above a surface with sticky properties like tape or some kind of adhesive spray [38].

Another different case is the preparation of isolated particles for spatially resolved analysis. Compared to bulk analysis, the particulates still need to be fixated, but as single particle and not as agglomerates or overlapping with each other. No physical or chemical processes can be introduced which may compromise the spatial information (e.g. pelletization and fusion). Using embedding, it’s difficult to prepare isolated particles, avoid agglomeration during hardening and provide easily accessible particles at the surface, since they tend to sink into the resin. The retention of particles on a sticky sample carrier seems to be the only approach with some prospect. However, compared to pelletization, fusion and embedding, which are well established processes, for the use of the sticky sample carrier approach improvements are required.

It can be stated that even in direct analysis, in the case of powders with ETV or LA at least some measure of sample preparation is necessary. Solutions for the above-mentioned problems are discussed in chapter 3.

2.2. QUANTIFICATION OF TRACE CONSTITUENTS IN POWDERED SOLID MATERIALS

Quantification strategies in ICP-OES and ICP-MS are based on external calibration using standards of predefined concentration. When analyzed, those standards yield signal intensities, either as intensity of emitted light (OES) or as counts of detected ions (MS). With those intensities, a relation can be obtained between standard concentrations and signals. This relation is used as calibration function to derive unknown sample concentrations from their respective signals. To discuss the challenges for accurate quantification of solid materials, the analytical process needs to be split in four steps: aerosol generation, aerosol transport, atomization/ionization and detection. In Table 1 these steps are displayed with further subdivisions. Most of them are dependent on overall sample composition - the matrix. If the standard used for calibration and the sample are too differing in matrix, obtaining accurate and precise results is challenging to say the least. Some effects can be compensated by correction factors (e.g. formation of interfering ions) or adding internal standards. But processes like aerosol generation and aerosol transport are too complex to account for with models, which increases method uncertainty. Depending on the desired accuracy and uncertainty the considered approaches need to be carefully optimized and validated.

If there are none or only minor differences in sample-matrix and standard-matrix accurate quantification is easily achieved. However, simple aqueous calibration, as commonly used in liquid ICP-OES and ICP-MS, is usually not possible for solid samples. In solid analysis, calibration can be done by using one of the following options: certified reference materials (CRMs), in-house matrix-matched standards, standard addition or isotope dilution in case of ICP-MS detection [39].

Although CRMs are well characterized, they need to be matched not only in matrix composition but also in the order of magnitude of analyte concentration and the selection of target analytes. The availability of such materials is limited especially for complex and uncommon matrices.

In-house matrix matched standards are derived from reference standard solutions or powdered solid CRMs. By diluting them as liquid or mixing them with other additives as pellets they can be designed to meet the matrix composition and analyte concentration needs. Pelletization and fusion are the most commonly used methods. However, quality control and extensive validation need to be conducted.

For standard addition, the sample is spiked once or several times with different amounts of analyte containing standard material during sample preparation. Liquid or a solid addition may be used, whereas in general, liquid addition offers a higher homogeneity. Even though the results are often of the best quality, the workload is tremendous. For each standard addition concentration level, a separate sample needs to be prepared.

Isotope dilution, which is only available for mass spectrometry and not for optical emission is not discussed in this work.

In this work, to achieve accurate quantification of solids for routine applications, pelletization is favored for LA and external calibration with standards for ETV analysis. Both approaches are discussed in chapter 3.

Table 1: Parameters influencing accurate quantification in ETV-ICP-OES and LA-ICP-MS analysis

	aerosol generation	**aerosol transport**	**atomization/ ionization**	**detection**
ETV-ICP-OES	sample composition temperature program modifier carrier gas	gas/particulate form particle size particle shape carrier gas flow	plasma load/ temperature particle composition particle size/shape residence time (gas flows)	spectral overlaps background correction
LA-ICP-MS	sample composition sample morphology laser parameters carrier gas			ion extraction ion focusing ion separation

2.3. DISTRIBUTION INFORMATION ANALYSIS FOR ISOLATED PARTICLES

As already mentioned, the first challenge for spatially resolved analysis with LA is the fixation of the target particles without compromising the initial analyte distribution. Furthermore, the powder needs to be retained as isolated single particulates without overlaps or agglomerates. The only reasonable retention approach is to disperse the sample over a sticky surface and then to look for isolated particles. The profile of retained particles needs to be taken into consideration as well as particle size distribution. So far, this has been done just by manually scattering a small sample amount above a sticky template, an approach leading to unreliable repeatability.

Another major challenge is accessing the spatial information. Analytical techniques applied for particle characterization provide either sufficient spatial resolution or adequate sensitivity, but seldom both. For example, scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM-EDX) is often utilized because of its very good lateral resolution. The sensitivity, however, is not sufficient for adequately detecting minor and trace components. In addition, SEM-EDX is a surface sensitive technique, thus only a layer of some µm thickness can be investigated, making analysis of a particle’s core impossible when the particles are some tens of micrometers in diameter.

When using LA-ICP-MS, one approach is to just drill through a particle and obtain the information via depth profiling. In ns-LA this method is limited due to thermal effects like melting of the sample surface during laser application. Thereby the depth-profiles become blurred, reducing resolution and information quality. Moreover, in case of environmental particles, their relatively rigid nature often leads to particle destruction during laser drilling. Tackling the problem by ablating the whole particle in one swoop is also not feasible since target particulates diameters are usually in the range from 25 to 100 µm. When trying to ablate the whole particle layer by layer, melting effects may again alter the composition prior to analysis. Another approach, commonly used in material analysis, may be to somehow access cross-sections of particles. In metallographic material analysis the previously embedded samples are usually cut to achieve a surface which represents the bulk distribution and can be analyzed directly. These cross-sections are then ground, polished and/or etched and investigated with microscopy or other techniques (e.g. SEM-EDX). However, this procedure is not directly applicable to “soft” environmental particles which would be destroyed in the process. If such particle cross-sections could be prepared, these newly created surfaces could then be accessed easily and would be representative for the lateral particle composition (elemental distribution).

3. METHODS APPLIED TO TACKLE THE CHALLENGES

3.1. BULK ANALYSIS

For bulk analysis, after some consideration, pelletization was chosen as suitable approach. The required equipment like a press, mill, ultrasonic bath and vortexer is simple, cheap and easily accessible in most laboratories. A defined amount of dried sample material is weighed, mixed with some additives and pressed to a pellet. Therefore, powder samples as well as standard materials can be combined with a binder. Thereby the analytes are diluted to some extent, but at the same time matrix influences are reduced considerably when using LA as sample introduction technique. Basically, the binder is used as uniform matrix matching material. Instead of producing standard materials matching one sample, all investigated samples and standards are adjusted to better match each other. Sodium tetra borate was introduced as binder material. An internal standard, silver oxide, was introduced to monitor and compensate for remaining variations in ablation efficiency, transport effects, changes in plasma temperature, etc. The addition of optical absorbents (e.g. caffeic acid) has been investigated but yielded no promising results.

3.1.1. ETV-ICP-OES

The advantages of slurry sampling have already been discussed in the previous chapter. With the slurry approach, standard addition calibration can be easily achieved by just spiking the solution. An internal standard can be added likewise. The concentration levels can be easily adjusted by varying slurry dilution. However, the desired quantification strategy for routine analysis needs to reduce the workload. One single external calibration to provide accurate results for a variety of samples should be the goal. When employing ETV as introduction technique, the following aspects can be used to considerably reduce matrix influences: utilizing a temperature program to separate target analytes from interfering matrix constituents and introducing a modifier to affect the boiling points of matrix or analytes for more effective separation.

The temperature program needs to be adjusted depending on the (organic) matrix, the amount of inserted material and the target analytes. Pyrolysis and atomization temperature as well as the heating rate need to be adapted to keep the ICP from extinguishing while transferring analytes apart from matrix components to the ICP as a stable aerosol. Depending on instrument configuration even gaseous modifiers can be introduced. As multi-element modifiers, usually chlorinating or fluorinating agents are used to convert the analytes into more volatile chlorides and fluorides, compared to carbides or oxides. The introduction of liquid modifiers like PTFE-solution in conjunction with the gaseous modifier Freon R12 was also investigated but with no positive effects observed. After careful optimization, successful calibration just with aqueous standards could be achieved as is presented in detail in section 5.2.2.

3.1.2. LA-ICP-MS

Pelletization, as described earlier, is a feasible approach to provide in-house standards, based on CRMs. However, even with matrix adaption and utilizing an internal standard there are still some effects in LA-ICP-MS which can hamper successful quantification. Even though, using up to 80 % binder material and other additives, the remaining 20 % can still have large variations in elemental composition (e.g. comparing NIST SRM2709 - San Joaquin Soil and BCR144 - sewage sludge). Different elemental species may form during atomization if varying matrix elements like C, N, O, Si, P, or S are present. To overcome such influences problematic in quadrupole mass spectrometry collision/reaction cell technology can be employed. By introducing a collision gas like a He/H_2 mixture prior to the mass filter, polyatomic interferences can be suppressed. These interferents tend to have larger effective cross-sections than atomic ions and thereby more collisions occur, reducing the kinetic energy of the interferents. With a kinetic energy barrier those interferents are then prevented from entering the mass filter. Alternatively, for specific analytes or matrix interferences, a reaction gas (e.g. ammonia) can be introduced to react with either analyte or interference yielding a different m/z ratio then before. However, collision/reaction cell technology needs to be carefully optimized to achieve the desired interference separation without significantly reducing sensitivity for analytes. Combining the sample material with sodium tetra borate as binder and silver oxide as internal standard a uniform matrix was generated. By applying collision/reaction cell technology the remaining polyatomic matrix influences could be compensated. Four different CRMs have been combined to derive a linear calibration function which can be used to quantify environmental samples, when prepared according to the procedure developed in this thesis.

3.2. SPATIALLY RESOLVED ANALYSIS

For the preparation of suitable sample carriers, adhesive layers of hairspray can be employed to fixate target particles. To scatter the particles in a more reproducible manner, a cyclone spray chamber, usually implemented in liquid ICP-OES analysis, can be used. A defined sample amount can be dispersed inside such a device in a controlled stream of Ar and then be transferred to a sticky sample carrier ready at the only exit orifice. This method allows preparation and fixation of isolated particles of the desired size distribution on a carrier ready for LA-ICP-MS analysis by adjusting the introduced sample amount as well as the gas stream. The parameters were carefully optimized and investigated with optical microscopy. The samples particle distribution, which was determined by a particle analyzer, was compared to the deposited particle by visual and computer assisted means.

3.2.1. IMAGING

After successfully preparing suitable sample carriers with retained isolated particles for LA-ICP-MS spatially resolved analysis needed to be carried out. The "cross-section-approach" common in material testing had to be applied to the relatively rigid environmental particles with diameters from 25 up to 100 µm. To access the particles' cross-section, the entire upper part of them was ablated under smooth laser conditions with a beam covering the whole particle. Those fresh surfaces were then analyzed with line patterns as base for image generation. The new cross-sections were investigated with scanning electron microscopy (SEM) prior to LA-ICP-MS analysis. It was initially expected that environmental particles (e.g. originating from MWI) are very inhomogeneous, which was confirmed by visual inspection of SEM images. Some particles are conglomerates rather than a homogeneous bulk. Some areas of particles appeared as structures with a distinctly confined geometry while the major portion was constituted of a crumb-like material. These large visible inhomogeneities even within single particles already indicate the high complexity of the environmental particulates. Further analysis was carried out with LA-ICP-MS. The achieved cross-sections were ablated in a line-scan pattern. Some optimization has been done on gas flows and line-scan parameters to achieve sufficient resolution. The line-scan data was processed to images using ImageLab (v.1.02, Epina GmbH, Pressbaum, Austria) [40]. The data was overlaid with the SEM images and the geometry observations from SEM and LA-ICP-MS results were in good alignment. To validate the LA-ICP-MS findings, SEM-EDX-imaging was done to fresh particle cross-sections prior to LA-ICP-MS analysis. After calculating both results with ImageLab the data could be compared and was in very good agreement as is discussed in detail in 5.2.3.

With this method, particles can be easily characterized by their analyte distribution. Particles can be distinguished regarding target analytes in: surface enriched particles, bulk concentrated particles, particles with locally enriched inclusions or particles with even analyte distribution.

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5. SCIENTIFIC PUBLICATIONS

5.1. RESEARCH CARRIED OUT DURING THE PHD THESIS

This thesis is composed of four publications. The challenges described in chapter 2 are discussed in those articles implementing the solutions outlined in chapter 3. Furthermore, four poster contributions are included in this work. They provide some steps of initial work done on the same topics as the publications and some additional work which was not pursued any further.

The first publication is entitled "Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry" (Analytical and Bioanalytical Chemistry, 407 (2015) 6593 – 6617). It is a review article about different approaches how to achieve quantitative information with LA-ICP-MS. One chapter is focusing on quantification of powdered samples and was prepared during the literature study for this doctoral thesis (article pages 6601 – 6605). The chapter contains a (at the date of publication, and to the best of the author's knowledge) comprehensive list of quantification approaches for powdered samples. The application of CRMs and in-house standard materials is discussed as well as some improvements done with standard addition and isotope dilution. Also, some specific approaches are described for applications.

The second publication within this thesis is entitled "Quantitative analysis of trace elements in environmental powders with laser ablation inductively coupled mass spectrometry using non-sample-corresponding reference materials for signal evaluation." (Spectrochimica Acta Part B, 113 (2015) 63-69). This article discussed the combination of pelletization and the use of powdered certified reference materials as a solution for quantification in LA-ICP-MS. Since CRMs are not always available in suitable matrix and analyte composition, by applying the same preparation procedures to samples and CRMs, the matrix influences could be reduced significantly. Combining the sample material with sodium tetra borate as binder and silver oxide as internal standard a uniform matrix was generated considering the ablation process. Still different elemental compositions in sample matrices can form different species and interferences during atomization and ionization. By applying collision/reaction cell technology even those matrix influences could be compensated. The use of optical absorbents has also been investigated but yielded no promising results. Four different CRMs have been combined to derive a linear calibration function which can be used to quantify environmental samples, when prepared according to the procedure as outlined in this publication.

The third publication enclosed in this thesis is entitled "ETV-ICP-OES analysis of trace elements in fly-ash samples - A fast and easy way for simplified routine determination." (Microchemical Journal, 137 (2018) 496-501). This article focuses in more detail on the combination of the slurry approach with the application of a gaseous modifier and quantification via external aqueous calibration. Using slurry sampling, the samples can be easily spiked with an internal standard and transferred to analysis. Furthermore, matrix-matched standards can be prepared without difficulty, yielding accurate results. By applying a temperature program and adding Freon R12 as gaseous modifier the organic matrix can be separated and the analytes can be aerosolized without major interferences. Liquid modifiers like direct addition of PTFE solution inside the graphite boat were investigated but no positive effects were observed. Finally, to reduce the workload and number of calibration standard measurements, after careful optimization, successful calibration with aqueous standards has been demonstrated in this paper.

The fourth article is entitled "Analysis of single fly ash particles using laser ablation ICP-MS – an approach achieving lateral elemental distribution information via imaging." (RSC Advances, 7 (2017) 20510-20519). In this publication, successful spatial resolved analysis was demonstrated by combining the "cross-section-approach", common in material analysis, with the LA-ICP-MS-imaging capabilities. For the preparation of suitable sample carriers, antistatic spray and hairspray were employed to fixate target isolated particles. To scatter the particles in a more reproducible manner, a cyclone spray chamber, usually implemented in liquid ICP-OES analysis, was used. A defined sample amount was dispersed inside in a defined stream of Ar and transferred to the sticky sample carrier ready at the only exit orifice. The samples' original particle size distribution as well as the size distribution of the particles retained at the carrier have been investigated and compared to a satisfactory result. With this method, by adjusting the introduced sample amount and gas stream, isolated particles of the desired size distribution can be prepared and fixated on a carrier ready for LA-ICP-MS analysis. To access the particles' cross-section, the upper part was ablated under smooth laser conditions with a beam covering the entire particle. Those fresh surfaces were then analyzed with line patterns as basis for image generation. With imaging, semi-quantitative analysis was demonstrated revealing presence, absence or enrichment of the respective target analytes spatially resolved over single particles with diameters up to 100 µm.

5.2. SELECTED PUBLICATIONS

5.2.1. PART A

This part of the thesis contains two articles on the topic of quantification of environmental particulates with external calibration via LA-ICP-MS.

ARTICLE 1 (REVIEW-ARTICLE)

Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry. Review Article.

Andreas Limbeck, Patrick Galler, Maximilian Bonta, **Gerald Bauer**, Winfried Nischkauer and Frank Vanhaecke.

Analytical and Bioanalytical Chemistry, 407 (2015) 6593 – 6617.

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One chapter of this review article – analysis of powdered samples - was written by Gerald Bauer and this part (pages 6601 – 6605 of the published article) should therefore be considered part of this doctoral thesis. The other chapters of the review article are provided to give the reader a full picture of the review article.

Anal Bioanal Chem
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REVIEW

Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry

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Abstract Laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) is a widely accepted method for direct sampling of solid materials for trace elemental analysis. The number of reported applications is high and the application range is broad; besides geochemistry, LA-ICP-MS is mostly used in environmental chemistry and the life sciences. This review focuses on the application of LA-ICP-MS for quantification of trace elements in environmental, biological, and medical samples. The fundamental problems of LA-ICP-MS, such as sample-dependent ablation behavior and elemental fractionation, can be even more pronounced in environmental and life science applications as a result of the large variety of sample types and conditions. Besides variations in composition, the range of available sample states is highly diverse, including powders (e.g., soil samples, fly ash), hard tissues (e.g., bones, teeth), soft tissues (e.g., plants, tissue thin-cuts), or liquid samples (e.g., whole blood). Within this article, quantification approaches that have been proposed in the past are critically discussed and compared regarding the results obtained in the applications described. Although a large variety of sample types is discussed within this article, the quantification approaches used are similar for many analytical questions and have only been adapted to the specific questions. Nevertheless, none of them has proven to be a universally applicable method.

Keywords LA-ICP-MS · Quantitative analysis · Certified reference material · Matrix-matched standards · Internal standard correction · Liquid standards

Introduction

Laser ablation (LA) in combination with inductively coupled plasma–mass spectrometry (ICP-MS) is a powerful technique for the direct elemental analysis of solid samples. This technique provides major, minor, and trace element information with a wide elemental coverage, excellent limits of detection, and a linear dynamic range of up to 10 orders of magnitude, while also enabling microanalysis, depth profiling analysis, and 2-dimensional elemental mapping. Further advantages of LA-ICP-MS are minimal sample preparation, high sample throughput, access to isotopic information, and the possibility of analyzing both conductive and non-conductive and opaque and transparent materials [1–4].

However, two fundamental aspects of processes involved constrain the ability of LA-ICP-MS to act as a universal method for direct analysis of solid samples. The first major drawback of LA-ICP-MS is that the abundances of the ions detected after m/z separation are often not entirely representative of the composition of the original sample. In the literature, this problem is often referred to as "elemental fractionation" [5, 6], although this term is also used to describe time-dependent changes in the composition of the ion beam in the mass spectrometer. Besides the ablation process itself (e.g., non-stoichiometric effects due to the preferred ablation of more volatile compounds), the transport of the aerosol particles

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from the ablation chamber into the ICP (e.g., differences in gravitational settling between smaller and larger particles) and vaporization, atomization, and ionization in the ICP (less efficient for larger particles) are also important contributors to fractionation effects. A detailed discussion of the individual contributions to elemental fractionation and the strategies developed for minimizing the influence exerted can be found in the literature [7–14].

The second major problem connected with the use of LA-ICP-MS for direct analysis of solid samples is the difference in the interaction between the laser beam and the sample surface observed for various matrices, causing changes in the mass of analyte ablated per pulse due to differences in the properties of the matrices investigated (e.g., absorptivity, reflectivity, and thermal conductivity). The aerosol particles produced during ablation of different matrices may vary in size and geometry, thus having an effect on the sample transport efficiency from the ablation cell to the plasma [15]. Both effects contribute to differences in the mass load of the plasma and give rise to matrix effects, since the vaporization, atomization, and ionization efficiencies of the analytes introduced into the plasma depend on the mass load [16]. Sample-related “matrix effects” therefore jeopardize the accuracy of LA-ICP-MS analysis and complicate quantification [2–4, 17–20].

As a result, elemental fractionation and matrix effects occur simultaneously, leading to LA-ICP-MS signals that are not representative of the elemental composition of the sample investigated. The sensitivity or absolute signal intensity can vary significantly for samples with the same analyte concentrations, but different matrix compositions and/or physical properties. At this point, it has to be mentioned that mass spectrometric separation and detection of the ions generated can also contribute to the bias in LA-ICP-MS results. However, an explanation of the corresponding sources of bias is beyond the scope of this work; details on these issues can be found in a recently published review article [21]. Figure 1 schematically summarizes the individual steps of LA-ICP-MS analysis prone to elemental fractionation and matrix effects.

As a consequence of the increasing interest in the use of LA-ICP-MS in various scientific fields, research has been devoted to overcoming the aforementioned drawbacks. In the few last years, attempts were made to address the limitations of LA-ICP-MS by improving the instrumental parameters relevant to aerosol formation. Most of this work focused on the influence of the wavelength of the laser radiation (especially important for transparent materials) and the pulse duration (especially important for metallic samples). With the use of shorter ultraviolet wavelengths and pulse durations in the femtosecond (fs) range, instead of the nanosecond range, a significant reduction of elemental fractionation and matrix effects is enabled. Furthermore, the laser beam profiles were changed from Gaussian to (pseudo) flat-top profiles, leading to optimized ablation performance. However, complete elimination of these effects is still not possible. Ongoing research is therefore dedicated to methodological developments that permit correct quantification with the currently available instrumentation for LA-ICP-MS analysis.

The purpose of this review is to summarize state of the art procedures and recent developments in quantitative LA-ICP-MS analysis of samples originating from the fields of life sciences and environmental chemistry. In addition to traditional approaches, novel concepts for the preparation of matrix-matched standards, such as the deposition of elemental coatings or thin polymeric films containing an internal standard on the sample surface, as well as quasi-simultaneous measurement of standard and sample using a spinning platform will be presented. Capabilities and limitations of the different approaches will be compared, critically examined, and evaluated on the basis of their suitability for general use.

Common concepts for quantification in LA-ICP-MS

Even though the application range of LA-ICP-MS is wide and the sample types analyzed are various, some approaches for quantification are applied to a large variety of sample types. The basic principles of the methods described below are the same, while modifications thereof will be presented in the sections dedicated to specific sample types.

External calibration utilizing certified reference materials (CRMs) which match the composition of the sample to be investigated to the largest possible extent—preferably exactly—is the most reliable method for accurate quantification in LA-ICP-MS [20, 22–24]. If this prerequisite is met, ablation, transport, atomization, and ionization of sample and standard can be considered to be (nearly) identical, enabling reliable quantification. For each CRM, a detailed certificate is available containing information regarding component concentrations. Additionally, in the literature, preferred concentration values are available for non-certified sample constituents [25]. However, the lack of appropriate CRMs for the majority of sample types (in particular for samples from environmental, biological, or medical origin) limits the applicability of this approach. Thus, alternative quantification strategies are mandatory.

A promising approach for quantification is the preparation of matrix-matched calibration standards, prepared from material with the same matrix as the sample [26–29]. Procedures for sample preparation preceding LA-ICP-MS analysis reported in the literature include fusion with borate, embedding in a polymer resin, or preparation of a pressed disk in the presence of a binder. Benefits of these sample preparation approaches are that they facilitate the addition of one or more internal standards, known amounts of the analyte(s) of interest (for standard addition purposes) or isotopically enriched spikes (for isotope dilution purposes), as well as the possibility to

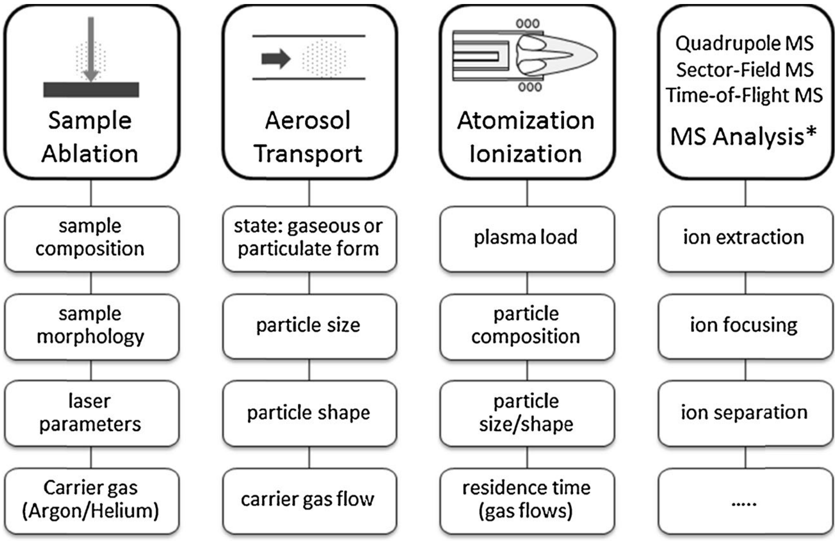

Fig. 1 Sources of error in LA-ICP-MS analysis, * not discussed within this review

adjust the analyte concentrations as required (dilution). A major drawback is the applicability to powdered samples only; samples that are compact in their native form require additional sample pretreatment (i.e., milling, grinding). Furthermore, it has to be considered that this type of adjustment of the sample matrix is automatically accompanied by analyte dilution, which decreases the detection power of the analysis approach.

A frequently applied method in combination with external calibration (i.e., CRMs and in-house standards) is signal normalization to an internal reference or internal standard [30–33]. This approach can be used to further improve the accuracy of the quantification results, since the influence of remaining differences between sample and standard can be minimized. Variations in sample ablation and transport as well as ICP-related alterations in signal intensity (e.g., changing plasma conditions) can be corrected for using an internal standard. A precondition for the successful application of this method is that the internal standard element and the analyte element are homogeneously distributed within the sample, and that their behavior during ablation, transport, and ionization is similar. In this course, crucial parameters are, e.g., the form in which the element is transported from the ablation cell into the ICP (gaseous or particulate) and its mass and ionization potential. The element being used as internal standard can either occur naturally in the sample or is added during the sample preparation process. Optimally, the concentration of the element used as internal standard in the sample is known. However, for successful application it is sufficient that the concentrations in the standard and sample are equal.

"Solid–liquid" calibration in which a dual flow system allows simultaneous introduction of a nebulized aqueous standard solution and laser ablated material is an attractive alternative to the use of matrix-matched solid standards [3, 34, 35]. In this procedure, the carrier gas flow coming from the ablation cell is mixed with an aerosol generated by nebulization of an aqueous standard solution. Besides the addition of aerosol to the gas lines leading to the ICP [36], the use of micronebulizers has also been proposed to add the aerosol to the gas flow directly at the site of material ablation [36, 37]. Not only standards with natural isotopic composition [36] but also isotopically enriched standards [37] have been used for such experiments. Standard and blank solution are alternately added to the sample stream, such that the accompanying difference in signal intensity can be used to quantify the analyte concentrations in the sample. A correction for the differences in ablation efficiency is required and when aiming to maintain the advantages of "dry plasma" conditions, such as a reduced level of oxide interferences, the wet aerosol must be desolvated prior to its mixing with the sample aerosol. However, for special applications, wet plasma conditions may also offer improved measurement conditions, e.g., in terms of signal stability [38]. This method enables quantification based on aqueous standards, and can compensate for matrix-related ionization differences. However, possible variations in ablation efficiency or altered transport efficiencies cannot be accounted for.

Although the quantification approaches mentioned above have been successfully applied in several research fields, including material sciences, geo- and cosmochemistry, environmental chemistry, biology, and medicine [3, 4, 14, 19, 22, 23, 39], their successful application to any kind of sample is not guaranteed. Thus, further improvements are required, which could be achieved either by reducing the extent of matrix effects by using optimized instrumental parameters (e.g., laser radiation wavelength, pulse duration, robustness of ICP) or by developing alternative strategies for quantification.

Analysis of hard tissues and compact samples

Naturally occurring compact materials, such as rocks and minerals, bones, teeth, claws, feathers, or nails, require no pretreatment like milling or pressing prior to LA-ICP-MS analysis. However, often it might be necessary to flatten the exposed sample surface using a grinding and/or polishing step. Within this review, only samples of biological origin will be discussed. Samples of geological origin will not be described in detail here; for this kind of samples, detailed information can be found in journals devoted to geology and geochemistry.

While quantitative determination of major, minor, and trace elements in the samples mentioned above is the main field of application of LA-ICP-MS, the technique also offers the possibility of performing spatially resolved analysis, which is of interest for studying element distributions (mapping or imaging and depth profiling analysis) or inhomogeneities (solid or fluid inclusions) in many materials. Applications solely dedicated to visualizing elemental distributions are also beyond the scope of this paper, which focuses on those applications in which estimation of bulk or local concentrations forms at least part of the investigation and, possibly, some effort is made for cross-validation using an alternative analytical approach. Yet, calibration approaches discussed here can self-evidently also be deployed in mapping or imaging applications.

Biogenic carbonates: calibration

Although LA-ICP-MS lends itself specifically well to spatially resolved analysis, its application for bulk analysis is justified in cases where a dedicated area across a given set of samples has to be reproducibly analyzed in situ in order to enable comparison. This has been specifically exploited for the investigation of fish otoliths at their cores and edges for the purpose of origin determination of fish populations [31, 40–47], or for the investigation of changes in the prevailing conditions, reflected in the microchemistry of very narrow otolith bands [32, 48–50]. The daily accretion of calcium carbonate layers in otoliths and their permanent retention of chemical fingerprints in the form of various elemental impurities make them an ideal target for this type of investigation [51]. Similar incremental growth behavior and chemical matrix are found in mussel shells and corals. Combined with their immobility, it makes these objects valuable environmental monitors [26, 27, 52–54]. Also larvae tracking applications have been reported for mussels [55, 56]. This type of investigation can be summarized under the term *sclerochronology.*

The different NIST SRM glasses 610, 612, and 614 (National Institute of Standards and Technology, Gaithersburg, USA), with certified trace element concentrations over approximately three orders of magnitude, from the low microgram per gram level to hundreds of micrograms per gram, are by far the most frequently used materials for calibrating biogenic calcium carbonate measurements by LA-ICP-MS [31, 32, 40–43, 46, 48–50, 52–56]. Trying to improve the analytical results, Arkhipkin et al. compensated for the difference in matrix composition between the NIST SRM glass and biogenic calcium carbonate via the introduction of in-house correction factors [46]. However, according to Jochum et al., calibration using NIST SRM glasses as such already results in accurate values for the refractory elements, whereas a closer matrix-matching using calcium carbonate pellets has to be applied for low boiling point elements, such as Pb [53]. Another decisive parameter for measurement accuracy when using the NIST SRM glasses for calibration is the set of reference concentrations used for these materials [53, 57, 58]. Custom-made fused glasses are an alternative to the NIST SRM glasses for calibration purposes. Such glasses were prepared by Sinclair et al. by blending biogenic carbonate (coral powder) with silica in a ratio of 1:1, followed by fusion at 1650 °C and by Perkins et al. by blending $Li_2B_4O_7$ in excess with synthetic $CaCO_3$, MgO, and gravimetric additions of the analytes of interest, followed by fusion over a burner flame [26, 27]. Sinclair et al. obtained reference concentrations for their glasses using solution-based isotope dilution either by ICP-MS or thermal ionization mass spectrometry for all elements other than B, which was calibrated via LA-ICP-MS against NIST SRM 612 using B concentrations from the literature [26].

Besides NIST SRM glasses, carbonate pellets represent the second largest group of calibration materials in the field of biogenic carbonate analysis by LA-ICP-MS [27, 44, 45, 47, 52, 53, 59]. Different carbonate materials pressed into pellets have been used, including the commercially available synthetic calcium carbonates USGS MACS-1 and MACS-3 (United States Geological Survey, Reston, VA, USA) [44, 52, 53], fish otolith powder NRC FEBS-1 (National Research Council Canada, Ottawa, Canada) [47], synthetic in-house carbonates prepared by co-precipitation [45], or in-house standards prepared from gravimetric blends of the analytes of interest and either commercially available calcium carbonate or crushed biogenic carbonate [27]. In one case, the authors blended NIST SRM glasses and carbonate pellets to obtain calibration standards, without revealing whether all materials were used in the same calibration function [52]. However, despite the multitude of calibration materials obviously at hand, the fact that otoliths also contain a significant amount of organic matter is commonly not accounted for [27, 51].

Without exception, all authors use Ca as internal standard element for normalization, albeit with little agreement regarding their choice of the Ca nuclide used for this purpose. This is mainly a question of user experience, instrumental sensitivity, and the means available to overcome spectral interference. All Ca isotopes, apart from the most abundant (^{40}Ca) and the least abundant (^{46}Ca), have been reported in papers related to LA-ICP-MS analysis of biogenic calcium carbonates and referenced in this review. There is also a fair amount of disagreement with respect to the Ca concentration assumed or measured for otoliths, which is critical for obtaining accurate data. Whereas some authors calculate a theoretical Ca concentration based on $CaCO_3$ stoichiometry [32, 40, 41, 45, 48, 50], others measure it in advance using conventional solution nebulization ICP-MS or ICP-OES [31, 47]. As a result, reported Ca concentrations range from 35 to 40 %. Even when estimates are based on $CaCO_3$ stoichiometry only, some disagreement is possible.

Biogenic hard tissues: claws, feathers, fish scales, and hair: calibration

LA-ICP-MS also becomes an asset when minimally invasive sampling and analysis are required. LA-ICP-MS has been used for the quantitative analysis of animal claws, feathers, fish scales, snake tail clippings, animal hair, human hair, and human finger nails [60–71].

Ethier et al. and Kaimal et al. used the NIST SRM 612 glass as a standard in the context of multi-element analysis of badger claws and bird feathers, respectively [60–62]. Both teams used concentration data obtained via LA-ICP-MS for statistical classification of their results. Whereas Ethier et al. used S as an internal standard as a consequence of the high cysteine content of the sample matrix keratin [60, 61], Kaimal et al., used ^{42}Ca, assuming a homogeneous Ca distribution [62]. For Ethier et al., the use of S as internal standard, quantified in advance using conventional solution nebulization ICP-MS, required the introduction of inter-element sensitivity factors, established from the ICP-MS mass response curve obtained upon ablation of NIST SRM glass. The authors indicated that this approach only yields semiquantitative data. Human and animal hair, as well as human finger nails or clippings thereof, all predominantly comprised of keratin, have been the subject of many studies owing to their capability as a biomonitor of past (trace) element exposure [66–70]. The application of in-house hair or nail material for calibration is quite commonplace in this context [66–70]. Rodushkin and Axelsson used in-house finger nail material, powdered and pressed into a pellet, for calibration of finger nail measurements [70]. Reference concentrations were obtained from conventional solution nebulization ICP-MS after sample digestion. For hair analysis, the certified GBW07601 hair reference material (Institute of Geophysical and Geochemical Exploration, Lanfang, China) was used for calibration [70]. Similarly, Stadlbauer et al. used BCR CRM 397 hair reference material (Institute for Reference Materials and Measurements, Geel, Belgium), pressed into a pellet with polyethylene as a binder [71]. Bartkus et al. and Arriaza et al. both used whole in-house hair standards, quantified for Pb and As by conventional solution nebulization and hydride generation ICP-MS, for calibration of LA-ICP-MS measurements [68, 69]. Dressler et al. pursued calibration of LA-ICP-MS measurements of mouse and human hair by simultaneous aspiration of multi-element solutions (at several concentration levels) via a conventional nebulizer [66]. The wet aerosol was mixed on-line with the dry aerosol coming from the ablation chamber in the injector tube of the ICP torch. Differences in aerosol generation and transport efficiencies between solution nebulization and LA were assessed by ablating in-house hair material with known analyte element concentrations. The in-house hair standard material was prepared by immersion of hair strands in a multi-solution, subsequent drying, and digestion of the material thus obtained for the determination of reference concentrations via conventional solution nebulization ICP-MS. Sela et al. used a similar approach, but one based on standard addition using an ultrasonic nebulizer equipped with a desolvation unit [67]. The dry aerosol intended for calibration was directed through the ablation cell for mixing with the LA aerosol before introduction into the ICP. Concentrations were determined for single hair strands and hair powder, both fixed on carbon tabs. As for the internal standard, both ^{32}S and ^{34}S have been used for hair and finger nail samples [66, 67, 70]. Rodushkin and Axelsson report S concentrations of 4.77± 0.41 % and 3.30±0.56 % for hair and finger nails, respectively [70]. S concentrations were obtained on the basis of hair and finger nail samples of approximately 100 Swedish individuals. Stadlbauer et al. used a quadrupole-based ICP-MS instrument equipped with a reaction cell and adopted sulfur in the form of $(^{32}S^{16}O)^+$ as internal standard to avoid spectral overlap of the $^{32}S^+$ peak with that from the oxygen dimer ion $^{16}O_2^+$ at $m/z=32$ [71]. Also ^{13}C has been reported as an internal standard for LA-ICP-MS analysis [68, 69]. However, the use of ^{13}C as internal standard is associated with some major drawbacks. Those will be described in the chapter 'measurement of soft tissues and protein samples' in the section 'internal standards' in more detail.

Holá et al. and Flem et al. both developed LA-ICP-MS methods for trace element quantification in fish scales as an alternative to otolith sampling [63, 64]. Since fish scales contain (Ca-deficient) hydroxyapatite, Holá et al. used NIST SRM 1486 bone meal for external calibration [63]. In contrast, Flem et al. used not less than six different glass reference materials for calibration, namely NIST SRMs 610, 612, 614, 616, NIST SRM 1830 soda limestone float glass, and USGS TB-1 basaltic glass [64]. TB-1 was only introduced for calibration of Sr. Flem et al. commented that for the purpose of their study, normalized data only would have sufficed, yet calibration against the different glasses was included in order to be able to at least provide concentration estimates for later use. Both groups used Ca as an internal standard, determined by electron microprobe analysis in both cases [63, 64]. Flem et al. quote an average Ca concentration of 37.4±0.4 % for a set of fish scales [64], whereas Holá indicate Ca concentrations for three line scans on one fish scale ranging from 23.5 to 26.5 % [63]. Holá et al. also gave some indication of the homogeneity of Ca in fish scales through a spatial distribution map obtained by electron microprobe analysis [63]. Alternatively, calibration using spiked hydroxyapatite prepared as in-house calibration materials has been reported for LA-ICP-MS investigations of (human) bone and teeth [71].

The last example given describes the direct analysis of water snake tail clippings by LA-ICP-MS as an ecotoxicology tool [65]. Given the complexity of the sample material containing inorganic bone, calcium carbonate, muscle blood, and skin, Jackson et al. resorted to in-house preparation of matrix calibration standards from water snake tail sample material [42]. Reference concentrations were obtained from conventional solution nebulization ICP-MS and ^{13}C was used as internal standard for LA-ICP-MS.

Validation

It is not uncommon to omit validation from the analytical procedure entirely, which may be justified in cases where consistency of results is more important than accuracy, such as in statistical classification of the samples analyzed among different groups [40, 42, 43, 46, 62, 64]. In cases where analyte concentrations are obtained via LA-ICP-MS using non-matrix-matched standards, one should refrain from comparing results to other sets of data obtained for the same sample type by a different analytical approach without validating the quantitative results. Several approaches for this purpose were reported in the literature. Validation by re-measuring the calibration standard, in this case NIST SRM 610 glass, as a sample has also been described, but this is clearly a far from ideal assessment of measurement accuracy [32]. This is appreciated by some authors through the introduction of a reference material as an unknown in the analytical protocol. Different reference materials including USGS MACS-1 and MACS-3 synthetic calcium carbonate, NIES-022 fish otolith powder (National Institute for Environmental Studies, Tsukuba, Japan), and NRC FEBS-1 fish otolith powder have been used for this purpose, as have the limestone reference materials GSJ JLS-1 (Geological Survey of Japan, Tsukuba, Japan), GSR-6 (Ministry of Land and Resources, Beijing, China), and BAS CRM-393 (Bureau of Analysed Samples Ltd, Middlesbrough, UK) [27, 41, 44, 47, 53].

Some authors also validated their LA-ICP-MS results by conventional solution nebulization ICP-MS. Phung et al. performed LA-ICP-MS analysis in holes left by micro-drill sampling for solution nebulization ICP-MS analysis and subsequently compared results from both procedures involving two different LA-ICP-MS facilities [52]. Results agree generally within the quoted analytical errors, with a few exceptions depending on the hole analyzed. Sinclair et al. converted LA-ICP-MS line scans on corals into average concentrations for five elements and compared these to results from solution nebulization ICP-MS of a digest of the same sample [26]. Deviations ranged from approximately −3 to 30 % between the two methods. Dressler et al., Sela et al., and Rodushkin and Axelsson all compare their LA-ICP-MS results for human hair and nail samples to results from conventional solution nebulization ICP-MS [66, 67, 70]. Dressler et al. achieve agreement within analytical error [66], and the results of Rodushkin and Axelsson also showed a good correlation of LA-ICP-MS and solution nebulization ICP-MS results; generally, LA-ICP-MS results are within 30 % of solution nebulization ICP-MS results. Average LA-ICP-MS results obtained by Holá et al. for fish scales are generally higher than the corresponding solution nebulization ICP-MS data, which is also explained by the complexity of the sample matrix, i.e., analyte enrichment in the uppermost layer ablated from fish scales [63].

There is a general agreement between the authors regarding the use of gas blanks for baseline correction. Typically, limits of detection are calculated from three or ten times the standard deviation of the gas blank, divided by the slope of the calibration line or the instrumental sensitivity [31, 42, 44–46, 48]. However, as discussed by Rodushkin and Axelsson, detection limits in LA-ICP-MS depend on the volume of ablated material, the analyte mass, the ionization energy of the analyte, its isotopic abundance, and the ion transmission efficiency [70]. Aerosol size distribution and transport efficiency to the ICP-MS presumably play a role too. For the analysis of hair and nail, detection limits in LA-ICP-MS range from picograms per gram to nanograms per gram and are quoted as only marginally nferior to conventional solution nebulization ICP-MS as a result of sample dilution after digestion for the latter approach.

Measurement of soft tissues and protein samples

In recent years, LA-ICP-MS has also become a technique of growing interest in the life sciences. The effect of variations in trace elemental concentrations, and especially metal–protein interactions are increasingly studied in biological and biomedical investigations [72]. The sample types reported on vary from native samples, such as plant material [73–76], and thin sections of animal/human body tissues (e.g., liver [77], brain [78–80], eye tissue [81], kidney [82], and others), to electrophoretically separated metalloproteins [83, 84]. Typically, natural element distributions within the biological samples were investigated. In special cases, the use of isotopic analysis has been reported (e.g., as tracers for metal uptake in organisms). For example, Florez et al. exposed *Daphnia magna* to isotopically enriched Zn tracers and produced isotope ratio images with 30-μm spatial resolution [85]. A more detailed description of possibilities and limitations of isotopic analysis can be found elsewhere [86].

Like in every other field of LA-ICP-MS applications, quantification is a crucial aspect. Problems aggravating reliable quantification are the large variety of sample types and properties, as well as a lack of suitable standard materials. However, especially when thin sections of sample material are used (preparation of thin sections is common practice in the medical sciences), some aspects of quantification are facilitated, and some new issues may arise. Those thin-cuts typically have thicknesses of 5–20 μm, thus providing the opportunity to ablate the sample material (the entire depth) completely with a few laser shots, i.e., during one cycle of analysis. The analysis of thin layers renders the analysis of tissue sample much easier, since differences in penetration depth of the laser beam into the sample material do not need to be considered. This gives the opportunity of applying thin layers containing a standard for signal normalization above or below the sample. Those also have to be completely ablated along with the sample. Independently from the quantification strategy used, reliable quantitative analysis is only possible when the thin sections of the samples have equal thicknesses. Some quantification approaches that will be described in later sections rely on this assumption as they cannot compensate for varying layer thickness. If the tissue thicknesses are varying within one sample or the whole tissue sample can not be ablated in a single run, i.e., for thicker samples or bulk material, internal standardization has to be used as for many other types of samples described in this article.

Quantitative imaging approaches

A large number of LA-ICP-MS applications involving soft tissue samples aim to unravel the 2-dimensional trace element distributions (bioimaging or mapping) [87–89]. To preserve information on the spatial analyte distribution, tissue samples are analyzed as thin slices without any prior homogenization step. Three major problems have to be addressed to ensure reliable analysis results: material ablation and aerosol transport are highly matrix-dependent, the efficiency and location of the ionization process in the ICP are a function of the particle size distribution of the aerosol produced via LA [24], which, similarly, is matrix-dependent, and during the measurement time, instrument instability and signal drift may occur because of changing experimental conditions (e.g., cone conditions, vacuum pressure). As a result of those factors, even the measurement of reliable qualitative distribution maps is not self-evident; ensuring reliable quantitative results is even more challenging. Not all approaches that have been presented in the past are capable of adequately addressing the complete range of limitations mentioned.

Solid standard materials

Another method for quantification is the use of solid standard materials. Thereby, a suitable standard material can be manufactured for almost every sample type. CRMs for tissues are only scarcely available, and are in most cases not compatible with the specific experimental conditions (e.g., tissue types, trace elements selected, and/or concentration range).

While quantitative elemental analysis of homogenous materials using LA-ICP-MS can often rely on matrix-matched standards, biological samples may significantly differ in their composition even within several sections of a single sample, and therefore different methods are needed to ensure accurate quantification. Various approaches have been proposed and used to facilitate and improve the quantification of trace elemental distributions in biological tissues and to overcome the problem of often pronounced sample inhomogeneity. Even though many alternative methods for quantification have been proposed, the classical and still most often used method is the use of matrix-matched standards [90]. Those have to be prepared in-house and tuned to the specific application. The preparation of matrix-matched tissue standards has been described by Hare et al. [90] in detail. In short, the selected tissue is homogenized and spiked with an aqueous standard containing the elements of interest; the spiking process is performed at different concentrations enabling the determination of calibration functions. An aliquot of the homogenized and spiked tissues is acid digested for determining the actual analyte element concentrations in the standards. After freezing of the standard, a cryo-cut of desired thickness is prepared for LA-ICP-MS measurement. Alternative approaches for quantification in LA-ICP-MS analysis of biological tissue using solid standards aim at rendering the process of standard preparation easier. Approaches to facilitate the manufacturing process of standard materials use gelatin [91], agarose gel [92], or sol-gel [93] standards, spiked with appropriate amounts of the elements of interest. The preparation of those materials is similar to that of matrix-matched tissue standards, but less tedious. The goal is to minimize the handling of biological materials and still end up with standards with a similar matrix composition (mostly in terms of carbon content and density). One approach uses a polymeric film, spiked with the elements of interest, applied to a glass slide before attaching a thin section of the sample [94]. Assuming simultaneous ablation of standard and sample material, this approach will lead to correction for matrix effects during the measurement—similar to a single standard addition approach. Another way to facilitate standard preparation for analysis of biological tissues is printing of standards onto paper using a commercially available office inkjet printer [95, 96]. Conventional paper can be used for standard preparation, and the inks may be spiked with elements of interest. This method has been successfully used to quantify trace elements in different biomaterials. Reifschneider et al. proposed a method to reduce matrix effects by embedding biological tissues into epoxy resins [97]. In the embedding method used, complete penetration of the resin into the tissue material was ensured. The standards are prepared from epoxy resins without embedded tissue; as the main matrix material is the epoxy resin, no major difference in matrix composition exists between standards and samples. All methods discussed so far try to simulate the ‘average’ matrix conditions in the tissues presented. But, a biological sample can be very inhomogeneous and matrix compositions may vary significantly, even within a single sample. Local variations in the matrix composition can lead to inaccurate quantitative results because of alterations in material ablation, aerosol transport, and analyte ionization efficiencies. The approaches for quantification described can reduce such matrix-related effects on the ablation and analyte ionization. Still, those approaches offer no possibility for the correction of instrument instability and/or signal drift or for the reduction of signal variations originating from inhomogeneities in the sample matrix.

Internal standards

Similar to conventional solution ICP-MS measurements, an internal standard can help to correct for changes in the signal intensity originating from instrument instability and/or signal drift. During the long measurement times of imaging experiments (usually 4–30 h), gas flow rates, cone and vacuum conditions, and other experimental conditions may vary. Furthermore, the pronounced inhomogeneity of the samples investigated with profoundly changing matrix compositions require the use of (an) internal standard(s) for reliable quantification [98]. In most publications, carbon has been proposed as the internal standard, as it is abundant in every biological sample and is often uniformly distributed across the sample. However, it has been shown that carbon is not an optimal internal standard [99], as its ionization potential is significantly higher than those of commonly investigated elements, such as most transition metals, and an altered carbon load in the plasma may change the ionization efficiency of some of the analytes monitored substantially. Furthermore, the transport of carbon into the ICP can partly occur in the form of carbon dioxide, which will lead to transport properties and efficiencies that can markedly differ from those elements that are transported as particulate matter only [99]. Therefore, normalization to carbon as internal standard may lead to distortions of the actual analyte distribution, causing inaccurate quantification results. Sulfur has also been proposed as a sample-inherent internal standard [77]; however, it is not evenly distributed in most tissues and, because of its high first ionization energy, similar problems as mentioned for carbon may be expected. Therefore, alternative approaches for signal normalization have been developed to improve the existing quantification methods. Both online addition of wet aerosol [36, 37] and the method with the spiked polymer layers [94] or the epoxy resin [97] have used signal normalization as part of the quantification approach. However, in the first two approaches mentioned, no internal standard in the traditional meaning was used, as ablation of sample and internal standard take place subsequently, and not simultaneously. Another way to normalize the analyte signal which was proposed by Konz et al. [100] and shown to be feasible for quantification [81, 95] is the sputtering of the samples with a thin gold layer; however, this approach only provides a pseudo-internal standard for the same reason. Only the epoxy embedding method provides a true internal standard. The tissue samples are immersed in the epoxy resin containing the internal standard; the resin completely penetrates the tissue material. Therefore, the internal standard is ablated simultaneously with the sample material. Combining the preparation of external standards with matrices similar to the sample material with the use of an internal or pseudo-internal standard can counteract the matrix-related effects on the material ablation, aerosol transport, and analyte ionization, as well as that of instrument instability and/or signal drift.

The necessity of instrumental drift correction was described by Hare et al. [20] and shown by Bonta et al. [95] in later experiments. As mentioned earlier, the long measurement times of LA-ICP-MS imaging experiments may cause significant changes in the instrument sensitivity. This was illustrated in an imaging experiment of a printed pattern with blue ink [95]. Blue ink contains copper, which was investigated as the analyte of interest. The pattern has been coated with a thin gold layer for use as a pseudo-internal standard. Features with equal amounts of ink deposition (i.e., copper concentration) measured at different time points were compared regarding the signal intensity. Figure 2 shows the signal of ^{65}Cu with and without correction to the gold signal. During the 4.5-h measurement time, the absolute signal intensity for ^{65}Cu decreased by 25 %, indicating a strong sensitivity drift. Normalization to gold as pseudo-internal standard corrects for this drift and keeps the sensitivity constant throughout the measurement time. Thus, the necessity and feasibility of signal normalization is underlined as the results show that an

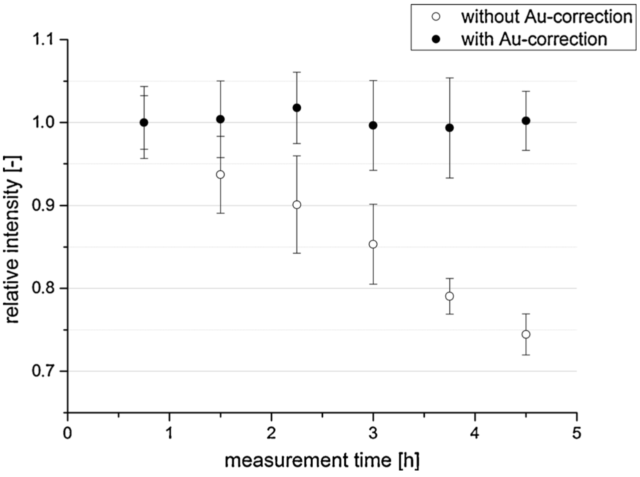

Fig. 2 Signal intensities at different time points with and without gold normalization; averages of 25 data points are displayed (n=25)

internal standard is necessary for reliable LA-ICP-MS imaging experiments.

In summary, quantitative determination of trace elements in biological tissues using LA-ICP-MS is still a challenging task, requiring extensive knowledge of sample composition and properties. Until now, no universal method has been established. Even though the preparation of matrix-matched standards seems to be the most straightforward method, some problems still remain. None of the other alternative methods are recognized as a reliable alternative to matrix-matched tissue standards because, as with every method, some limitations have to be considered.

Electrophoretically separated metalloproteins

Besides the analysis of native soft tissues, also other soft sample materials can be analyzed using LA-ICP-MS. A major group of samples are electrophoretic gels. Separation of proteins or peptides in porous gel matrices is a commonly used bioanalytical method [101, 102]. The biomolecules can be separated on the basis of their mobility in a gel matrix, and visualized using staining methods. Subsequent identification (e.g., using mass spectrometry) can be performed. With the increasing knowledge on metalloproteins, metal detection within the separated proteins has also gained importance. Sensitive elemental analytical techniques that allow for direct analysis of the metals from the gels, like LA-ICP-MS, are a powerful tool to obtain quantitative information on the metal content after electrophoretic separation of the proteins. Quantification of metal contents in electrophoretically separated gels is significantly different from trace element quantification in biological tissues, as a result of the homogeneous composition of the separation gel. However, some crucial aspects also have to be considered to ensure reliable results. Micronebulization of an aqueous standard at the ablation site using either standards with natural isotopic composition [36], or isotopically enriched solutions [37], has been proposed for quantification. In those approaches, changes in ablation and/or ionization behavior of the analytes are not taken into account and therefore an approach with species-specific isotope dilution was proposed by Konz et al. [103]. While in all other methods, the standard is added after material ablation, this method relies on direct addition of the standard to the sample and provides the possibility to compensate for all changes that affect the protein of interest. However, the disadvantage of the method is the fact that the protein of interest has to be available in pure form with an isotopically enriched metal cofactor.

Because the thickness of the gels is typically in the order of 1 mm, the entire thickness is not ablated during a few laser shots. Therefore, the use of carbon as internal standard has been proposed [104]. Still, transferring the proteins to a membrane after separation (blotting) is used far more often, as this allows one to avoid direct analysis of the gel. The investigation of so-called Western blot membranes using LA-ICP-MS has been described in detail elsewhere [105, 106]. In contrast to tissue analysis, the variety of proposed methods in the field of protein analysis is smaller. As with tissue samples, thus far, no optimal quantification method has been found.

Analysis of powdered samples

Sample preparation

Most LA-ICP-MS applications in the fields of environmental research and life sciences focus either on obtaining bulk information (with high precision and accuracy) or on obtaining spatially resolved information, sometimes only semiquantitatively. In contrast to the compact samples discussed in the previous sections, powdered samples require some kind of pretreatment prior to LA-ICP-MS measurement. The approaches most frequently applied for the preparation of compact samples from powders include milling/grinding/sieving for sample homogenization, combined with pelletization [107–112], fusion to sample disks [29, 107, 113–115], or mounting/embedding [110, 116–119] of the sample in a polymeric resin. In some cases, alternative approaches such as ablating standard and sample in quick succession by placing them on a rotary platform or electroplating have been reported [28, 33, 120–125].

During pelletization, the sample powder is compacted using a hydraulic press. Usually, the sample is mixed with a binder to improve powder grain adhesion and to produce stable pellets. Also additives (in liquid or solid form) can be introduced for internal standardization, quantification (e.g., for standard addition or isotope dilution purposes), or to affect laser–sample interaction (i.e., increased energy absorption at the applied laser wavelength). To achieve a better homogeneity, the components are often milled or ground prior to mixing. The pressing step is usually optimized in terms of press power and pressing time. Depending on the ratio of binder to sample, target analytes may be diluted by up to a factor of 10. Thereby, matrix differences between samples will be reduced, but the detection power is decreased. Pelletization is a very easy approach without the need of high-tech equipment. The homogeneity achieved in pressed pellets is sufficient for most applications. However, in some cases the reproducibility achievable is constrained by the sample homogeneity.

For fusion, the sample powder is usually combined with lithium tetraborate or lithium metaborate or a mixture of both. At high temperatures (over 1000 °C), the sample is dissolved in the molten flux and, after cooling, very homogeneous fusion disks are obtained. Like with pelletization, additives can be introduced for internal standardization or quantification. Also by diluting with flux, the matrix similarity increases, while the sensitivity decreases. Fully automated fusion generators are available, reproducibly delivering homogenous samples and requiring only little analyst effort. Compared to pelletization, borate fusion offers a better homogeneity. However, fusion may be problematic for analytes with low boiling points (below 1000 °C), like As, Cd, or Zn. Analyte losses cannot be eliminated and therefore might give rise to systematic errors. Of course, with this type of sample preparation, information on Li and B as analyte elements is also lost.

The third approach that is frequently used is mounting/embedding. By mounting, the powdered samples are attached on an adhesive surface, like sticky tape or not completely dried epoxy resin. The surface can be coated before or after sample exposition to vary adhesive effects, or to introduce standards. Mounting is mostly used for qualitative and semiquantitative analysis. Adhesiveness is a limiting factor since the surface must be sticky enough to retain powder particles even after the nearby surface has been subjected to laser irradiation; total damage of the investigated particles or removal of particles next to the ablation site has to be prevented. The sample particulates can also be embedded completely in epoxy resin. After embedding, the resins usually need to be cut and polished prior to LA analysis. During preparation of the epoxy resins, standards and other supplements (e.g., surfactants for particle isolation) can also be added to improve the results. With both methods, information on individual particles can be obtained, which is not possible with pelletization or fusion. This aspect extends the possibilities of LA-ICP-MS (e.g., for 2-dimensional mapping), but the sample preparation is very tedious. However, as a result of the possibly widely different composition of the single particles, reliable quantification is practically impossible.

Quantification strategies

Application of CRMs and in-house standards

Signal quantification using solid standards could be accomplished using either CRMs or in-house prepared standards. Usually, sample and standard need to be converted into a compact sample pellet or disk by one of the methods described in the previous section. Regardless of the sample preparation technique used, in all cases an element initially present in the sample and standard or added during sample preparation is used as an internal standard to correct for differences in ablation, transport, and ionization efficiencies. Concentrations of the internal standard in the sample and standard must be determined by complementary techniques (e.g., SEM-EDX, energy dispersive x-ray analysis) or must be sufficiently well known on the basis of stoichiometry.

Hondrogiannis et al. [108] used LA-ICP-TOF-MS to successfully classify 25 vanilla samples according to their origin. Three grams of vanilla powder was directly pressed into a sample pellet. External calibration was achieved versus NIST SRM 1549 (non-fat milk powder), NIST SRM 1575a (trace elements in pine needles), NIST SRM 1515 (apple leaves), NIST SRM 1547 (peach leaves), and NIST SRM 1570a (trace elements in spinach leaves). The method was validated using NIST SRM 1573a (tomato leaves). Eze et al. used LA-ICP-MS to investigate the composition of coal fly ash [33]. Fusion disks of each sample were prepared according to an automatic gas fusion procedure (Claisse M4 gas fusion instrument) with Claisse Flux as binder material. Quantification of 18 elements was achieved via external calibration versus NIST SRM 612 and using ^{29}Si as an internal standard. USGS BCR-2 or BHVO 2G CRMs were used for method validation. Scarciglia et al. investigated soil and paleosoil samples [123]. Thin sections were prepared for LA-ICP-MS analysis and for calibration NIST SRM 612 was relied on because of the lack of soil CRMs. SiO_2, quantified with SEM-EDX, was used as an internal standard. Relative standard deviations (RSDs) were less than 8 % for all elements and less than 5 % for most of them. Further applications include the analysis of Sahara dust samples [118], desert varnish [121], soil samples [116], biomass ashes [29], fly ash samples [113], ash related deposits [120], coral skeletons [125], and forensic investigations [110]. Detailed information can be found in Table 1.

If no suitable CRMs are available, or the range of analytes cannot be covered, the preparation of in-house standards is another possibility for quantification. Coedo et al. determined six elements in electric arc furnace flue dust [111]. Samples were pressed into pellets using paraffin and cellulose/*N*-butylmethacrylate. Standards were prepared by spiking synthetic ZnO/Fe_2O_3 matrix (1:1) with multi-element solution standards and Rh as an internal standard. The approach was validated with four reference materials. Su et al. [112] determined the distribution of metals in single wood fibers. The fibers were fixed by pressing them onto pellets with graphite powder. For quantification, matrix-matched pellets were prepared with cellulose powder and softwood pulp, doped with multi-element standards. The difference in the amount of ablated material was compensated for by introducing a mass coefficient. Fitzpatrick et al. investigated sol-gel processes to establish in-house calibration standards [28]. They showed that S and Se can be added up to 3 % of the total xerogel concentration, while for transition metals the corresponding maximum level is 0.01 %. The xerogels thus obtained were used for calibration in the LA-ICP-MS analysis of NIST SRMs 610 and 612 (trace elements in glass), achieving satisfactory results with RSDs comparable to those achieved using glass CRMs. According to their work, xerogels seem to be a feasible alternative for glass CRMs. However, no accurate results could be produced for samples with high sulfide contents.

Improved standard approaches

Compared to the reported approaches using CRMs and in-house prepared matrix-matched standards, the quantification

Table 1 Pretreatment and quantification approaches for powdered samples

	Sample type	Sample preparation	Quantification	IS	Validation	Recovery	RSD	Ref.
Standard procedures	Vanilla samples	Pressed pellets	NIST SRM 1549, NIST SRM 1575a, NIST SRM 1515, NIST SRM 1547 and NIST SRM 1570a		NIST SRM 1573a	83–106 %	6.2–14.3 %	108
	Coal fly ash	Borate fusion	NIST SRM 612	Si	USGS BCR-2 or BHVO 2G			29
	Soil samples	Thin sections	NIST SRM 612	Si			<5–8 %	123
	Sahara dust samples	Adhesive tape	NIST SRMs 612 and GSD-1G	Si	USGS W-1 and BCR-2, MPI-DING T1-G and GSJ JG-1a	75–125 %	<15 %	118
	Desert varnish	Direct analysis	NIST 61X series		NIST SRM 612	80–120 %	<20 %	121
	Biomass ash	Borate fusion	NIST SRMs 610 and 612					33
	Fly ash samples	Borate fusion	NIST SRM 2691					113
	Ash related deposits	Embedded in epoxy resin	NIST SRM 2691					120
	Soil samples	Ashing, mounting in epoxy resin	NIST SRM 2691 and NIST SRM 1633b				15–40 %	116
	Coral skeletons	Glass-fused/cut into thin sections	NIST SRMs 610 and 612 and MPI-DING KL2-G	Ca	USGS MACS-1/NIST SRM 614	80–120 %	<4–15 %	125
	Forensic applications	Tape mounting and pelletization	USGS PACS-2, NIST SRM 2704, NIST SRM 2710 and NIST SRM 2710a	Sc, Lu			<15 %	110
	Furnace flue dust	Pressed pellets	Synthetic ZnO/Fe_2O_3 matrix	Rh	CRM 876-1, AG-6203, AG-6201, and AG-SX3705	85–115 %	<7 %	111
	Wood fibers	Pressed pellets	Pellets prepared with cellulose powder, softwood pulp					112
	Glass, silicate	Xerogel disks	NIST SRMs 610 and 612					32
	Aerosol samples	Direct analysis	Standard addition				<10–18 %	124
	Sunflower leaves	Direct analysis	Standard addition					73
	Compost samples	Pressed pellets	BCR-144R and CRM029-050 and standard addition				<10 %	109
Improved procedures	Various CRMs	Borate fusion	Isotope dilution		NIST SRM 1944, 2586, 2702, 2710a, 2711a, and 2780	95–120 %	<3 %	114
	Various CRMs	Pressed pellets, borate fusion	On-line isotope dilution		NIST SRM 610, 612, and 614, MESS-2 and PACS-2 and NIST SRM 2710a, 2711a, 1944, 2702, and 2780	85–110 %	3–21 %	107
	Oxide grains	Mounted on epoxy resin	On-line isotope dilution, ratio analysis		SRM U950a and U010 as well as natural uraninite grains		0.4–2.7 %	117
Specific approaches	Environmental samples	Borate fusion	Standard addition		NIST SRM 612	85–115 %	~10 %	115
	Carbonate	Adhesive tape	MPI-DING reference glasses		NIST SRM 610	90–110 %	1.6–24 %	119
	Soil & dust samples	Electroplating	Ratio analysis		NIST SRM 4353			122

strategies can be even further improved by exploiting the concepts of single standard addition, multiple standard additions, or isotope dilution. Thus, remaining differences between sample and standard can be further compensated for, enhancing the quality of LA-ICP-MS analysis. Okuda et al. used LA-ICP-MS to analyze aerosol samples collected on cellulose nitrate filters [124]. The filters were directly ablated and 15 elements were investigated. Calibration was achieved by spiking the filters with standard solutions. Precisions better than 10 % RSD could be achieved, except for Al (11 %) and Cu (18 %).

da Silva and Arruda [73] prepared sample pellets for the measurement of Se and S in sunflower leaves, which were spiked with different amounts of the elements of interest. Different certified materials were used for validation of the method. Jiménez et al. [109] investigated compost samples for the presence of toxic metals. The samples were homogenized, ground, sieved several times, and pressed into pellets (200 mg). Quantification was achieved by external calibration versus matrix-matched standards (BCR-144R and CRM029-050) and standard addition with aqueous standards. The RSDs for quantification were better than 10 % for most elements. Particle size and therefore milling time were identified as factors having a high impact on the method precision.

If applicable for the target analyte(s), the addition of isotope-enriched spikes is also feasible, enabling analyte quantification using isotope dilution. This approach offers best results in terms of precision and accuracy, but is also expensive and limited to elements for which at least two isotopes can be measured interference-free. Malherbe et al. investigated the potential of this approach for the analysis of different CRMs. Prior to LA-ICP-MS measurement, sample disks were prepared by borate fusion [114]. NIST SRM 1944 (New York/New Jersey waterway sediment), NIST SRM 2586 (trace elements in soil containing lead from paint), NIST SRM 2702 (inorganics in marine sediment), NIST SRM 2710a (Montana I soil), NIST SRM 2711a (Montana II soil), and NIST SRM 2780 (hard rock minewaste) and a meteorite sample were analysed. The results obtained were in good agreement with the corresponding certified values and the precision was better than 3 % RSD for all elements investigated. For the analysis of powdered samples, the previously described concept of liquid standard nebulization is also used for quantification of LA-generated aerosols. Fernández et al. [107] proposed a quantification method with on-line double isotope dilution for a wide range of matrices. Samples were either analyzed directly (NIST SRMs 610, 612, and 614), pressed into pellets (USGS MESS-2 and PACS-2), or fused with lithium borate (NIST SRMs 2710a, 2711a, 1944, 2702, and 2780). The ablated aerosol of either standard or sample is mixed with the nebulized isotope-enriched spike solution or blank solution. The RSDs ranged from 6 to 21 % for pressed pellets and from 3 to 21 % for borate fusion. Lloyd et al. analyzed uranium oxide grains, retrieved from soil and dust samples [117]. The grains were mounted on epoxy resin; the latter was then ground and polished to access the interior of the grains. As a result of the lack of a suitable standard reference material containing ^{236}U, quantification was achieved by introducing liquid reference materials NBL U950a (uranium particles) and NBL U010 (uranium isotopic standard) via a desolvating nebulizer. Natural uraninite grains were used as tertiary reference material to correct for mass bias. U isotope ratio analysis was implemented successfully with precisions of 0.4 % and 2.7 % RSD for $^{235}U/^{238}U$ and $^{236}U/^{238}U$, respectively.

Specific approaches

Claverie et al. [115] proposed a new approach for quantification of six elements of environmental concern, e.g., in soil or sediment samples, using pellets fixed on a spinning platform. Samples as well as standards were prepared by lithium borate fusion. By placing standard and sample next to each other on a platform, which is spinning at a high speed during laser ablation, quasi-simultaneous ablation of sample and standard is achieved. The mixed ablation aerosols are analyzed and quantification is based on standard addition or isotope dilution. For five standard reference materials and meteorite rock, an average precision of 10 % RSD could be achieved. The experimental results obtained compared well with the corresponding certified values with maximum deviations of 15 %. Lu et al. [119] tried to overcome the need for an internal standard for LA-ICP-MS analysis of carbonate materials. Using an equation-based approach, the so-called MRM-NoIS calibration strategy, a successful quantification of different carbonate minerals was achieved by using four reference materials (NIST SRM 610, USGS MACS-3, USGS GP-4, MPI-DING). For trace elements RSDs of less than 10 % and for rare earth elements (REEs) and major compounds RSDs of less than 5 % were observed. Cizdziel et al. investigated plutonium in US soil and dust samples [122]. Pu was spiked with a tracer, leached from the sample, and extracted from the leachate by anion exchange chromatography. Afterwards, the recovered analyte was electroplated on a stainless steel planchette disk for LA-ICP-MS analysis. LA-ICP-MS results were compared with liquid ICP-MS results, which were validated using NIST SRM 4350b (river sediment, radioactivity), NIST SRM 4353 (rocky flats soil number 2), and IAEA 385 (radionuclides in Irish Sea sediment). The authors reported a successful fingerprinting of Pu in soil and dust samples with LA-ICP-MS.

Figures of merit

Since detection limits and data for the level of reproducibility achieved have not been published in any of the reviewed contributions, this section aims at providing a comparison between the methods, accounting for all special applications.

Besides the approach used for preparation of compact samples, the quantification strategy also has to be taken into consideration. Furthermore, sample homogeneity is another limiting factor (especially for pressed pellets). Also, the concentration ranges of the target analytes as well as the instrumentation applied influence the quality of the results obtained.

In general, detection limits (LOD) were found to vary between several micrograms per kilogram and some milligrams per kilogram, depending on the instrumentation used and the analyte of interest. With pelletization, LODs around 0.035 mg kg^{-1} were obtained for different elements in vanilla samples [108]; for compost samples [109], values ranging from 0.01 to 0.8 mg kg^{-1} were reported. For fusion, the LODs varied from 0.02 to 4 mg kg^{-1} [114] with SF-ICP-MS and Q-ICP-MS. For tape mounting analysis and subsequent LA-ICP-MS analysis using SF-ICP-MS, detection limits from 0.3 μg kg^{-1} to 10 mg kg^{-1} were observed [118]. LODs varying from 0.001 to 0.5 mg kg^{-1} were reported for direct analysis of the sample without pretreatment [121].

In contrast to sensitivity, the reproducibility of a measurement is less dependent on the MS instrumentation used. Overall, reported RSDs were in the order of less than 3 to 50 %. The pelletization approach resulted in measurement reproducibilities varying between 6 and 21 % for the elements Pb, Rb, and Sr [107], and 6 to 14 % for 11 elements in vanilla [108] and less than 15 % for 12 elements in soil [110]. Fusion approaches showed comparably lower RSDs, a result which could be attributed to the improved sample homogeneity obtained with this approach. Published results vary between less than 3 % [114], 3 and 21 % for Pb, Rb, and Sr [107], and 10 % for six elements in environmental matrices [115], depending on target element and calibration strategy. For applications using the mounting/embedding approach for sample preparation, RSDs ranged from 15 to 50 % for the halogens Cl, Br, and I in ashed soil samples [116], and 15 to 25 % for 60 elements in dust samples using fs-LA-ICP-MS [118]. Poorer RSDs often result from the low analyte signals observed when analyzing single particles, which give rise to very small amounts of ablated material only.

Dried droplet analysis of liquid samples

As demonstrated in the previous sections, LA-ICP-MS is a versatile tool for solid sampling, suited for both bulk analysis and for mapping analyte distributions, as well as for combinations thereof. Consequently, the vast majority of samples being analyzed by LA-ICP-MS today are solids, especially since LA-ICP-MS circumvents the sometimes cumbersome digestion procedures otherwise required. For liquid samples and sample solutions, sample introduction in ICP-MS analysis is traditionally accomplished using a nebulizer. Pneumatic nebulizers are available in numerous modifications to suit practically any kind of liquid matrix [126]. However, heavily matrix-loaded liquid samples, such as urine or blood, present a challenge even for the most matrix-tolerant nebulizers. Such demanding matrices require at least dilution or partial digestion, which results in an increased workload. If high sample throughput is required, alternative sample introduction methods are therefore necessary.

As an alternative to pneumatic nebulization, laser ablation of dried liquids offers the aforementioned matrix-tolerance and sample throughput. In this section, the concept and some practical aspects of dried droplet laser ablation will be discussed. The performance of the method, as well as instrumental limitations will be highlighted, and a comprehensive overview of the related literature, including application examples, will be given.

The concept of dried droplet laser ablation

The basic concept of dried droplet laser ablation consists of depositing a well-defined volume of liquid sample on a solid support, evaporating the solvent, and examining the remaining dried residue by means of LA-ICP-MS. To unmistakably state that only the dried residue of a liquid sample is being analyzed, the term “dried droplet laser ablation” will be used throughout. To the best of our knowledge, Yang et al. introduced this method to ICP-MS in 2005 [127]. The present review will focus exclusively on the ablation of dried liquid samples, although it has been demonstrated that direct liquid ablation is also possible [128, 129].

As simple as the concept of dried droplet laser ablation may seem, its implementation can hold some pitfalls. One risk is to compromise the natural homogeneity inherent to the liquid sample. Method development in dried droplet laser ablation should therefore aim at preserving the sample’s original elemental composition throughout the analytical process, or at providing a sound strategy to compensate for any inhomogeneities introduced artificially during sample preparation. There are some methods reported in the literature that appear to be similar to dried droplet laser ablation in the sense that some part of a liquid sample is dried and analyzed by laser ablation. However, with those methods, the homogeneity of the liquid sample is abandoned by design. Hence, it is difficult or impossible to obtain quantitative information. Such methods are, for example, the combination of thin-layer chromatography with laser ablation [130–134] or the analysis of substrates which are immersed in a sample, removed from the liquid, and subsequently dried [135, 136].

The motivation for using dried droplet laser ablation instead of more established sample introduction techniques is in all cases reported to be (a combination of) the following four features: coverage of (sub-)microliter sample volumes, while offering (sub-)microgram per liter detection limits in case of ICP-MS detection, removal of solvent to allow coupling ICP-MS as an element-specific detector to chromatographic systems and to obtain less polyatomic interferences arising from the solvent, simplification of sample logistics, as well as direct sampling of challenging liquid matrices. Although some of these features could also be achieved with alternative solid sampling methods, such as solid sampling graphite furnace AAS or electrothermal vaporization (ETV) ICP-MS, dried droplet laser ablation offers two significant advantages over graphite furnace techniques. First, it is a genuine multi-element technique as opposed to conventional AAS, or compared to high-resolution continuum source AAS with limited multi-element capabilities. Secondly, LA allows complete desorption of the sample, whereas in ETV carbide formation may hamper correct quantification (e.g., [137, 138]). Such problems are not observed with LA [139]. In some cases, sample throughput was found to be higher with dried droplet laser ablation than with ETV-ICP-MS [139] but this certainly depends on the measurement protocols deployed and cannot be generalized.

Preparation of dried droplets

As stated above, the key aspect of dried droplet laser ablation is to preserve the inherent homogeneity of the liquid sample throughout sample preparation and measurement. If an artificial inhomogeneity is newly introduced, this should be done in a reproducible way, in order to be able to fully compensate for it. From everyday experience, it is well known that dried residues, e.g., coffee stains in the kitchen, are usually far from being homogeneously shaped. It is the scope of this section to provide some very basic physical insights into the processes involved in droplet-drying, although the literature on this topic is vast and the interested reader is referred to the numerous specialized reviews. Three parameters play a major role in terms of dried droplet shape: (a) choice of the surface used for droplet deposition, (b) drying conditions, and (c) the matrix of the liquid sample:

(a) When drying droplets on hydrophilic surfaces, ring-shaped residues are frequently obtained. This “coffee stain effect” was described by Deegan et al. [140, 141] to be caused by a radial flow, which transports liquid from the core of the droplet to its perimeter, where the solvent evaporates more easily. This radial flow is the consequence of one precondition inherent to this physical model: the contact line (the perimeter of the droplet) does not shrink during the drying process. Several authors provided experimental data to support this model (e.g., [142–144]). Contrarily, in the case of a hydrophobic surface, deposition of concentric rings or small spots in the center of the droplet can be observed [145–147], as the contact line continuously or periodically shrinks while drying.

(b) In addition to the flow patterns that lead to ring deposition, the interaction of dissolved or colloidal matter with the contact area, as well as convective currents can contribute to the dried pattern [144, 148]. Such convective currents are related to the drying rate, which in turn depends on temperature, relative humidity, and heat conductivity of the substrate [144, 149, 150]. Hence, the experimental setup might also influence the shape of the dried residue.

(c) Finally, the matrix of the sample (e.g., salt or protein concentration) also influences the shape of the dried residue [151, 152]. In the first publications that describe dried droplet laser ablation, small sample aliquots of 20 μL were pipetted onto hydrophobic polystyrene plates and dried under ambient conditions [127, 139, 153]. Owing to differences in the matrix (purely inorganic salts in the case of standards, with organic constituents in case of samples), the shape and size of the dried residue depended strongly on the sample matrix [127].

In view of the aforementioned three parameters, a drying droplet is a complex system and it is easy to understand that the morphology of the final dried residue is difficult to predict. Although the references provided show that it is indeed possible to control the morphology of the dried residue, such experiments are most likely beyond the scope of analytical laboratories. However, it is possible to minimize the influence of those factors, which have the most pronounced effect. As the choice of the solid substrate plays a major role in terms of droplet morphology, this factor was considered and optimized in most reported cases of dried droplet laser ablation. The following three types of solid substrates were applied: 1. hydrophobic surfaces, 2. filter paper (paper diameter much greater than droplet diameter), and 3. confined, circular, and hydrophilic areas (diameter of circular area no greater than droplet diameter). For visualization, examples of these approaches are provided in Fig. 3.

Method I Using a hydrophobic surface for droplet deposition results in a small dried residue, as described above. Typical diameters of dried residues are around 100–1600 μm, depending on droplet volume and sample matrix (Table 2). As the droplet shrinks continuously, the coffee stain effect will be observed only at a very late stage of the drying process, or not at all. Hence, it is straightforward to ablate the entire dried residue with only a few laser pulses. Hsieh et al. [154, 155] demonstrated that this approach allows for external calibration when quantifying metals in whole blood. Yet, as other authors have found, the extreme preconcentration on a small spot has the disadvantage of pronounced matrix effects by co-existing sample constituents. For example, Yang et al. [127] showed significant signal suppression by sodium present in the sample. On the other hand, deposition of droplets on a substrate

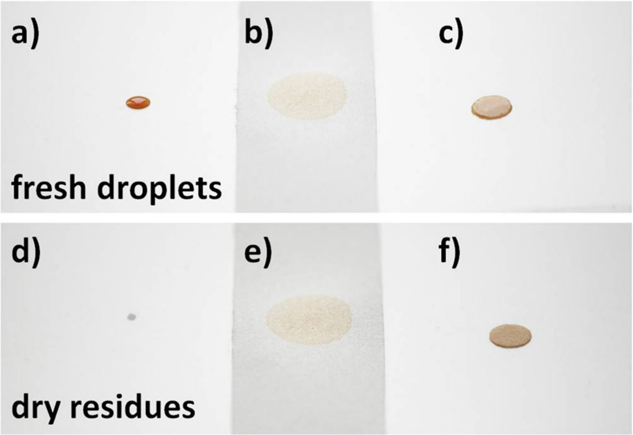

Fig. 3 Strategies for sample application in dried droplet LA analysis. Deposition of a defined sample volume on hydrophobic surfaces (**a**), filter paper with dimensions much greater than droplet diameter (**b**), and confined, circular, hydrophilic areas with diameter of circular area no greater than droplet diameter (**c**). Dried residues after evaporation of the solvent on a hydrophobic surface (**d**), filter paper (**e**), and precut filter disks of filter paper (**f**)

that enhances sample ablation as a result of strong interaction with the laser light has been demonstrated [156, 157], in combination with automated deposition of liquids. Table 2 summarizes the literature that applied the approach of hydrophobic surfaces.

Method II Applying a droplet on a large piece of filter paper makes sample preparation very easy, as the liquid is immediately absorbed by capillary action [158, 159]. Once dried, the residues can be easily transported and stored as the analyte is incorporated in the paper fibers [160]. Consequently, blotting cards are widely used in clinical settings [161], e.g., in collection of blood samples. Yet, even if the dispensed volume of sample is well defined, differences in viscosity can lead to a different migration behavior on the paper, combined with chromatographic effects [162, 163]. Careful design of laser ablation patterns is therefore required. Table 3 gives an overview of papers that report on analysis of "freely migrated" droplets on filter paper, via LA ICP-MS. Also, typical diameters of dried residues and applied sample volumes are given.

Method III By providing a hydrophilic area with a clearly defined border, samples can only migrate within this area. Therefore, samples with low viscosity or challenging matrix are confined on the same area as purely aqueous samples. This approach was used by Choi et al. [164] to analyze photo-resist, deposited on micro-machined polymer pillars. A somewhat different approach was presented by Aramendía et al. [160] who applied precut disks of filter paper on a hydrophobic surface. By doing so, large volumes of sample could be applied on a small area, thus enhancing sensitivity 10-fold [160]. However, the coffee stain effect is very pronounced with this type of sample preparation, since the precut filter disk is the ideal model of a fixed contact line (as described above, a fixed contact line results in a constant droplet area during the drying process. As the evaporation on the rim of the droplet is faster than in the center of the droplet, a liquid flow is created which transports material to the rim of the droplet which is the origin of the coffee stain effect). Crater-shaped analyte distributions were therefore obtained [18, 160, 165]), as also observed in MALDI-MS [166]. Table 4 gives an overview of the related literature and typical sample loadings (microliters per millimeter squared).

Quantification approaches, sensitivity, and reproducibility

The quantification process also needs to be adapted to the approach used for sample preparation. The sensitivity is influenced to a large extent by the analyte loading, i.e., the amount of sample per unit area (e.g., microliters per millimeter squared). In Tables 2–4, this value can be compared for the three application modes (methods I–III), and in general, highest analyte loading is observed with method I. However, as discussed above, matrix effects are most pronounced with this approach; therefore, lower analyte loadings (method II or method III) can be beneficial, depending on the individual analytical setup and sample type.

In the case of sample preparation on a hydrophobic surface (method I), the small residue can be ablated completely using spot, grid, or line patterns. Thus, the entire signal is collected in a short time, giving rise to a sensitivity which is comparable to that achievable with conventional nebulizer systems. Yang et al. [127] even demonstrated a 2–7-fold improved absolute sensitivity (counts per nanogram) compared to pneumatic nebulization when analyzing aqueous standard solutions. This finding is also due to the fact that the transport efficiency of laser ablation systems is superior to that of pneumatic nebulizer systems [127]. The general sensitivity of dried droplet laser ablation in combination with hydrophobic surfaces obtained in practice can therefore be expected to be similar to that with pneumatic nebulization (see Table 2).

Partial ablation of freely deposited droplets (method II) might result in erroneous results, as demonstrated in [160], unless closely matrix-matched standards are used [158]. The reason for this is that sample-to-sample variations in terms of viscosity result in different sample spread across the filter. The complete consumption of the dried residue [159] is a feasible way to avoid this problem, but requires specialized laser equipment. If the deposited volumes are very small [167, 168], quantitative ablation from filter paper becomes easy, especially in the presence of substances that improve the laser ablation yield, such as black ink deposited prior to the droplet [167, 168].

Table 2 Method I: droplet deposition on hydrophobic surface

Sample matrix	Droplet volume	Size of dried residue	Sample loading[a]	Surface material	LOD	Reproducibility	Additional information	Ref.
Drinking water, yeast extract	20 μL	150–500 μm	10^{-4}–10^{-3} μL μm^{-2}	PS	0.08–0.12 ng mL^{-1} (aqueous), 0.06–0.09 ng mL^{-1} (standard addition), 0.05–0.08 ng mL^{-1} (isotope dilution)	4.6–23 % RSD (aqueous with I.S., n=4), 4.7–8.2 % RSD (standard addition with I.S., n=4), 3.5–3.9 % RSD (isotope dilution, n=6); 0.5 % RSD (Se in yeast, isotope dilution, n=5)	NaAc matrix was added to water samples	[127]
HPLC fractions of yeast extract	20 μL	600 μm	7×10^{-5} μL μm^{-2}	PS	36–110 μg g^{-1} (Se)	0.55–0.77 % RSD (species-specific isotope dilution)	No matrix required due to high salt load of samples	[153]
Digested biological tissue, nearshore seawater, and river water	20 μL	100 μm 1.6 mm	10^{-5}3×10^{-3} μL μm^{-2}	PS	0.033 pg mL^{-1} (Pu), 0.051 pg mL^{-1} (Th), 0.072 pg mL^{-1} (U).	8 % RSD (with I.S., n=10)	Chromogenic matrix investigated	[137]
Cr species via capillary electrophoresis	100 nL	100–500 μm	5×10^{-7}–10^{-5} μL μm^{-2}	PETG	0.2–6.5 μg L^{-1}	Below 3 % RSD	α-Cyano-4-hydroxycinnamic acid	[156]
Blood reference materials	0.5 μL	700–900 μm	8×10^{-7}–10^{-6} μL μm^{-2}	Other	0.1 ng mL^{-1}	Below 10 % RSD for all samples	Methylene blue as indicator and to improve ablation yield	[154]
Cell cultivation medium and cell lysate	<20 nL	<300 μm	3×10^{-7} μL μm^{-2}	PETG	26 fg Cu (100 nL droplet, therefore 26 ng L^{-1})	5 % RSD under optimized conditions for samples	Rhodamine B added for visibility	[157]
Cr species via liquid-liquid micro extraction, synthetic seawater	7 μL	5 mm	4×10^{-7} μL μm^{-2}	PS	0.11 μg L^{-1}	4–8 % RSD	Organic matrix, internal standard	[169]
Various “meat” reference materials (oyster tissue, etc.)	50–100 μL	1 cm	6×10^{-7}–10^{-6} μL μm^{-2}	PTFE, PS	0.05–6 μg kg^{-1} dry mass (corresponds to 1.25–240 ng L^{-1})	5–10 % RSD	No additive, organic digest	[170]
Mineral water, tap water, swimming pool water, and water from two artificial lakes	1 μL	600 μm	4×10^{-6} μL μm^{-2}	PTFE	0.05–0.81 ng mL^{-1}	~5 % RSD (for n=3, recovery experiment)	Methylene blue added for visibility	[171]
Seronorm blood reference material	0.5 μL	–	–	PTFE	0.14–29 ng mL^{-1} (Be–Mg)	6 % RSD within-run precision, 4–8 % RSD between-run precision	Methylene blue added for visibility	[155]
SLRS-4 river water reference material, lake water, and synthetic seawater	1 μL	480–850 μm	2×10^{-6}–6×10^{-6} μL μm^{-2}	PTFE	0.03–0.2 pg mL^{-1} (enrichment factor 32)	2–5 % RSD	Methylene blue added for visibility	[172]
Human urine from Fabry disease patient and control	1 μL	–	–	PTFE$^{)}$	0.003–0.58 μg g^{-1}	<20 % RSD	Spiked samples for calibration	[173]

PS polystyrene, *PETG* poly(ethyleneterephthalate)glycol, *PTFE* polytetrafluoroethylene, *Other* “hydrophobic filter membrane”

[a] Sample volume/area of dried residue (assuming a circular spot)

Table 3 Method II: droplet deposition on large filter paper sheets

Sample matrix	Droplet volume	Size of dried residue	Sample loading[a]	Surface material	LOD	Reproducibility	Additional information	Ref.
Blood spotted on paper, from a lab proficiency test	–	–	–	Whatmann filter paper	0.9 μg dL^{-1} (Pb)	7 % RSD (in-between droplets and also within droplet)	Sample directly spotted without any other treatment	[158]
Co in a drug preparation, Pb in whole blood, and Sn in food samples	500 nL	–	–	Filter paper with additive	1–60 ng L^{-1}	10 % RSD (spot-to-spot)	Different additives to improve laser yield	[168]
Pb and Cd in BCR-634 whole blood reference material	200 pL	–	–	Filter paper with additive	0.5 pg Pb 0.02 pg Cd (equal to 2.5 and 0.1 ng L^{-1} with 200 nL of sample)	25 % for Pb and 8 % for Cd with standard solutions using ^{13}C as internal standard, for samples: 5 % for Pb and 35 % for Cd	Repeated deposition of 65 pL droplets, ablation of several droplets at the same time	[167]
Blood (reference materials and real samples)	5 μL	5–6 mm	3×10^{-7} μL m^{-2}	Filter paper	0.040–0.054 μg L^{-1}	3–9 % RSD (quantitative) 1500 ppm (isotope ratios)	Analysis vial split aerosol-flow (single-collector/multi-collector ICP-MS)	[159]

[a] Sample volume/area of dried residue (assuming a circular spot)

Table 4 Method III: droplet deposition on confined, circular, and hydrophilic areas

Sample Matrix	Droplet volume	Size of dried residue	Sample loading	Surface material	LOD	Reproducibility	Additional information	Ref.
Photo-resistant used in photolithography	64.7 pL	150 μm	4×10^{-6} μL μm^{-2}	PDMS-columns (micro-machined)	2.33, 15.4, 5.72 ng mL^{-1} (Al, Cu, Pb)	17.1–46.9 % RSD (due to extremely low sample volume)	No matrix added, photo resist	[164]
Human urine from supposedly healthy patients	300 μL	16 mm	10^{-6} μL μm^{-2}	Filter paper (precut saturated filter disks)	0.1–13 μg L^{-1}	2–5 % RSD	No additive	[160]
Cu isotopes in urine of Wilson's disease patients, treated patients and one control patient	300 μL	16 mm	10^{-6} μL μm^{-2}	Filter paper (precut saturated filter disks)	–	200–500 ppm RSD intra-spot, and 540 ppm RSD inter-spot	No additive, corona ablation with 10 kHz	[18]
Phosphorus in fermentation media	10 μL	5 mm	5×10^{-7} μL μm^{-2}	Filter paper (precut saturated filter disks)	10 μg mL^{-1} (ICP-OES detection)	10 % RSD	Analysis via laser ablation ICP-OES	[165]

[a] Sample volume / area of dried residue (assuming a circular spot)

Table 5 Selection of frequently applied procedures for signal quantification in LA-ICP-MS analysis

Quantification approach	Biogenic carbonates	Hard tissues	Soft tissue	Powdered samples	Liquid samples
CRM/SRM	27, 38–48, 50–54	58–62		108, 118, 121, 123	154
In-house prepared standards					
Non matrix-matched standards					
Use of well-characterized materials	43	64–68			158
Thin films on sample or substrate			94		
Gelatin, agarose gel, sol-gel standards			91, 92, 93	32	
Printed pattern			95, 96		167, 168
Dried droplets (aqueous standards)					127, 138, 154, 157
Matrix-matched standards					
Preparation of pellets	69			71, 109, 111, 112	
Fusion to disks	31, 32			29, 33, 113–115	
Embedding into polymer resin			97	116, 120	
Homogenized tissues			90		
Matrix-adjusted dried droplets					155, 164, 169–173
Specific approaches		63, 66, 67			
Nebulized liquid standards					
Calibration/standard addition	64, 65		88, 89	117	
IDMS			89, 103	107	
Internal standard correction					
Sample-inherent element	27, 28, 38, 39, 43, 46	58–67	75, 104	29, 118, 123, 125	
Homogeneously spiked to the sample			90, 97	110, 114	127, 139, 160, 169
Applied as thin layer on/below sample			79, 94, 95, 100		160
On-line addition of dried aerosol			88, 89		

In the case of uniform sample geometry due to circular hydrophobic areas (method III), the coffee stain effect is very pronounced, as discussed above. Although a quite homogeneous analyte distribution is obtained in the center of the droplet, the extent of ring formation will depend on the sample matrix. Therefore, standard addition or isotope dilution is required if the laser is focused onto the center of the filter disk. In a recent publication, Nischkauer et al. [165] showed that the bias resulting from this centrosymmetric distribution of analytes can be easily compensated for. Instead of performing laser ablation only in the center [160] or only in the rim [18] of the precut filter disk, it was proposed to perform radial line scans that pass across the entire sample, including the center. The resulting U-shaped signal was then integrated and was found to be proportional to the concentration in the initially liquid sample, without the need to ablate the entire filter disk, and without the need for matrix-matching or the use of an internal standard [165].

The reproducibility of dried droplet laser ablation is intrinsically compromised, compared to pneumatic nebulization, as a result of the additional error introduced by repeated droplet deposition and by the transient signal mode. Interdroplet reproducibilities range between 3 % and 23 % RSD for samples measured directly, with typical values ranging between 3 % and 10 % RSD [127, 137, 154, 155, 157, 158, 160, 165, 167–173]. When automated, droplet deposition can be achieved with greater precision [174, 175], but the higher uncertainty inherent to solid sampling techniques will most likely persist. In case of isotope dilution and isotope ratio measurements, better reproducibility was reported (540 ppm RSD interspot [18], 0.55–0.77 % RSD for species-specific isotope dilution [153]) than in the case of pure quantitative measurements.

Conclusions

Although geoscience is still the main field of application of LA-ICP-MS, its use in the fields of environmental research and life sciences increased continuously during the last few years. High sensitivity combined with excellent spatial resolution is the main reason for using LA-ICP-MS in the analysis of hard and soft tissues, as well as of powdered environmental samples. The capabilities for performing imaging studies or isotope ratio measurements are additional advantages of LA-ICP-MS. The applications published so far cover a wide range of sample matrices, target analytes, and concentration ranges. Nevertheless, they have one common problem—reliable quantification. The strategies used to circumvent the influence of elemental fractionation and matrix effects in LA-ICP-MS analysis, which are considered as the main problems hampering reliable quantification, are rather similar, although the resulting interferences differ between individual applications. Table 5 presents a compilation of the most frequently applied approaches for quantification, indicating that the use of in-house prepared standards in combination with an internal standard is the dominating strategy. Improved concepts for sample preparation as well as for application of matrix-matched standards will further enhance the potential of LA-ICP-MS for the analysis of environmental, biological, and biomedical samples. The choice of an appropriate internal standard is still of major concern in many applications, especially when no sample-inherent element is available. Thus, further methodological developments are required, e.g., in the case of tissue analysis the application of polymeric layers or thin metal coatings has been shown to be promising. Special attention should be paid to the application of fs-laser systems, which offer distinct improvements in terms of matrix effects and elemental fractionation. Another prerequisite for the acceptance of LA-ICP-MS as an alternative to traditional procedures for the quantitative determination of trace elements is the availability of appropriate reference materials. Especially for life science applications, the development and production of a larger range of CRMs is highly desirable. In contrast, for environmental samples (soil, fly ash, dust, etc.) a wide variety of CRMs is available. However, as those materials have been designed for liquid analysis after mineralization, none of them is applicable for direct LA-ICP-MS analysis because of their inhomogeneity on the microscale. Particularly considering the comparability of measurement results, the availability of at least a couple of compact standard materials with sufficient homogeneity should be aspired to.

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ARTICLE 2

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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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

Table 1
Instrument parameters for LA-ICP-MS analysis.

Laser ablation system	NWR213, ESI	ICP-MS	iCAP Q, Thermo Scientific
Type of laser	Nd:YAG 213 nm	RF power (W)	1550
		Carrier gas flow rate (L min^{-1})	0.4
Ablation mode	Raster (lines)	Plasma gas flow rate (L min^{-1})	12
		Auxiliary gas flow rate	0.8
Spot size (µm)	100/200	Collision/reaction gas	He with 7% H_2
		CR gas flow rate (mL min $^{-1}$)	4
Fluence (J cm^2)	0.65–15	Kinetic energy barrier (V)	3
		Acquisition time per isotope (ms)	10
Frequency (Hz)	10	Measured isotopes	^{58}Ni, ^{60}Ni, ^{63}Cu, ^{64}Zn, ^{65}Cu, ^{66}Zn, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{114}Cd
Scan speed (µm s^{-1})	300		
He gas flow (L min^{-1})	0.75	Isotopes used for quantification	^{111}Cd, ^{60}Ni, ^{63}Cu, ^{66}Zn,

depth investigations were started by ablating a larger area at the surface level while decreasing the margin by 100 µm for each repeated measurement, starting with a 900 × 900 µm spot at the top level, resulting in a 600 × 600 µm spot at the fourth depth level. Thus potential "wall effects" (repeated ablation of an already measured layer, together with a lower layer) were reduced. For signal evaluation, the same 600 × 600 µm total spot size was used at all times.

3. Results and discussion

3.1. Selection of CRMs

CRMs used for method development were selected because of their differences in matrix composition, even though they are all categorized as environmental samples. Since these materials originate from different sources, they show distinct deviations in their bulk as well as trace element composition. Furthermore, they are available in powdered form, which is the only requirement to apply the procedure presented in this contribution. According to the reference data sheets, the CRM particle size distributions d(0.9) varied from 30 µm for NIST1648a to 90 µm for BCR144 and BCR723.

BCR144, trace elements in sewage sludge, is originating from water treatment plants and therefore consists mostly of dried organic matter with relatively high phosphorus and comparably low silicon content. NIST1648a, urban particulate matter, on the other hand, consists of atmospheric particulates collected in an urban area with noticeable contents of elemental carbon. NIST2709, San Joaquin Soil, is agricultural soil with a dominating silicon fraction and high aluminum content. Due to preparatory reasons, the total carbon content is only about 1.2% in this CRM. Finally, BCR723, road dust, is a mixture of mainly silicon oxides and different carbon species. When comparing these CRMs, the silicon content (calculated as silicon dioxide content for comparing reasons) varies from 13% for BCR144 to over 63% for NIST2709. Although detailed information about the contribution of organic material, elemental carbon, and water-soluble ions is not available for all CRMs, severe differences were also expected for these principal constituents, substantially influencing the laser–sample interaction. In addition to the mentioned deviations in bulk composition, the selected CRMs show also distinct differences in the analyte concentrations. For example are the trace metal concentrations in NIST2709 (San Joaquin soil) up to two orders of magnitude below the levels of NIST SRM1648a (urban particulate matter). Table 2 [29] presents concentrations for target analytes as well as for selected matrix constituents.

3.2. Pellet investigation

These reference materials are commonly applied for demonstration of accuracy in liquid ICP-MS analysis using external calibration after sample digestion. To make powders applicable to LA analysis, pelletization was chosen as sample preparation procedure since it is easy, time saving, and the equipment is available in most analytical laboratories. To keep the procedure as simple, fast, and mild to the sample as possible only pre-drying of the materials, mixing and one pressing step were applied. Overall, the previously described pellet preparation routine takes 40 min (mixing of sample with prepared binders/additives and pressing). The prepared CRM pellets showed no degradation over time if stored under clean and dry conditions. One pellet can be used for more than 500 analyses, considering 600 × 600 µm patterns, since the whole surface and at least 50% of the bulk material can be utilized in ablation until the pellet integrity is lost.

The most important property for successful analysis in LA-ICP-MS is the homogeneous distribution of analytes throughout the pellet. The average signals of each spot (within one sample layer, as well as within the 4 consecutive layers) were statistically evaluated for all investigated elements ($\alpha = 99\%$, data not shown). RSDs were around 10% for BCR144, NIST1648a, and BCR723, indicating general homogeneity of the pellets. For NIST2709, an enhanced RSD of around 20% was observed, which can be explained by the explicitly lower analyte concentrations when compared to the other investigated CRMs. Since no significant difference in precision could be found when comparing the average signals obtained during depth analysis with the ones from surface analysis, all further precision and comparison measurements were done directly on the surface (RSDs of 600 × 600 µm spots, $n = 6$).

When examining the local analyte distribution of each 600 × 600 µm spot, the transient signal characteristics showed some small fluctuations within the analyzed area. Since these fluctuations were identical for all measured analytes, sample in-homogeneities could be excluded as source for the observed signal variations. Thus, local variations in ablation and/or transport efficiency are more likely to account for differences in the amount of sample introduced into the detection system. To overcome these problems and to further improve signal stability, silver oxide was introduced as internal standard during pellet preparation. The silver oxide content was set to 1% of total pellet mass. An excellent correlation between transient signal patterns of Ag (IS) and sample constituents was observed, indicating a homogeneous distribution of all components.

Table 2
CRM mass fractions for target analytes (values and uncertainties taken from the respective reference data sheets).

Reference material	Cd (mg kg^{-1})	Cu (mg kg^{-1})	Ni (mg kg^{-1})	Zn `(mg kg^{-1})
BCR 144	3.41 ±0.25	713 ±26	942 ±22	3143 ±103
NIST 1648a	73.7 ±2.3	610 ±70	81.1 ±6.8	4800 ±270
NIST 2709	0.38 ±0.01	34.6 ±0.7	88 ±5	106 ±3
BCR 723	2.5 ±0.4*	226 ±3**	171 ±3*	1660 ±100*
Matrix constituents	SiO_2 (%)	total carbon (%)	Fe (%)	Ca (%)
BCR 144	13.6		4.43	4.06
NIST 1648a	27.4	12.7	3.92	5.84
NIST 2709	63.5	1.2	3.5	1.89
BCR 723	32.1	10*	3.29	6

* Indicative values.

** Uncertain value[29] (confirmed within this work by microwave assisted digestion of the material using mineral acids and subsequent analysis with standard procedures).

Thus Ag has been used as IS in all further investigations. After IS correction, RSDs were decreased to below 8% for most elements in BCR144, NIST1648a, and BCR723. RSDs for NIST2709 remained unchanged, an outcome which could be explained with the low concentration levels prevailing in this CRM, thus measurement precision is not only influenced by the ablation process but also by measurement uncertainty during ICP-MS analysis. Summing up, by using a laser beam diameter of 100 μm, a scan speed of 300 μm s^{-1} and by introducing an internal standard, sufficient reproducibilities for the LA-ICP-MS analysis of the prepared pellets could be obtained. Further improvements were anticipated by preliminary grinding of the samples, thereby existing differences in particle size between binder, IS, and the investigated CRMs could be cleared, leading to pellets with increased homogeneity.

Similar findings for LA-ICP-MS investigations of sample pellets were reported in literature (Table 3) [30–38]. O'Connor et al. [10] achieved RSDs of around 20% with their pelletization procedure using ^{13}C and ^{65}Cu as IS which is comparable to the results obtained for NIST2709. Shaheen et al. [13] investigated a large number of elements using epoxy resins as matrix material, obtained RSDs varied from 2.4% to 49% with most elements around 15% using silicon as IS. The higher RSDs corresponded to low analyte concentrations in the respective analyzed materials. Kleiber et al. [39] achieved RSDs of 10–20% while performing trace metal analysis of coal with various IS. In their research they compared continuous sampling (3 sites, 60 s line scan each) with sequential sampling (15 sites, 20 s line scan each) with RSDs of about 10% for continuous and 10–20% for sequential sampling respectively.

3.3. Method development

For signal quantification, the known CRM contents of the prepared pellets and the respective certified/indicative trace element concentrations (Table 2) were used. In each experiment, one CRM was investigated while the other three were used to create a linear calibration curve. The concentration of the investigated CRM was calculated according to formula 1.

$$c_{unk} = \frac{i_{unk} - d_{cal}}{k_{cal}} \tag{1}$$

c_{unk}	Concentration of investigated CRM in mg kg^{-1} (presumably unknown).
i_{unk}	Blank and IS corrected signal intensity corresponding to in counts s^{-1}.
d_{cal}	Axis intercept of calibration curve
k_{cal}	Slope of calibration curve

3.4. Standard mode

The prepared pellets were measured with ICP-MS using standard conditions as shown in Table 1. To determine the concentrations of the investigated sample, formula 1 was applied to the data after blank and internal standard correction. This process was repeated 4 times for each data set changing the investigated CRM and calculating the calibration curve with the remaining three standards. Linear calibration curves were achieved for all combinations (R^2 between 0.90 and 0.95); the element concentrations found for the individual CRMs match the right order of magnitude. However, compared to the reference values, the resulting concentrations were well beyond the confidence region in most cases. When calculating concentrations for BCR144 the deviations between determined and certified content ranged from 40% to 133% and for NIST1648a from 47% to 174% of the certified contents. Looking at NIST2709, deviations from 113% to 275% and at BCR723 from 36% to 132% were found.

Observed differences between measured and certified CRMs/SRM contents indicate that matrix-induced variations in the ablation

Table 3
Comparing recently published environmental work using pelletization and borate fusion with LA-ICP-MS regarding accuracy (relative standard deviation).

Sample matrix	Internal standard	Pellet matrix	Number of analytes	Achieved RSD
BCR144 NIST1648a NIST2709 BCR723	Ag	Sodium tetra borate	5	4–15% 2–8% 5–20% 3–7%
Sediment [9]	None	$Li_2B_4O_7/LiBO_2$	5	3%
Sediment [10]	C, Cu	No binder, Polyvinyl alcohol, Vanillic acid, Nicotinic acid, Pyrazinoic acid	1	20%
Fly ash [12]	None	Cellulose, Silver powder, Caffeine, Maleic acid, Cinnamic acid, $Li_2B_4O_7/LiBO_2$	10	1–117% (Pellets) 1–57% (Fused beads)
Flue dust [24]	Rh	Paraffin, cellulose/N-methacrylate ZnO/Fe_2O_3	6	7%
Soil [30]	Sc, Lu	No binder	12	15%
Compost [31]	None	No binder	9	10%
Solid [32]	None	No binder	3	6–21%
Vanilla [33]	None	No binder	11	6–14%
Environmental [34]	None	$Li_2B_4O_7/LiBO_2$	6	10–15%
Soil and sediment [35]	Ag, Ni	No binder	8	5–14%
Soil, sediment, ash [36]	None	ZnO/2-methoxy-4-(2-propenyl)phenol	3	<20%
Road sediment [37]	Ca	No binder	3	10%
Agricultural soil [38]	Ge, Au, Sc, Pd	Ag powder, Al powder	8	2–8%
Coal [39]	C, Rh, Mo	No binder, KBr	10	10–20%
Soil and sediment [40]	Ge, Y	No binder	16	2–10%

behavior of the investigated samples are not or only partially corrected with the use of an IS. Even though possible matrix effects have been reduced due to the preliminary sample dilution by a factor of 10, the remaining matrix-induced variations which are still resulting in a limited accuracy. Consequently, the next development step focused on the ablation process.

3.5. Addition of optical absorbant

The interaction of the laser beam with the sample depends on the optical properties of the investigated sample (e.g. absorbance). Thus, samples with different matrix composition might be ablated in a different way even when using identical conditions [4–7]. An attempt to overcome this problem is the introduction of a material with absorbance capabilities at the used laser wavelength. Thus, differences in the absorbance of sample and standard could be minimized. O'Connor et al. [10] reported positive effects when using vanillic acid, pyrazinoic acid, or nicotinic acid. Stankova et al. [12] achieved improvements with the addition of maleic acid.

In this work, caffeic acid was chosen as modifier because of its good absorbing characteristics at a wavelength of 213 nm. To the knowledge of the authors, caffeic acid has not been used as optical laser absorbant in LA-ICP-MS so far. The absorbant was added with 40% total pellet mass by replacing the respective part of the binder material. Otherwise, the same preparation procedure was applied and the pellets were again measured using the conditions described before.

Data evaluation was performed as explained in the previous chapter. Overall, the addition of caffeic acid as optical absorbant did not significantly improve the results. Compared to experiments conducted without absorbant addition no improvements in accuracy were obtained, thus matrix-induced variations in ablation behavior and/or transport of different CRMs are not compensated by the addition of caffeic acid. No distinct improvements regarding the slopes or R^2 of the calibration curves could be observed. Also differences between certified and measured contents remain basically the same ranging from 39 to 123% for BCR144 and from 37 to 177% for NIST1648a. For NIST2709, deviations from 115 to 267% were found and for BCR723 deviations ranged between 39 and 112%. However, in the presence of caffeic acid, the analyte RSDs for NIST2709 were improved considerably below 6% for all investigated elements. At the same time, the RSDs for NIST1648a increased up to 60%. These changes in the reproducibility of measurement could not be attributed to insufficient sample in-homogeneity. Other possible explanations for these findings are impurities or interferences introduced by the addition of caffeic acid. Even though blanks were prepared and measured according to the described procedures, no significant improvements in accuracy could be achieved. Thus, contaminations of the used chemicals could be excluded as source for poor results with insufficient accuracy and reproducibility, the only remaining reason are therefore spectral interferences in ICP-MS analysis.

3.6. Collision/reaction cell technology (CR-mode)

The influence of spectral interferences on accuracy of analysis is well known from the field of liquid ICP-MS analysis. There, polyatomic ions with m/z values non-resolvable (with the used mass analyzer) from the target analytes are created from the plasma gas Ar with solvent and/or matrix constituents. In case of LA-ICP-MS measurements, the contribution of the solvent is not present; nevertheless, the formation of interferences from sample components and carrier or plasma gas is still possible. In the present study, binder (sodium tetra borate) and internal standard (silver oxide), which were both introduced during sample preparation, have to be considered as further sources for polyatomic interferences. Simple blank measurements for correction of generated interferences are considered to be not straightforward, since the polyatomic ions formed during LA-ICP-MS analysis of the prepared sample pellets are assumed to be different for the investigated matrices. For example, vary the concentrations of potentially interference-forming elements such as C, N, O, Si, P, or S distinctly between the individual CRMs, thus affected m/z values and extent of the created interferences are supposed to be different for each CRM.

A successful way to overcome polyatomic interferences in quadrupole ICP-MS analysis is the use of collision or reaction cells [7]. In this study, a combined collision/reaction (CR) mode was used by introducing a gas mixture (helium with 7% hydrogen) with simultaneous application of the kinetic energy discrimination (KED) approach. For optimization of the CR-mode conditions, the $^{40}Ar^{23}Na$ interference on ^{63}Cu has been selected, as this interference originates primarily from the added chemicals and not from the investigated samples. Hence, the signals observed for ^{63}Cu and ^{65}Cu in blank pellets prepared with sodium tetra borate and silver oxide were used for development of the CR method. While for ^{65}Cu, signals close to the background level were found, indicating the absence of any Cu-contaminations in binder and internal standard, significant signals were found in experiments without collision/reaction gas and a KED value of 0 V at an m/z ratio of 63. These signals were assigned to the formation of $^{40}Ar^{23}Na$ ions. With increasing flow rate of the used He/hydrogen mixture and/or kinetic energy barrier value, a decrease of the $^{40}Ar^{23}Na$ signal was observed. Simultaneously, the signal of the silver isotopes dropped, but with a different extent, when compared to the examined polyatomic interference. Best results in terms of minimum polyatomic interference (signal at the m/z value of 63) with maximum intensity for the internal standard (^{107}Ag signal) were reached when introducing the CR gas at a flow rate of 4 mL min^{-1} and a KED value of 3 V. Therefore, all sample measurements were performed using these conditions (detailed parameters in Table 1).

For quantification, the same procedure for signal evaluation was used as described previously. Again a linear calibration function was achieved for all combinations with considerably increased coefficients of determination ($R^2 > 0.99$ for all elements). Based on the signals derived for sample and blank pellets, the respective limit of detection (LOD) was determined for each investigated element. LODs (3 σ) were calculated from the standard deviations of blank measurements ($n = 6$), yielding results of 1.7 μg kg^{-1} for Ni, 9.5 μg kg^{-1} for Cu, 9.8 μg kg^{-1} for Zn, and 0.3 μg kg^{-1} for Cd. For all materials, a satisfying precision was accomplished with average RSDs of 11.1% for NIST2709 and 7.6% for BCR144 as well as 4% and below for NIST1648a and BCR723 for Cu, Ni, and Zn. For Cd in CR-mode, all RSDs were elevated to around 20% except for NIST1648a, which can be explained by the low concentrations of this element in the other CRMs and the reduced sensitivity of the ICP-MS analysis in the CR-mode. Comparison to recent LA-ICP-MS literature shows that findings for reproducibility of analysis expressed as RSD are similar or even better to published data (Table 3); further improvements have been reported only when using isotope dilution for quantification.

Using the developed procedure, all four investigated CRMs could be accurately quantified; achieved results were in good agreement with the certified values (Fig. 1). Due to the wide range of the analyte concentrations, the common logarithm of all values was calculated for comparison of the measured values with the certified concentrations. Slopes of the calculated linear regression functions (varying from 0.987 to 1.012) are not significantly different from the value of 1 for all four presented cases ($\alpha = 0.05$), indicating no systematic error resulting from the calibration with different CRMs. Intercepts of the respective functions do not differ significantly from 0 ($\alpha = 0.05$).

Obtained results were for all investigated elements and CRMs except Ni in BCR 723 (road dust) within the uncertainty of the reference values, indicating that matrix effects in sample ablation and measurement were reduced to an extent not affecting the accuracy of LA-ICP-MS analysis anymore. Absolute deviations between measured and certified values varied between less than 1% (Cu in NIST1648a) and approximately 17% (Cd in BCR144). For most elements and samples, differences in the order of 5% only were obtained; larger deviations were only observed for elements with concentrations close to the respective limit of detection. Similar findings were reported from Malherbe et al. [9],

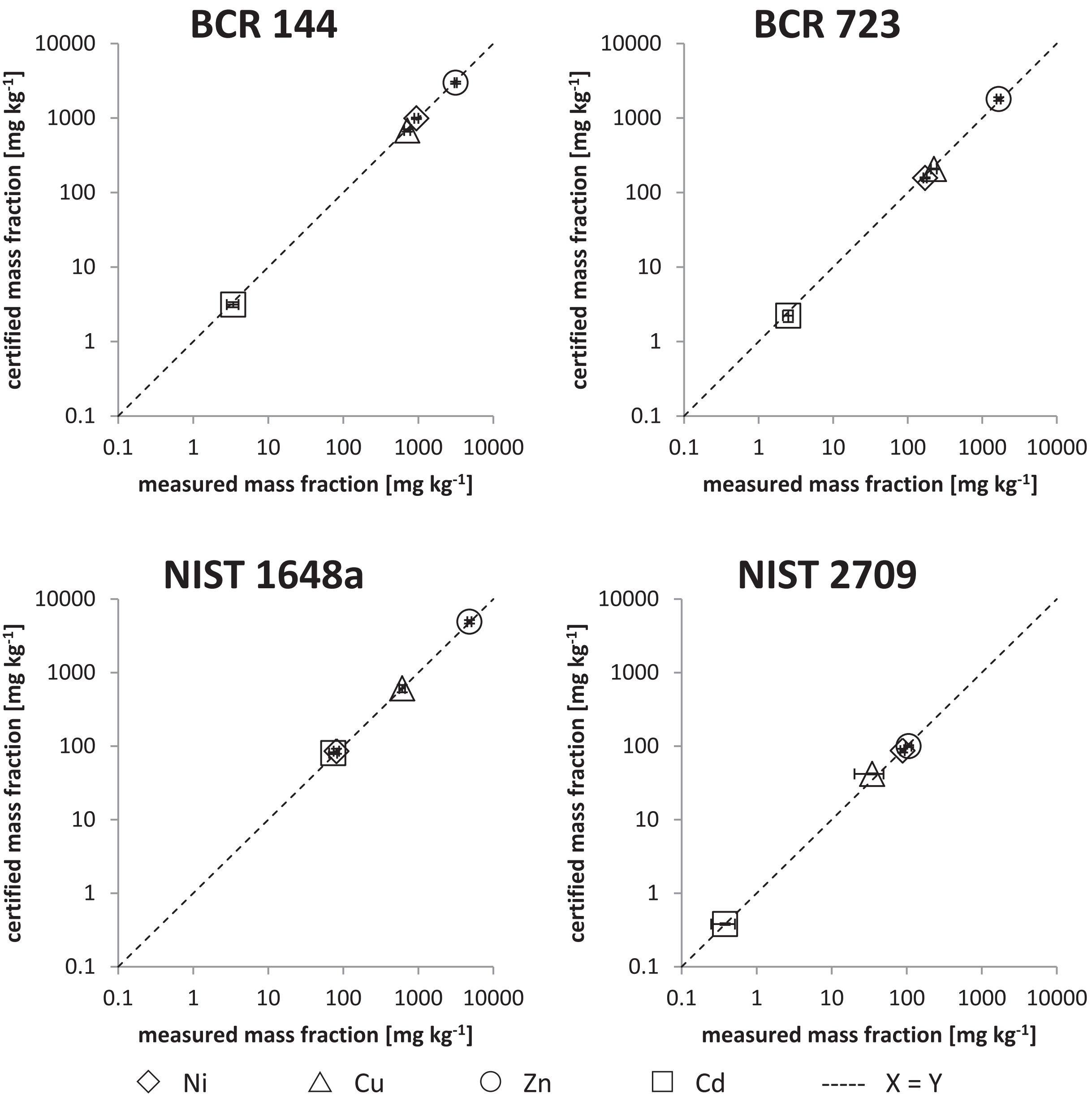

Fig. 1. Comparison of certified and measured mass fractions for Cd, Cu, Ni, and Zn (RSDs shown as error bars, α = 0.05, n = 6).

who found a good agreement with Ba, Cr, Pb, Sr, and Zn in 6 CRMs when using isotope dilution for signal evaluation, despite requiring considerably higher workload. All other examples found in literature were in the same level of accuracy with limitations to elements in lower concentrations (e.g. Cd, Cr, or Hg). For example, Claverie et al. [34] achieved an agreement between measured and certified values for most investigated elements even though absolute deviations of 23% were reported in some cases. Arroyo et al. [40] reported recoveries ranging from 3% to 16% with RSDs of 1–10%. by grinding the particulate samples to a particle size below 1 μm.

4. Conclusions

In this contribution, an improved approach for quantitative LA-ICP-MS analysis of environmental powders such as urban particulate matter, soil, sewage sludge, or road dust is presented. By using sodium tetra borate as binder material and silver oxide as internal standard during pellet preparation, differences in ablation, transport, and ionization behavior were minimized for the investigated environmental samples. Furthermore, polyatomic interferences formed during ICP-MS measurement, originating from sample constituents, additives, carrier gas, or plasma gas were eliminated using collision/reaction cell technology. Thus, in contrast to common approaches for signal quantification, the application of CRMs with distinct differences in composition becomes possible, enabling accurate quantification without the use of reference materials showing narrow matrix similarities to the investigated sample. Moreover, the use of CRMs with different analyte contents allows the determination of calibration functions for extended concentration ranges. Improvements in reliability of LA-ICP-MS analysis are further advantages of the proposed multiple standard approach when compared to conventional single-standard calibrations. Applicability of the developed procedure was demonstrated by the successful analysis of the trace elements Cd, Cu, Ni, and Zn in four different CRMs (NIST 1648a, NIST 2709, BCR 144, BCR 723).

Using this procedure, the range of samples evaluable with existing CRMs can be increased drastically. One major benefit is that environmental applications become possible where currently no reference materials are available. Another advantage of the developed procedure is the possibility to overcome problems related to the number of included elements or the sometimes inadequate concentration levels of available CRMs. Furthermore, the proposed procedure is not limited to environmental samples; with some modifications, the concept should be also applicable for LA-ICP-MS analysis of other sample materials such as cement, ceramics, or plant material. The only requirements are samples in powdered form and the existence of reference materials with suitable element contents.

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POSTER 1

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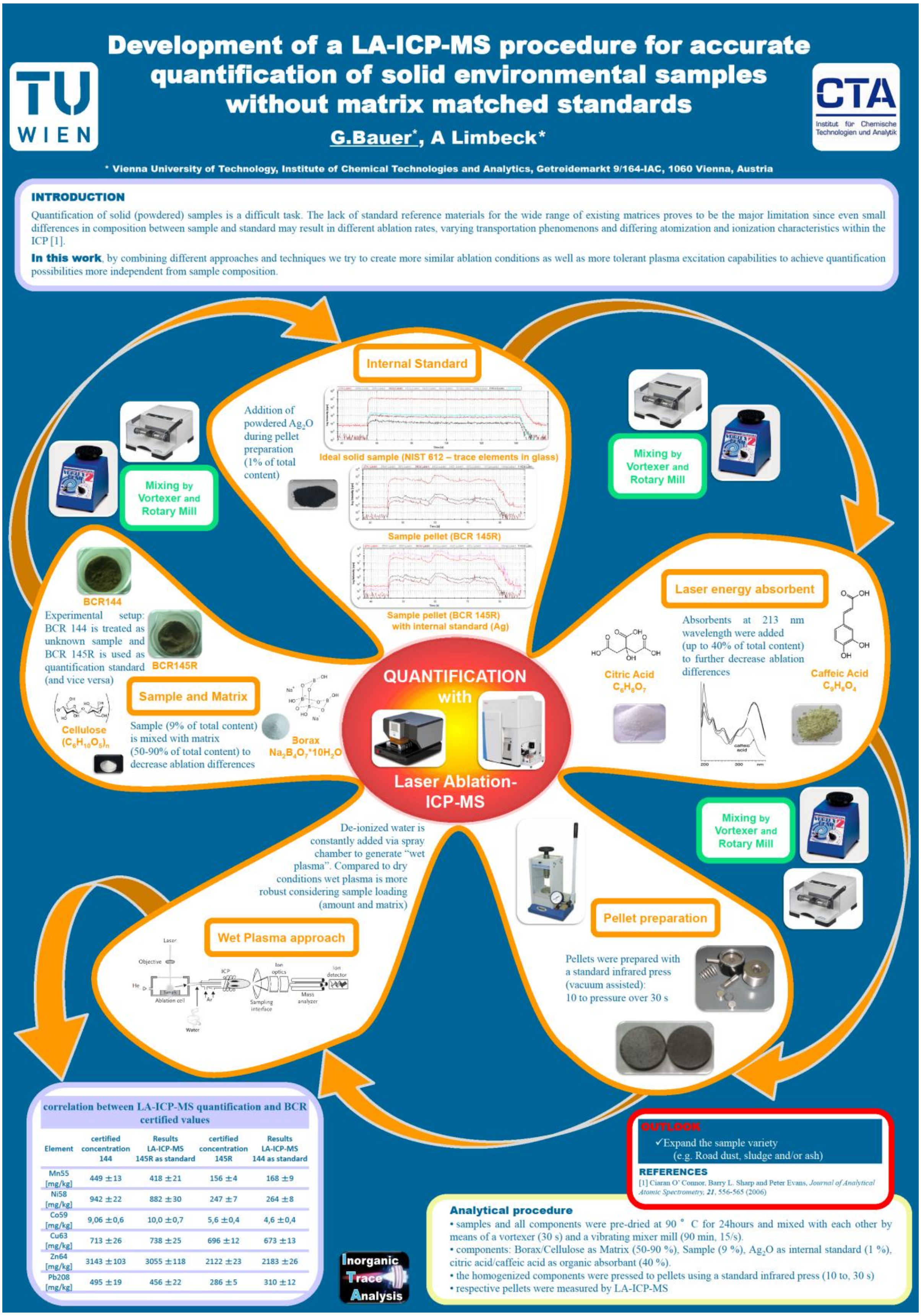

Development of a LA-ICP-MS procedure for accurate quantification of solid environmental samples without matrix matched standards

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INTRODUCTION

Quantification of solid (powdered) samples is a difficult task. The lack of standard reference materials for the wide range of existing matrices proves to be the major limitation since even small differences in composition between sample and standard may result in different ablation rates, varying transportation phenomenons and differing atomization and ionization characteristics within the ICP [1].

In this work, by combining different approaches and techniques we try to create more similar ablation conditions as well as more tolerant plasma excitation capabilities to achieve quantification possibilities more independent from sample composition.

Internal Standard

Addition of powdered Ag_2O during pellet preparation (1% of total content)

Ideal solid sample (NIST 612 – trace elements in glass)

Sample pellet (BCR 145R)

Sample pellet (BCR 145R) with internal standard (Ag)

Mixing by Vortexer and Rotary Mill

Laser energy absorbent

Absorbents at 213 nm wavelength were added (up to 40% of total content) to further decrease ablation differences

Citric Acid $C_6H_8O_7$

Caffeic Acid $C_9H_8O_4$

Mixing by Vortexer and Rotary Mill

Pellet preparation

Pellets were prepared with a standard infrared press (vacuum assisted):
10 to pressure over 30 s

Wet Plasma approach

De-ionized water is constantly added via spray chamber to generate "wet plasma". Compared to dry conditions wet plasma is more robust considering sample loading (amount and matrix)

Sample and Matrix

BCR144

Experimental setup: BCR 144 is treated as unknown sample and BCR 145R is used as quantification standard (and vice versa)

BCR145R

Sample (9% of total content) is mixed with matrix (50-90% of total content) to decrease ablation differences

Cellulose $(C_6H_{10}O_5)_n$

Borax $Na_2B_4O_7{}^*10H_2O$

Mixing by Vortexer and Rotary Mill

QUANTIFICATION with Laser Ablation-ICP-MS

correlation between LA-ICP-MS quantification and BCR certified values

Element	certified concentration 144	Results LA-ICP-MS 145R as standard	certified concentration 145R	Results LA-ICP-MS 144 as standard
Mn55 [mg/kg]	449 ±13	418 ±21	156 ±4	168 ±9
Ni58 [mg/kg]	942 ±22	882 ±30	247 ±7	264 ±8
Co59 [mg/kg]	9,06 ±0,6	10,0 ±0,7	5,6 ±0,4	4,6 ±0,4
Cu63 [mg/kg]	713 ±26	738 ±25	696 ±12	673 ±13
Zn64 [mg/kg]	3143 ±103	3055 ±118	2122 ±23	2183 ±26
Pb208 [mg/kg]	495 ±19	456 ±22	286 ±5	310 ±12

OUTLOOK

✓Expand the sample variety
(e.g. Road dust, sludge and/or ash)

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Analytical procedure

- samples and all components were pre-dried at 90 ° C for 24hours and mixed with each other by means of a vortexer (30 s) and a vibrating mixer mill (90 min, 15/s).
- components: Borax/Cellulose as Matrix (50-90 %), Sample (9 %), Ag_2O as internal standard (1 %), citric acid/caffeic acid as organic absorbant (40 %).
- the homogenized components were pressed to pellets using a standard infrared press (10 to, 30 s)
- respective pellets were measured by LA-ICP-MS

5.2.2. PART B

This part of the thesis contains one article and one poster focusing on the quantification of environmental powders with ETV-ICP-OES. Also, some additional work has been done with ETV-ICP-MS which has been published as conference poster and is included in this chapter.

ARTICLE 3

ETV-ICP-OES analysis of trace elements in fly-ash samples - A fast and easy way for simplified routine determination.

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ETV-ICP-OES analysis of trace elements in fly-ash samples - A fast and easy way for simplified routine determination

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ABSTRACT

Distinguished procedures for routine assessment of metal contents in powdered environmental samples need to be simple, fast, reliable and accurate. Using ICP-based measurement techniques usually sample digestion is necessary prior to liquid analysis. In this work, a method is presented which allows accurate quantification of Cd, Co, Cr, Cu, Mn and Ni in fly ash samples by means of electro-thermal vaporization (ETV) in combination with ICP-OES detection. Thus, time demanding sample digestion could be circumvented. For analysis slurries of the powdered samples are prepared and measured without any further complex sample preparation. The method was validated by analysis of BCR 176R (fly ash), demonstrating that calibration with aqueous standard solutions allows accurate quantification. Derived detection limits ranged from 2 μg/g to 25 μg/g, providing sufficient sensitivity for analysis of metallic contaminants in fly ash. The method was successfully applied to the analysis of municipal waste incineration ash samples from Spittelau, Vienna's municipal waste combustion plant.

1. Introduction

Municipal waste incineration produces fly ash, ash and sludge, containing various metals in major, minor and trace concentrations. The composition and trace metal amounts of these products depend mainly on the input materials during the incineration process and the applied incineration conditions. Releasing such materials containing toxic elements like Cr or Tl poses risks to health and the environment. On the other hand, increasing waste from ceramics, electronics or superconductors give prospects to profitable recycling. Therefore, to effectively determine hazard or recycling potential, a fast, simple and reliable procedure is needed to investigate metal content of waste materials like ashes and sludge.

For routine multi element analysis of the mentioned solid particulate samples, the usual approach is sample digestion combined with subsequent analysis of the derived solution with inductively coupled optical emission (ICP-OES) or mass spectrometry (ICP-MS) [1–6]. This method is well established and delivers accurate results for a wide range of analytes and concentration levels. However, sample analysis is time demanding and labour intensive due, often concentrated mineral acids or oxidants as well as high pressure and/or temperatures are required for complete sample dissolution. However, pre-treatment poses risks of sample contamination and/or analyte losses. Depending on the involved materials (e.g. silicates) in unknown samples the digestion step must be carefully optimized to achieve quantitative analyte recovery.

To overcome these limitations direct analysis of the solid sample can be performed. For this purpose several destructive and non-destructive techniques are reported in literature [7].

X ray based techniques like X-ray fluorescence spectrometry are widely used, but not applicable for trace level investigations due to limited sensitivity. If used hyphenated with electron microscopy, again, sample preparation and automatization are an important issue [8]. Another direct approach for solid sample materials is the use of laser ablation (LA) [9–13] in combination with ICP-based detection techniques. For bulk materials, LA is considerably faster with less workload than digestion. However, for accurate quantification certified reference materials (CRMs) are required, which are not available for every sample composition. Furthermore, LA requires compact samples for analysis. Therefore, powdered samples must be fixed onto a substrate or converted to a compact sample either by pelletization, embedding or fusion which reduces sensitivity and increases preparation time [12].

Another approach for direct analysis of solid samples is electro thermal vaporization (ETV) in combination with ICP-OES or ICP-MS detection [14–21]. By applying a temperature program, the analytes can be separated from more or less volatile matrix constituents (e.g. organic matrix, in the particular case of fly ash or sludge). After the vaporization, the analytes are transported to the detector via a carrier gas stream. For quantification, simple external calibration with aqueous standards can be performed. However, in the case of challenging samples like road dust or fly ash, CRMs are still required for quantification. To overcome this limitation, alternative quantification approaches like isotope dilution for MS [15,16,22] or standard addition [15,20,21,23] have been reported.

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One drawback of ETV analysis is the limited amount of sample material which can be introduced in the graphite boat. Usually, sample intakes in the order of several mg are applied, but when handling dry powdered material, for representative analysis, a minimum amount of solid sample is required to compensate for sample inhomogeneity. Using the slurry sampling approach in ETV-ICP-OES has distinct advantages compared to conventional analysis of the powdered sample. In slurry ETV-analysis the powdered sample is suspended in a suitable liquid, for measurement a defined aliquot is pipetted into the graphite boat, enabling multiple measurements from the same sample slurry. Moreover, the pipetting step is much easier and faster than using a scale. Also, sample amounts which are limited by the accuracy of the scale can be easily managed by just increasing the slurry volume or the amount of solid dispensed in the slurry.

In this work, a slurry-ETV-method is presented using simplified aqueous calibration which allows fast, routine quantification of powdered environmental samples of interest. After careful optimization, direct determination and accurate quantification of Cd, Co, Cr, Cu, Mn and Ni in fly ash samples has been demonstrated. The method has been validated with certified reference material BCR 176R - fly ash and applied to the analysis of municipal waste incineration samples.

2. Experimental

2.1. Chemicals & consumables

High purity water was obtained by purifying de-ionized water (reverse osmosis/ion exchange combination Euro 20 plus, SG Water Systems, Germany) with an Easypure 2 system (Thermo Barnstead, USA). All chemicals needed for standard preparation (nitric acid, Triton X, PTFE solution, Multi Element Standard Solution VIII, Indium ICP Standard) were purchased from Merck, Germany or Sigma-Aldrich, USA and were of the highest available grade. Sample slurries were prepared and stored in 15 mL and 50 mL centrifuge vials from Sarstedt, Germany. EC JRC IRMM Certified reference material BCR 176R was used for method validation.

2.2. Preparation of samples and standards

Municipal waste fly-ash samples were collected at Spittelau, Vienna, Austria, a community heating combustion waste-to-energy plant. Samples were analyzed without further per-treatment (homogenization, sieving or mixing).

Prior to analysis samples and solid reference material standards were dried at 90 °C for at least 24 h and stored in a desiccator. For analysis, a defined amount (15 mg to 500 mg) of sample was weighed into a 15 mL or 50 mL vial, consecutively adding nitric acid (1 wt%) to a volume of 10 and 50 mL respectively. The vials were shaken for 15 s in a Vortexer (Vortex Genie 2 from Scientific Industries, USA) and then placed for 15 min in an ultrasonic bath (Sonorex TK 30, Bandelin, Germany). Prior to measurement the Vortexer was used again for 5 s to suspend sedimented material.

Liquid standards were prepared just before use by pipetting a defined amount of standard solution (multi-element) to a 15 mL vial and diluting it with nitric acid (1 wt%) to achieve the desired concentration.

In some cases, also Triton X was added during preparation (0.02 wt%). Indium was added as internal standard in liquid form to achieve a concentration of 50 μg mL^{-1} in all final standard solutions or sample slurries.

2.3. Sample analysis

An iCAP 6500 ICP-OES (Thermo Scientific, Bremen, Germany) radial view spectrometer equipped with an ICP-torch with a corrosion-resistant ceramic injector tube was used for analysis. Sample introduction and vaporization was done with an ETV 4000A system (Spectral Systems, Fürstenfeldbruck, Germany). Both instruments were coupled using PTFE tubing (50 cm length, 4 mm inner diameter). Samples were introduced into the ETV furnace using standard graphite boats. A fully automated temperature program was applied. Through the addition of the gaseous modifier Freon R12 ($CHClF_2$, 1.5 mL min^{-1}) the sample elements were converted to volatile chlorides and fluorides, which can be evaporated much easier compared to the respective carbides or oxides. Successful transport of the formed sample aerosol from the graphite furnace to the ICP was achieved with the use of an additional argon stream (bypass gas).

Samples were analyzed as slurries, for analysis a volume of 20 μL was directly pipetted into a pre-cleaned graphite boat. Each analysis was carried out with a minimum of three replicates. The boats were pre-dried via an IR-lamp for solvent evaporation and then placed inside the ETV 4000A furnace. After insertion of the prepared graphite boat into the furnace, the temperature program was applied and the ICP-OES measurement was started. The background-corrected signal was recorded and processed by Thermo iTEVA software. The peak area of the transient ETV-signals was used for data evaluation with data points collected every 0.5 s. Detailed parameters of the used ETV-ICP-OES procedure are shown in Table 1.

3. Results & discussion

3.1. Method development

3.1.1. Slurry stability

A key factor for sensitivity and accuracy in slurry procedures is the slurry stability. If the slurry is not stable enough, particulates settle down immediately resulting in unpredictable analyte losses during transfer from the sample vial to the graphite boat. The particle size influences sedimentation processes. Since no sample pre-treatment was applied, the effect of particle size wasn't investigated any further. In literature, some measures are reported to enhance slurry stability like increasing density or viscosity of the applied solution [15,16,21,23]. One common approach to overcome flocculation effects in slurry-ETV-ICP-OES is the introduction of surfactants like Triton X.

Table 1
Instrument parameters.

ETV-System	4000A ETV, Spectral Systems	ICP-OES	iCAP 6500, Thermo Scientific
Modifier gas [mL min^{-1}]	1.5	RF power [W]	1300
Bypass gas [L min^{-1}]	0.38	Carrier gas [L min^{-1}]	–
Carrier gas [L min^{-1}]	0.14	Plasma gas [L min^{-1}]	12
Temperature program:		Auxiliary gas [L min^{-1}]	0.6
Ramp to 400 °C in 60 s		Observation height [mm]	12
Hold 400 °C for 10 s		Signal acquisition mode	Transient
Ramp to 2150 °C in 0 s			
Hold 2150 °C for 20 s			
Wavelengths [nm]		Cd 226.502, Co 228.616, Cr 267.716, Cu 327.396, In 230.512, Mn 293.930, Ni 231.604	

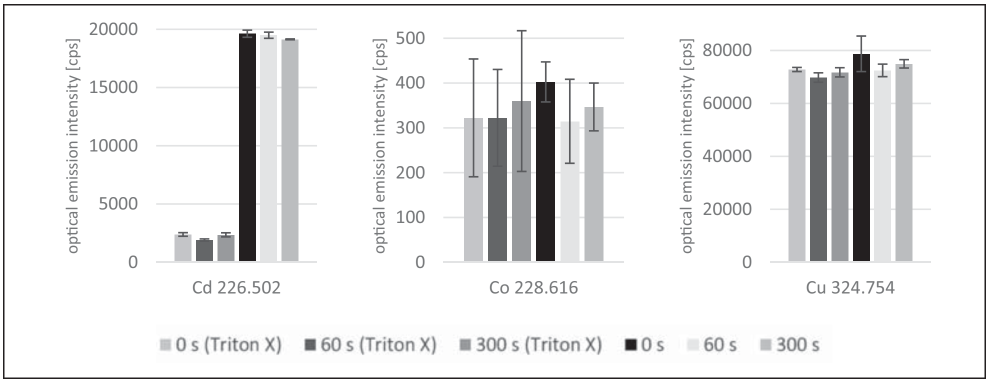

Fig. 1. Slurry stability comparison: slurry concentration 10 mg mL^{-1}, transfer to graphite boat 0 s, 60 s and 300 s after 5 s vortexing (n = 4).

As optimization goal, a slurry stability of one minute was considered sufficient for the proposed procedure. Solutions were prepared as described in chapter 2.2 with and without addition of Triton X. Prior to analysis the sample slurries were again vortexed for 5 s and then transferred to three different graphite boats for each replicate. The first boat was filled directly after vortexing, the second after letting the slurry settle for 1 min and the third after waiting 5 min without further stirring.

At first, samples spiked with Triton X were investigated and compared to un-spiked samples. For Cu and Mn, no significant change in slurry stability could be found, neither with nor without Triton X (Fig. 1). For Cd however, the addition of Triton X seemed to have a dampening effect, reducing the analytical emission signal by 90% compared to direct measurement. Possibly Triton X alters volatility of Cd causing evaporation at lower temperatures resulting in analyte losses during sample pyrolysis. It was concluded that no significant positive effect could be observed for the addition of Triton X.

Comparing the results for the slurries after different waiting times from the last stirring step, no significant changes in signal intensity could be observed for a waiting time up to 5 min. Measurement of Cd and Cu exhibited relative standard deviations (RSD) in the order of 5% to 8%. For Co and Ni, comparably high RSDs were found (up to 17%), which can be explained by the low content in the sample, yielding signals comparable to those of procedural blanks. Even though 5 min slurry stability is suited to handle the pipetting step and respective replicates without decreasing the methods accuracy, all sample solutions were vortexed prior to every working step and transferred immediately. For details see Fig. 1.

3.1.2. Temperature program

One advantage of ETV-procedures is the ability to separate volatile matrix constituents by applying a temperature program. Thereby, the matrix (organic interferents in case of MWI samples) is removed prior to the actual analyte evaporation. However, low heating rates are required when introducing large amounts of organic samples to prevent the ICP from extinguishing due to the sudden generation of vapor. Usually, higher temperatures improve the removal of organic matrix. However, for volatile elements (such as Cd), analyte losses are possible. Therefore, a careful optimization of the ETV temperature program is required, in particular suitable conditions for matrix pyrolysis and analyte atomization are required. The pyrolysis temperature was varied between 400 °C and 900 °C and atomization temperatures of 1850 °C, 2000 °C and 2150 °C were studied. For all investigated elements, the ICP-OES signals decreased with increasing pyrolysis temperature resulting in lowest signals for 900 °C. Especially for Cd, which is the most volatile of all target analytes, the signal was reduced by >90%. Best multi-element conditions in terms of signal intensity and standard deviation were found at a pyrolytic temperature of 400 °C. Regarding atomization best results were achieved at 2150 °C. Higher temperatures were avoided to preserve the graphite boat and graphite heating tube in the oven.

Thus, 400 °C for pyrolysis and 2150 °C for atomization were applied in all further measurements.

3.1.3. Modifier

Modifier is introduced, either to decrease the boiling points of target analytes or to improve the thermal stability of analytes, enabling a more efficient separation of analytes and matrix constituents. Modifier processes are still not well understood and are defined by experimental experience rather than theoretical knowledge in most cases. Fluorinating and/or chlorinating modifiers are usually applied in multi trace metal analysis with ETV [16,21,24]. The modifier type, gaseous or liquid depends mostly on instrument configuration. In this study, gaseous as well as liquid modifier addition was investigated. Liquid PTFE suspension was used for direct addition during sample preparation and Freon R12 was used as gaseous modifier introduced during temperature program application. The conditions for modifier gas and ETV cumulative gas were treated as constant to not negatively affect aerosol generation and transport into the ICP. The slurry concentration was varied with both modifiers to achieve different ratios of analyte material to available modifying atoms/molecules. Sample preparation steps were carried out as described in Section 2.2.

Without modifier addition, analysis results were very poor. Very low signals were observed for most elements, coupled with high RSDs. These findings indicate that analytes were not or only partially vaporized. Furthermore, memory effects and analyte carry-over in-between measurements were observed.

With addition of gaseous or liquid modifier improved signals were observed. A direct comparison of both approaches yielded better results for Freon. Combining liquid and gaseous modifiers in one measurement for further improvement of the ETV procedure leads to plasma extinguishment. Even with the use of a slower heating rate until pyrolysis temperature with this approach still too much vapor was generated for the ICP to handle. Since no extra preparation step is necessary for the Freon addition, it was used in all further experiments.

Varying the analyte to modifier ratio had no significant effect on the results. Thereby it was concluded that by introducing Freon R12 with a flow 1.5 mL min^{-1} enough modifier is present to enable ETV-analysis for target analytes up to 10 mg mL^{-1} slurry concentration.

Table 2
Limits of detection for the analyzed elements based on 3 σ (n = 6).

Element	Cd	Co	Cr	Cu	Mn	Ni
LOD (3 σ) [ng/boat]	0.05	0.35	0.25	0.4	0.25	0.5
LOD [μg/g]	2.1	17.5	11.2	18.8	12.3	23.5

Table 3
Method validation by comparison of reference values for BCR 176R with measured values achieved by ETV-ICP-OES with aqueous calibration standards and standard addition (n = 3), slurry concentration 1 mg mL^{-1}, except for Co & Ni - 10 mg mL^{-1}.

BCR 176R	Cd 226.502	Co 228.616	Cr 267.716	Cu 327.396	Mn 293.930	Ni 231.604
Reference value [mg/kg]	226 ± 16	26.7 ± 1.6	810 ± 70	1050 ± 70	730 ± 50	117 ± 6
RSD [%]	7.1	6.0	8.6	6.7	6.8	5.1
Measured value slurry [mg/kg]	203 ± 6	23.7 ± 2.1	717 ± 67	993 ± 46	700 ± 28	101 ± 7
RSD [%]	2.1	8.8	9.3	4.7	5.0	7.1
Measured value standard addition [mg/kg]	226 ± 2	31 ± 4	739 ± 108	1030 ± 43	705 ± 27	110 ± 26
RSD [%]	0.9	13	15	4.2	3.8	24

3.1.4. Slurry volume & concentration

Finally, the effect of sample amount was investigated by introducing different volumes of slurry solution into the boat. Additions of three different volumes were investigated: 20 μL, 30 μL and 40 μL. The slurry concentration was varied from 1 mg mL^{-1} to 10 mg mL^{-1}.

No significant differences between comparable final analyte amounts in the boat could be observed. E.g., a 20 μL droplet with 2 mg mL^{-1} sample yielded similar results to a 40 μL droplet with 1 mg mL^{-1} sample concentration. These results demonstrate the robustness of the selected temperature program in the tested sample amount range. Since sample pre-drying with the IR-Lamp takes longer for larger volumes, all further measurements were carried out with 20 μL sample volume. The slurry concentration level depends on analyte concentration and can be changed accordingly.

3.2. Figures of merit

In all measurements Indium was used as an internal standard by adding a liquid spike solution to slurries as well as aqueous standards. Although no significant improvement in precision was observed when using internal standard correction, it was still considered a useful tool to monitor the overall performance of the ETV-ICP-OES system.

To assess sensitivity and linear range of the optimized ETV procedure, aqueous calibration standards with concentrations ranging from 0.05 to 5 μg/g, which results in total analyte amounts varying from 0 to 100 ng per boat, were analyzed. Signal intensities (in counts per second) obtained for the investigated analytes were normalized using In as internal standard and correlated with the injected analyte masses, showing for all elements a linear behaviour (correlation coefficients above 0.99) throughout the investigated concentration range. In a next step, procedural blanks were compared to technical blanks. For measurement of technical blanks, empty graphite boats without any solution were inserted in the ETV-oven. For the analysis of procedural blanks, nitric acid (1 wt%) blank solution containing In as internal standard was pipetted into the boat and all steps (e.g. IR pre-drying) were conducted according to Section 2.2. No significant differences were observed when comparing results of technical and procedural blanks, so it was concluded, that lab cleanliness and reagent integrity was sufficient. Limits of detection (LOD) were calculated from 6 procedural blanks using the 3 σ criterion. For all elements, the respective LODs were below 0.5 ng of analyte in the boat and the limit of quantification (LOQ − 10 σ) was below 1.5 ng per boat. Considering the sample intakes used for slurry preparation and the slurry volume applied for analysis (20 μL) these instrumental detection limits could be converted into method detection limits, which varied from 2.1 μg/g (Cd) to 23.5 μg/g (Ni). Details for all elements are shown in Table 2.

Reproducibility for this method was calculated from triplicate measurements of the test sample used for method development. Derived RSD ranged from 3% for Ni to 17.5% for Co (95% confidence) reflecting the concentration levels of target analytes in the sample material. Whereas Ni signals were well elevated from the baseline, for Cd the signal intensity was in the same order of magnitude as for the procedural blanks.

3.3. Validation

The certified reference material BCR 176R (fly ash) was used for method validation. Usually standard addition or at least matrix matched standards are required for accurate quantification in slurry sampling ETV-ICP-OES. Since the standard addition is easy to accomplish in slurry analysis, we started with this approach. Therefore, one unspiked sample with a concentration of 1 mg mL^{-1} slurry and three spiked samples (slurry concentration of 1 mg mL^{-1} with additional contents of

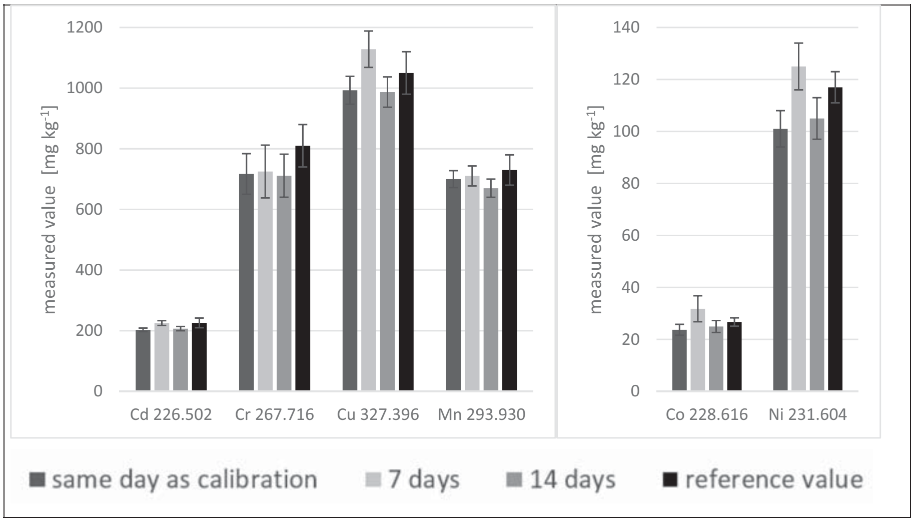

Fig. 2. Comparison of analysis results attributed to one calibration (day 0) with reference values, first results from the same day as the calibration, the other results from 1 to 2 weeks later, results derived by analyzing one middle range standard and using its value as correction factor with the initial calibration.

Table 4
Results for analysis of 3 MWI samples with ETV-ICP-OES (n = 3).

	Cd 226.502	Co 228.616	Cr 267.716	Cu 327.396	Mn 293.930	Ni 231.604
Sample 1	503 ± 15	<17.5	674 ± 16	1057 ± 88	94 ± 5	54 ± 1
Slurry level [mg mL^{-1}]	1	10	1	1	1	10
Sample 2	5.4 ± 0.7	<17.5	377 ± 60	12,580 ± 762	180 ± 11	80 ± 3
Slurry level [mg mL^{-1}]	10	10	1	1	1	10
Sample 3	119 ± 1.5	<17.5	258 ± 12	1384 ± 51	152 ± 8	137 ± 9
Slurry level [mg mL^{-1}]	1	10	1	1	1	10

standard solution resulting in final additions of 10 ng, 20 ng and 40 ng of analyte per 20 μl sample volume) were prepared and measured. A good linear correlation was achieved for all elements ($R^2 > 0.998$). For Co and Ni, the signals observed for the unspiked sample were close to the limit of quantification yielding RSDs of 13% and 24% respectively. All other investigated elements (Cd, Cr, Cu and Mn) showed distinctly reduced RSDs ranging from 5% to 8%. Results derived using the concept of standard addition are shown in Table 3, demonstrating a good agreement with reference values even at the threshold level.

However, this study aims at quantification just with aqueous standards to considerably decrease analysis time for calibration and reduce workload. Thus, in a next step, external calibration with aqueous standard solutions was performed. Again, a sample slurry with a concentration of 1 mg mL^{-1} was used for analysis. As can be deduced from Table 3 delivered this approach a good agreement between measured and certified contents for all target analytes except Co. BCR 176R contains target analytes in concentrations differing up to 3 orders of magnitude, and Co is the least abundant. Therefore, the measurement was repeated with a slurry concentration of 10 mg mL^{-1} and the results for Co as well as Ni (regarding RSD) were improved significantly. With a combination of 1 and 10 mg mL^{-1} slurry concentrations all measurement results were found in good agreement with the certified values.

The slopes of standard addition calibration and aqueous calibration were compared to check for possible inconsistencies in transport and atomization due to differences in composition between sample slurries and standard solutions. The slopes of the two calibration functions were in good agreement for all elements, indicating that the prevailing differences in sample matrix had no significant effect on signal generation and detection. Therefore, it was concluded that for this method, aqueous calibration is a suitable approach for quantification.

However, the usage of aqueous calibration, which reduces the number of samples in routine analysis drastically compared to standard addition, is only the first step. Furthermore, the external linear calibration was performed timely decoupled from sample analysis. After method optimization was finished, samples were analyzed in different batches, on different days and even weeks. When measuring samples, just blanks and one medium range standard were included. With the blanks, the uncertainty of the daily zero values was checked and with the medium standard a sensitivity factor was introduced. The factor was derived from the ratio of the signal intensity of the medium standard from initial calibration performed after method development (five concentrations levels, measured with 4 replicates per level) to the signal intensity of the same medium standard from daily calibration. This factor was then applied to the signals of the measured samples prior to calculating the analyte contents with the “old” calibration function. Samples and calibration have been analyzed at the same day and, one and two weeks apart.

Application of this concept resulted all three times in comparable findings for the investigated samples, and the CRM could be accurately quantified in all measurements (see Fig. 2). These results indicate that the number of standards can be reduced significantly in favor of sample analysis or time demand in general. Instead of 5 calibration standards with 4 replicate measurements per day only 4 replicates of one standard were necessary for analysis in this demonstration, still yielding results with the same accuracy. Thus, either a decrease of the total analysis time is possible, or the sample number can be increased, or the precision of the procedure can be enhanced by increasing the number of replicates.

3.4. Application

To further demonstrate applicability not only with a reference material but with other matrices, three MWI samples were analyzed. The samples were initially analyzed with the 1 mg mL^{-1} slurry concentration. After the first results, Ni and Co were found at LOD level and therefore the slurry concentration was increased to 10 mg mL^{-1}. With these conditions measurement of Ni was enabled, concentrations of Co were still below the LOQ. The amounts of the investigated elements varied considerably, for example in sample 2 the found copper concentration was approximately 10 times higher compared to sample 1 and 3. Similar variations were observed for Cd revealing concentrations ranging from 5 to >500 mg/kg. For details see Table 4.

4. Conclusions

With the proposed procedure, accurate quantification of Cd, Co, Cr, Cu, Mn and Ni in fly-ash samples is possible. The procedure is fast and easy, the sample just needs to be suspended, vortexed and can then be analyzed without further treatment. By using the gaseous modifier Freon R12 external calibration with aqueous standard solutions can be used for quantification. The achieved sensitivity and accuracy is comparable to standard liquid ICP-OES after digestion, but without all inherent risks (sample losses or contamination) and timely limitations. By using aqueous calibration, the number of standards needed for each sample batch can be decreased significantly. However, if the analyte concentrations vary by one or more orders of magnitude throughout the samples or between analytes, different slurry levels may be necessary. Also with unknown samples, the needed slurry concentration for each target element can be derived only after a first analysis.

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POSTER 2

Presented at Winter Conference on Plasma Spectrochemistry, Tucson, USA, 2012

FAST AND ACCURATE ETV-ICP-OES ANALYSIS OF TRACE METALS IN FLY ASH ORIGINATING FROM WASTE COMBUSTION

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INTRODUCTION

With implementing new technologies in daily life, the need for compounds in the fields of ceramics, electronics and superconductors is increasing drastically. Most of these complex products are dependent on special materials, e.g. noble metals. Due to limited access to these increasingly rare metals, caused by a regulating economic policy of the countries holding the biggest deposits, their initial scarceness or the absence of profitable extraction procedures, the investigation of alternate sources is getting more and more of an issue. One approach may be recycling coal fly ash, originating from waste combustion. Coal fly ash is known for its enriched metal contents but was studied mostly in the field of pollution monitoring and influences on the ecological system [1].

Our goal is to examine the possible recycling potential by determining the contents of target elements, usually metals like Au, In or Rh, which are present in trace concentration levels. Due to its harsh matrix properties, fly ash analysis is a challenging topic, usually demanding intensive sample pre-treatment. Typically some kind of digestion step is involved to dissolve the analytes and decompose the organic matrix. These approaches are labour and time demanding and propose the risk of sample-contamination during pre-treatment, furthermore sample dilution accomplished during sample digestion hampers sensitive measurement of target analytes.

In this work, we propose an ETV-based method for direct, fast and accurate ICP-OES-analysis. Sample preparation is reduced to simple dispersion of the particulate sample in diluted nitric acid. An aliquot of the derived slurry solution is transferred to a graphite-boat and introduced to an electro thermal vaporization unit coupled to an ICP-OES. By operating a defined temperature program and adding a gaseous chemical modifier, organic and volatile matrix compounds are removed prior to analysis. Target trace metal analytes are vaporized at higher temperatures according to the respective boiling points [2]. If the concentration of some elements are below the achieved LODs with ICP-OES, these elements will be investigated with ICP-MS.

ANALYTICAL PROCEDURE

- the fly ash samples were dispersed (concentration < 1 mg/10 ml) in nitric acid (10 % v/v) and engaged in a slurry state by means of ultrasonic agitation
- 40 µl of slurry solution were transferred into a graphite boat and the solvent was slowly evaporated by means of an IR-Lamp
- the graphite boat was planted into the ETV-4000 graphite furnace (Spectral Systems, Germany) an a temperature program (see **Figure I**) was applied.
- Depending on the anticipated amount of target elements the ETV 4000 was connected to ICP-OES (> 5 ng/boat) or ICP-MS (< 5 ng/boat). Emission signals were recorded in transient signal mode (intensity vs. time, see **Figure II**).

Figure I: optimized temperature program

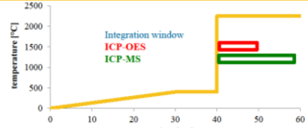
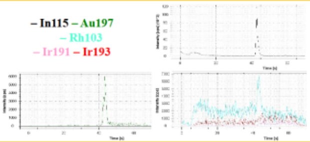


Figure II: Transient signals and peak shapes in ICP-MS (sample FLA)



SPECTROMETER OES

ICP-OES measurements were carried out on a Thermo Scientific iCAP 6500 ICP- OES equipped with radial view echelle optic. Wavelengths were chosen according to their intensity and the quality of their respective calibration curve (Au 267.595, Cd 226.502, Co 228.616, Cr 267.716, Cu 224.700, In 230.606, Ni 231.604, Pb 220.353, Rh 343.489). For detailed plasma parameters see **table I**.

SPECTROMETER MS

ICP-MS measurements were carried out on a Thermo Scientific XSeries2 ICP-MS. Analyte masses were chosen according to their abundance, possible interferences and to the quality of their respective calibration curve (Rh103, In115, Ir191, Ir193, Au197). For detailed plasma parameters see **table I**.

Table I: instrument parameters

		ICP-OES	ICP-MS
RF power	[W]	1250	1200
plasma gas flow rate	[L/min]	12	13
radial viewing height	[mm]	10	-
nebulizer flow rate	[L/min]	0.52*	0.52*
auxiliary flow rate	[L/min]	0.8	0.8
Freon modifier	[mL/min]	10	10

*sum of carrier gas and cooling gas

SAMPLES

The samples originated from the Vienna community heating combustion plant:

sample 1: **FLA**	**– fly ash**
sample 2: **KSA**	**– sludge ash**
sample 3: **Schlacke**	**– bed ash**

METHOD DEVELOPMENT

The temperature program was optimized using aqueous standard solutions. In a second step the best temperature conditions for pyrolysis and vaporization were investigated. In the last step matrix influences were tested with spiked fly ash slurries. The application of a gaseous modifier (Freon R12) was found to significantly increase both the signal intensity and the reproducibility.

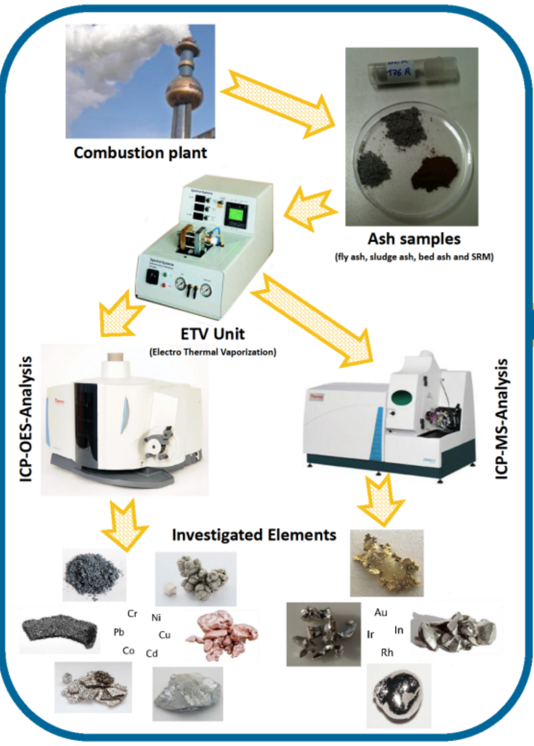


Table II	ETV-ICP-OES RSDs (n = 6): 5 – 10 %					
[ng/boat]	Au	Cd	Co	Cr	In	Ni
LOD (3 σ)	1.1	0.04	0.7	2.3	1.4	0.8
LOD (10 σ)	4.7	0.4	2.0	6.4	5.4	2.7

	ETV-ICP-MS RSDs (n = 6): 8 – 15 %			
[ng/boat]	Au	In	Ir	Rh
LOD (3 σ)	0.04	0.16	0.45	0.19
LOQ (10 σ)	0.08	0.17	1.37	0.30

METHOD VALIDATION

Standard reference material SRM BCR 17R was used

- to evaluate the signal quantification,
- to test the accuracy of the method and
- for comparison of aqueous and matrix adjusted calibration.

Figure III: comparison of calibration strategies

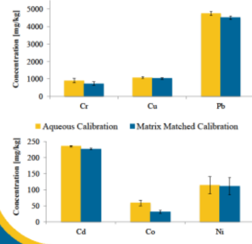


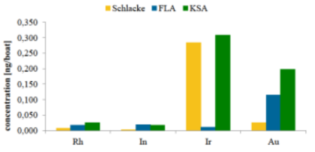
Table III: correlation between ICP-OES analysis and SRM certified values

[mg/kg]	Cd	Co	Cr
SRM certified concentration	226.0 ± 19.0	26.7 ± 1.6	810.0 ± 70.0
Results ICP-OES analysis	226.3 ± 2.2	30.8 ± 4.2	738.8 ± 108.4
	Cu	Ni	Pb
SRM certified concentration	1050.0 ± 70.0	117.0 ± 6.0	5000.0 ± 500.0
Results ICP-OES analysis	1030.6 ± 42.9	110.2 ± 26.1	4502.7 ± 108.9

RESULTS ICP-OES

The composition of the samples from percentage to trace metal range was determined and the ETV-sample introduction was proven to be a valid method for elemental analysis of fly ash. For elements like Au or Ir the concentrations were still below the LODs. For these elements ICP-MS analysis was carried out.

Figure III: sample comparison after ICP-MS analysis



QUANTIFICATION

In ICP-OES analysis the certified concentrations were obtained for all investigated elements. For details see **Figure III** and **Table II & III**.

In ICP-MS analysis so far only qualitative and semi-quantitative results were achieved.

RESULTS ICP-MS

The presence of Gold was confirmed for the samples FLA and KSA whereas KSA contains about 70 % more than FLA. For Iridium differences between the samples were found, but Ir showed a different transient signal peak (long and flat) than the other elements (edged). For details see **Figure II** and **Figure III**.

OUTLOOK

- ✓ Quantification for ICP-MS analysis (Au, In, Ir, Rh)
- ✓ Validation of ETV-ICP-MS analysis through digestion and liquid ICP-MS analysis

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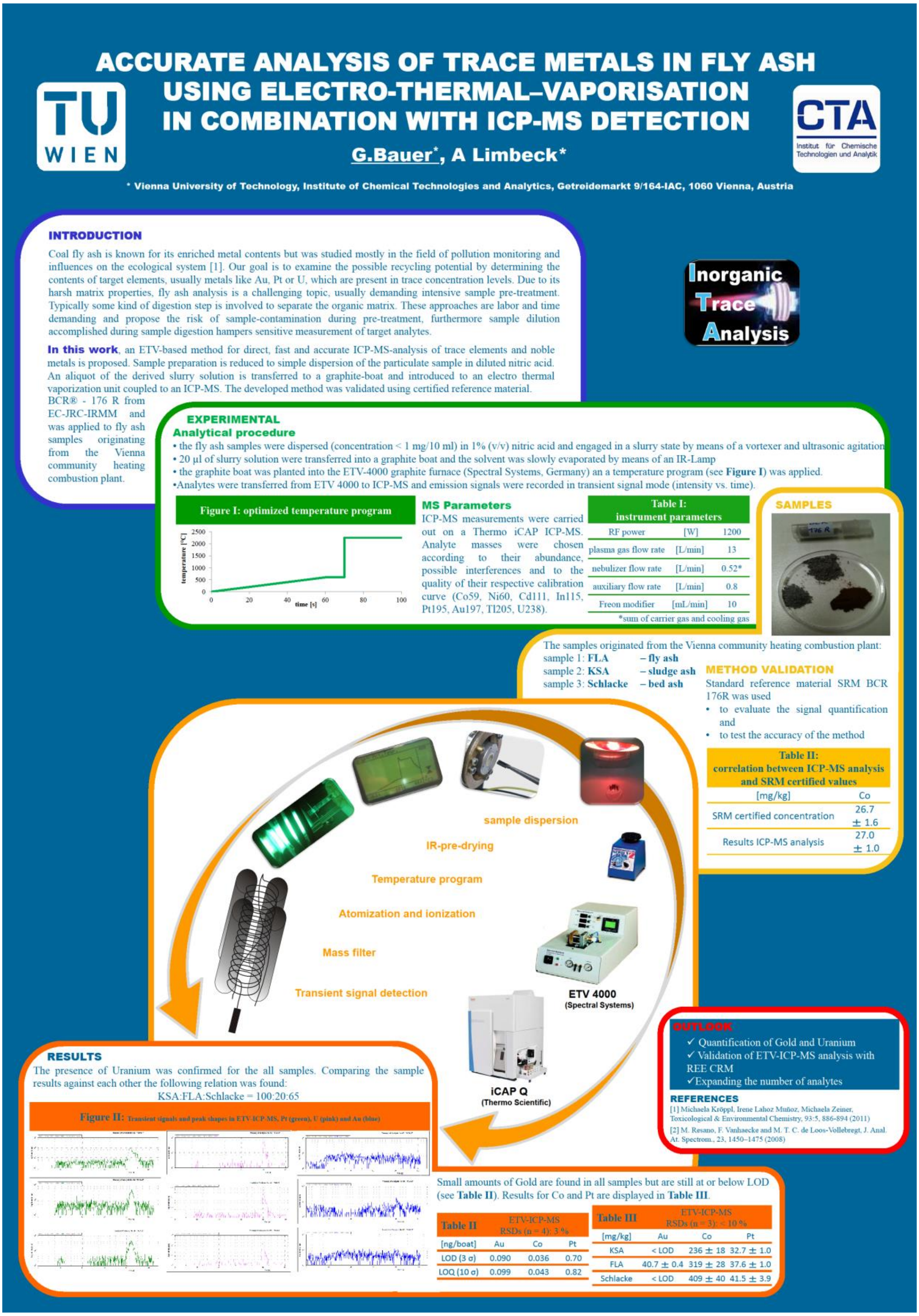
POSTER 3

Presented at Euroanalysis, Warsaw, Poland, 2013



ACCURATE ANALYSIS OF TRACE METALS IN FLY ASH USING ELECTRO-THERMAL–VAPORISATION IN COMBINATION WITH ICP-MS DETECTION

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INTRODUCTION

Coal fly ash is known for its enriched metal contents but was studied mostly in the field of pollution monitoring and influences on the ecological system [1]. Our goal is to examine the possible recycling potential by determining the contents of target elements, usually metals like Au, Pt or U, which are present in trace concentration levels. Due to its harsh matrix properties, fly ash analysis is a challenging topic, usually demanding intensive sample pre-treatment. Typically some kind of digestion step is involved to separate the organic matrix. These approaches are labor and time demanding and propose the risk of sample-contamination during pre-treatment, furthermore sample dilution accomplished during sample digestion hampers sensitive measurement of target analytes.

In this work, an ETV-based method for direct, fast and accurate ICP-MS-analysis of trace elements and noble metals is proposed. Sample preparation is reduced to simple dispersion of the particulate sample in diluted nitric acid. An aliquot of the derived slurry solution is transferred to a graphite-boat and introduced to an electro thermal vaporization unit coupled to an ICP-MS. The developed method was validated using certified reference material. BCR® - 176 R from EC-JRC-IRMM and was applied to fly ash samples originating from the Vienna community heating combustion plant.

EXPERIMENTAL

Analytical procedure

- the fly ash samples were dispersed (concentration < 1 mg/10 ml) in 1% (v/v) nitric acid and engaged in a slurry state by means of a vortexer and ultrasonic agitation
- 20 µl of slurry solution were transferred into a graphite boat and the solvent was slowly evaporated by means of an IR-Lamp
- the graphite boat was planted into the ETV-4000 graphite furnace (Spectral Systems, Germany) an a temperature program (see **Figure I**) was applied.
- Analytes were transferred from ETV 4000 to ICP-MS and emission signals were recorded in transient signal mode (intensity vs. time).

Figure I: optimized temperature program

MS Parameters

ICP-MS measurements were carried out on a Thermo iCAP ICP-MS. Analyte masses were chosen according to their abundance, possible interferences and to the quality of their respective calibration curve (Co59, Ni60, Cd111, In115, Pt195, Au197, Tl205, U238).

Table I: instrument parameters

RF power	[W]	1200
plasma gas flow rate	[L/min]	13
nebulizer flow rate	[L/min]	0.52*
auxiliary flow rate	[L/min]	0.8
Freon modifier	[mL/min]	10

*sum of carrier gas and cooling gas

SAMPLES

The samples originated from the Vienna community heating combustion plant:

sample 1: **FLA** – **fly ash**
sample 2: **KSA** – **sludge ash**
sample 3: **Schlacke** – **bed ash**

METHOD VALIDATION

Standard reference material SRM BCR 176R was used

- to evaluate the signal quantification and
- to test the accuracy of the method

Table II: correlation between ICP-MS analysis and SRM certified values

[mg/kg]	Co
SRM certified concentration	26.7 ± 1.6
Results ICP-MS analysis	27.0 ± 1.0

sample dispersion

IR-pre-drying

Temperature program

Atomization and ionization

Mass filter

Transient signal detection

ETV 4000
(Spectral Systems)

iCAP Q
(Thermo Scientific)

OUTLOOK

- ✓ Quantification of Gold and Uranium
- ✓ Validation of ETV-ICP-MS analysis with REE CRM
- ✓ Expanding the number of analytes

REFERENCES

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RESULTS

The presence of Uranium was confirmed for the all samples. Comparing the sample results against each other the following relation was found:

KSA:FLA:Schlacke = 100:20:65

Figure II: Transient signals and peak shapes in ETV-ICP-MS, Pt (green), U (pink) and Au (blue)

Small amounts of Gold are found in all samples but are still at or below LOD (see **Table II**). Results for Co and Pt are displayed in **Table III**.

Table II	ETV-ICP-MS RSDs (n = 4): 3 %		
[ng/boat]	Au	Co	Pt
LOD (3 σ)	0.090	0.036	0.70
LOQ (10 σ)	0.099	0.043	0.82

Table III	ETV-ICP-MS RSDs (n = 3): < 10 %		
[mg/kg]	Au	Co	Pt
KSA	< LOD	236 ± 18	32.7 ± 1.0
FLA	40.7 ± 0.4	319 ± 28	37.6 ± 1.0
Schlacke	< LOD	409 ± 40	41.5 ± 3.9

5.2.3. PART C

This part of the thesis contains one article and one poster that discuss the topic of spatially resolved analysis of isolated particles with imaging via LA-ICP-MS. The poster gives a fast and intuitive overview on the presented approach.

ARTICLE 4

Analysis of single fly ash particles using laser ablation ICP-MS – an approach achieving lateral elemental distribution information via imaging

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RSC Advances

PAPER

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Analysis of single fly ash particles using laser ablation ICP-MS – an approach achieving lateral elemental distribution information *via* imaging

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In environmental questions, particles at the micrometre scale are usually analyzed regarding their particle size and morphology using microscopic techniques. Thereby, their composition and trace element contents are neglected. However, when focusing on recycling and re-use of minor and trace elements in environmental particles like fly ash, originating from municipal waste incineration, information on elemental distribution within single particles may be of grave importance. In this work a procedure for the preparation of fly ash particles for LA-ICP-MS analysis is presented that also allows access to the spatial elemental distribution of each single particle. Herein the particles are dispersed and retained on a sticky substrate, followed by fixation. Roughly one half of the particle is ablated to access the particle cross-section. This cross-section is ablated with consecutive line scans to generate sufficient data to create an image. More than 60 particles with diameters between 25 μm and 100 μm have been analyzed using the presented procedure. General differences in the particle composition could be observed and the elemental distribution of minor constituents like Al, Cu, Pb, Si, Ti and Zn could be visualized for single particles with lateral resolutions down to 2 μm per pixel. Cu and Pb were found to be enriched at the surface, easily accessible for recycling techniques, whereas Ti was found predominantly in the particles' insides. Al, Si and Zn were mostly found to be evenly distributed within particles.

Introduction

When discussing single particle analysis with ICP-MS, usually particles at the nanometre scale are taken into consideration.[1,2] In this kind of analysis, typically a suspension of the nanoparticles is measured, and the resulting signals are used to determine the nanoparticle's size and number distribution.[3–5] However, with this traditional approach for single particle analysis it is challenging to gain information about the particle composition and entirely impossible to determine element distributions within the particles. When considering larger particles at the micrometre scale, such information may become of special interest to gain deeper knowledge about particle formation. Particles with such sizes are generated in various complex industrial but also environmental processes, leading to a much more inhomogeneous nature and composition than engineered nanoparticles.

An area of interest, in which large amounts of such particles are produced, is municipal waste incineration (MWI). Residues from MWI are of major importance for various reasons. So far, scientific concern has been focused mostly on processes regarding air pollution, release of toxic elements,[6–12] waste disposal and re-use for soil-improvements.[13,14] But the scrap also still contains a relevant fraction of elements like rare earths or other metals valuable for industrial re-use[15–17] and therefore is a potential source for recycling. To determine recycling potential and efficiency of such remains, they have to be investigated thoroughly with complementary analytical techniques. Up to now, mainly bulk concentrations were determined with ICP-MS techniques.[9,18] However, for sufficient characterization, the analytes of interest need to be investigated with a special focus on their prevailing chemical form (*e.g.*, metallic, oxide, sulphate, silicate) and also their relative distribution within the ash particles. Surface-enriched elements can be easily accessed and recovered with leaching, extraction or other processes involving heat, chemicals and/or mechanical procedures.[19,20] In recent years also biotechnological methods have been applied.[21,22]

Already in the 1980s, leaching experiments have shown to deliver shell-selective chemical information on the particle composition.[23] Even though very useful, also knowledge on the core material or even more detailed laterally resolved analysis would be of interest.

Two reasons can be identified for this lack of analytical data. Firstly, it is very delicate to prepare particulate samples for single particle analysis without compromising their composition and integrity. Fixation and isolation is mostly done by dispersing powders manually on a sticky medium (*e.g.*, double

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sided tape).[24] A typical problem of this approach is the complete transfer of a representative sample aliquot to the surface, without losing a relevant size or mass fraction; furthermore, reproducibility often cannot be guaranteed. Secondly, analytical techniques applied for particle characterization provide either sufficient spatial resolution or adequate sensitivity, but seldom both. For example, scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) is often utilized[25,26] because of its very good lateral resolution. The sensitivity, however, is not sufficient for adequately detecting minor and trace components. In addition, SEM-EDX is a surface sensitive technique, thus only a layer of some μm thickness can be investigated, making analysis of a particle's core impossible when the particles are some tens of micrometres in diameter. One powerful technique often applied for achieving lateral distribution information is secondary ion mass spectrometry (SIMS).[27,28] Although SIMS offers excellent sensitivity and depth resolution, the suitability for analysis of fly ash particles is also limited. Besides long analysis times, crater effects and surface roughening are considered to be the major problems.

An analytical technique which offers also the possibility of depth profiling and laterally resolved analysis is Laser-Ablation inductively-coupled Plasma-Mass Spectrometry (LA-ICP-MS).[29,30] The use of LA-ICP-MS for quantitative bulk-analysis of trace metals and minor constituents in a variety of environmental samples is frequently described in literature.[31,32] The sensitivity of LA-ICP-MS ranges from sub ng g^{-1} to μg g^{-1} depending on applied instrumentation, experimental conditions and the elements of interest. For imaging purposes, sensitivity may be reduced due to reduction of ablated material to improve lateral resolution.[31,33] In this work, an approach for the preparation of powdered fly-ash samples for spatially resolved analysis using LA-ICP-MS, a technique very well established for inorganic analysis, is presented.[34–37] The procedure proposed in this work allows dispersion and fixation of particles without exposing them to harsh sample preparation conditions. After exhibition of cross sections using laser ablation, 2D-imaging of particles with diameters in the range of 25–100 μm could be achieved, indicating distinct differences in the composition of individual fly ash particles but also in the distribution of minor elements, such as Al, Ti and Zn within the particles.

Experimental

Instrumentation

A commercially available Nd:YAG nanosecond laser ablation system (NWR213, ESI, USA) equipped with a standard, fast-washout-cell provided by the manufacturer and suitable for imaging applications[31,38–40] was used to ablate the samples. For analysis, the generated sample aerosol was transferred to a quadrupole ICP-MS (iCAP Q, Thermo Fisher Scientific, Bremen, Germany) using PTFE tubing. He (5.0) was used as ablation gas and mixed with a stream of Ar (5.0) as make-up gas prior to introduction into the ICP-MS.

Optical microscopy (DM2500M, Leica, Germany) was used to verify sample preparation techniques and scanning electron microscopy (SEM, Quanta 200, FEI, USA) equipped with an energy dispersive X-ray spectrometer (EDX – Octane Pro Silicon Drift Detector, Ametek) was used to validate elemental distributions from laser ablation experiments for the bulk elements Si and Al.

Sample preparation

Fly ash samples were provided by Wien Energie, collected at Spittelau, Vienna's municipal waste incinerator. Samples were characterized regarding particle size distribution using a laser diffraction particle sizer (Mastersizer 2000, Malvern instruments). Most of the fly ash particles were smaller than 100 μm in diameter ($d_{0.9}$ 96.5 μm) with a median at 26.2 μm $d_{0.5}$. Samples were stored at room temperature and dried (90 °C, 12 h) prior to preparation.

Standard petri dishes were used as sample carriers. The petri dishes were coated with a layer of anti-static spray (Antistatik 100, Kontakt Chemie®) to retain the dispersed particles. 10 mg of dried sample was weighed into an in-house constructed glass spray chamber setup. A petri dish, prepared as previously described was placed at the exit orifice of the setup. Subsequently, a constant argon stream was used to disperse the particles inside the spray chamber and to deposit them onto the pre-treated petri dishes. After dispersion of the particles, a layer of hairspray (Drei Wetter Taft, Schwarzkopf) was added for fixation of the particles. The solvent was allowed to evaporate at room temperature. After another fixation step by hairspray and subsequent drying, the so prepared samples were directly analyzed with optical microscopy and LA-ICP-MS.

LA-ICP-MS analysis

Prior to analysis, a daily performance check was conducted by tuning for maximum ^{115}In signal intensity while ablating NIST SRM 612 (trace elements in glass, National Institute of Standards and Technology, Gaithersburg, MD). After sample insertion, the ablation chamber was evacuated and consecutively flushed with He for 15 min. For analysis, the He flow rate was set to 750 mL min^{-1}. Settings were optimized in preliminary experiments. The laser output energy was adjusted to yield optimal ablation behaviour (*i.e.*, limited elemental fractionation as well as reducing surface damage and material re-deposition on adjacent sample areas). Before firing on the sample, the laser was allowed to warm up for 10 s to reach stable output intensity. Detailed instrumental parameters employed for sample analysis are shown in Table 1. Signals were recorded in transient signal mode with Qtegra software (version 1.5.1189.31) provided by Thermo Fisher Scientific.

LA-ICP-MS analysis of particles with diameters ranging from 25–100 μm was performed using two different procedures. For both approaches access to a cross section of the fly-ash particle is required. Thus, in a first step particles were ablated evenly to expose their cross section with a laser beam diameter exceeding the particle diameter. Usually ten to 25 laser shots with a fluence of 2.5 to 3 J cm^{-2} were sufficient.

The generated cross section of the particle was then analyzed using line scans with laser beam diameters ranging from 3 μm to 20 μm depending on the size of the investigated particle. Line

Table 1 Instrument parameters

Laser ablation system	NWR213, New Wave Research	ICP-MS	iCAP Q, Thermo Scientific
Type of laser	Nd:YAG 213 nm	RF power [W]	1550
Ablation mode	Raster (lines)	Carrier gas flow rate [L min^{-1}]	0.4
Beam diameter [μm]	5–20, 3/5 (imaging)	Plasma gas flow rate [L min^{-1}]	12
Fluence [J cm^{-2}]	4.5–17	Auxiliary gas flow rate [L min^{-1}]	0.8
Frequency [Hz]	4–20	Acquisition time [ms]	10
Scan speed [μm s^{-1}]	2–5	Cones	Ni
He gas flow [L min^{-1}]	0.75	Measured isotopes	^{27}Al, ^{29}Si, ^{48}Ti, ^{63}Cu, ^{66}Zn, ^{115}In, ^{208}Pb

scan parameters varied between 2 μm s^{-1} and 5 μm s^{-1} for scan speed and 4 Hz to 20 Hz for ablation frequency. Alternatively, for imaging purposes the prepared particle cross sections were analyzed by covering the whole surface area with adjacent line scans; laser beam diameters of 3 and 5 μm were used. The intensity data recorded for the measured line scan patterns were exported as csv files and processed with ImageLab (v.1.02, Epina GmbH, Pressbaum, Austria) as suggested by Bonta *et al.*[38] All 2D maps had squared pixels with pixel sizes of 3 × 3 or 5 × 5 μm^2, respectively.

Results & discussion

Sample preparation

To retrieve spatial information of particles *via* LA-ICP-MS or electron microscopy, the particulate sample needs to be transferred to a surface retaining the particles well enough to prevent them from breaking loose during laser irradiation or transfer into a vacuum (as necessary for SEM investigations). Moreover, the particles need to be isolated well enough for individual characterization. If particles are overlapping or agglomerating on the prepared surface, the achieved analytical information cannot be correlated with a specific particle. The development of sample preparation was done in two steps, focusing on particle dispersion and fixation.

Prepared samples were investigated using optical microscopy. The quality of sample collection was determined by visual comparison focusing on two objectives: particles on the substrate needed to be isolated well enough for individual analysis and all particle sizes according to particle size distribution should be present. Conditions for dispersion and fixation were modified to achieve well retained, isolated particle sizes in all relevant fractions. Argon with flows between 0.5 and 3 bar were applied as carrier gas and a defined sample amount (5 to 100 mg) was scattered on the prepared mounting base. Best results were achieved when using 10 mg of sample and an Ar stream of 0.5 bar (see Fig. 1). Image analysis (using ImageJ 1.50i, National Institute of Health, USA) of samples after particle deposition was carried out to ensure particle size distribution being comparable with the initial sample. For the optimized conditions, a median of 23.4 μm was found (assuming circular particles), which is not significantly different from the median of 26.2 μm measured for the loose fly-ash particles. However, the larger particles do not seem to adhere quantitatively to the substrate, as the 0.9-percentile ($d_{0.9}$) is shifted to 44.5 μm compared to 96.5 μm for the initial particles. Still it is possible to sample the particles of interest in a representative manner, which could be shown by quantitative image analysis.

LA-ICP-MS analysis

One of the simplest approaches to achieve spatial information from solid samples is applying a drilling-mode type of analysis. By constantly ablating the surface, the laser beam is penetrating layer by layer, resulting in depth-resolved information when displaying the transient signal. In the present case, however, environmental particles with maximum diameters of 100 μm are the target instead of hard bulk materials like ceramics or metals. Drilling was applied to the particles as initial approach. Even though particles were completely embedded in the hairspray-matrix, they were destroyed in most cases when using a laser beam diameter smaller than the particle itself. This effect can be mainly explained by the usually very rigid nature of the particles, leading to uneven crater formation and breakdown of the outer particle structure when exposed to the laser

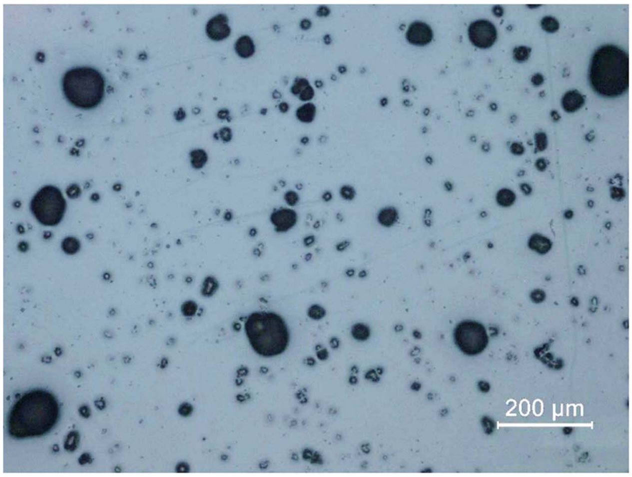


Fig. 1 Optical microscopy image of a finalized sample medium, showing the fixation of isolated particles prior to LA-ICP-MS analysis with anti-static spray below the hairspray layer; dispersal of 10 mg of sample, 0.5 bar Ar stream; a representative sample area is shown.

beam. In addition, thermal effects, such as partial sample melting, could be observed, leading to blurred depth-profiles – a problem which is often encountered when performing direct drilling using ns-LA.[41] Even if the number of destroyed particles could be reduced by using low-fluence ablation conditions, this procedure showed to reduce reproducibility of the drilling-mode measurements. Thus, drilling-mode experiments seemed not to offer favorable characteristics for the depth-resolved analysis of single fly-ash particles.

Preparation of cross-sections

To overcome the limitations of drilling, a different approach was required. When analyzing materials or ceramics in metallographic analysis, the samples, including the embedding material, are usually cut to achieve a surface which represents the bulk distribution and can be analyzed directly. These newly exposed surfaces are then ground, polished and/or etched and investigated with microscopy or other techniques. In this work, a similar approach has been attempted to be established. However, the environmental particles, embedded in hairspray could not be cut mechanically or treated the same way as hard and stable metallographic samples. The size and mechanical stability of the fly ash particles needed to be considered. Additionally, analyte smearing and cross-contamination might become a problem when grinding these samples. Instead of using mechanical processes, established laser etching techniques like FIB (focused ion beam)[42] could be used for particle cutting. Even though FIB is suitable to access cross-sections, when trying to cut larger particles, preparation of a representative number of particles would be extremely time consuming. To reduce time and cost, another method was established in this work. Virgin surfaces were exposed by ablating roughly half of the particle prior to the actual LA-ICP-MS analysis with the LA-laser system itself. Literature suggested good suitability of the 213 nm laser for this purpose.[43] These freshly created surfaces could then be analyzed using a line scan pattern without requiring depth-resolved investigations, thus eliminating the problems with depth profiling described in the previous chapter. In Fig. 2 the access of a particle cross section is sketched out.

In this cross-section mode the top of the target particle was ablated with a spot size of 10 μm to 15 μm larger than the actual particle diameter, respectively. This procedure was found to be beneficial to evenly ablate the particle and create a horizontally oriented cross-section. Very sensitive conditions were used to prevent effects like melting or particle break-up which would compromise the bulk distribution information of the cross-sections. By applying 10 to 25 laser shots with a fluence of 2.5–3 J cm^{-2}, depending on particle size, one third to a half of the particle top was removed, resulting in suitable cross-sections available for further analysis. The ablation conditions for accessing the cross-section were optimised by investigating SEM-pictures of ablated cross-sections.

It was initially expected that particles originating from a MWI are very inhomogeneous, which was confirmed by visual inspection of SEM images. When examining a SEM image, it can be observed, that some particles are conglomerates rather than a homogeneous bulk. An exemplary SEM image is shown in Fig. 3. Some areas of the particle appear as structures with a distinctly confined geometry (such as the areas marked by the black circle and the square in Fig. 3) while the major portion is constituted of a crumb-like material. These large inhomogeneities even within single particles already indicate the high complexity of the components of fly-ash. To investigate the origin of this observation, further chemical analysis of the particle's sub-structures is required.

Sample analysis using a single line scan

Line scans were performed across the complete diameter of the particle, starting and ending in embedding medium. A schematic sketch is shown in Fig. 4. This approach allowed a simple

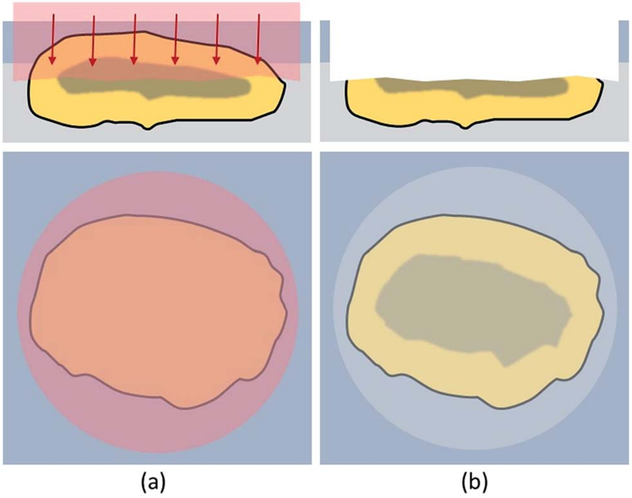


Fig. 2 Schematic description of the cross-section mode; the embedded particle is ablated with a laser beam diameter, covering the complete particle diameter and using very mild ablation conditions (a); the newly created cross section surface is subsequently accessible (b).

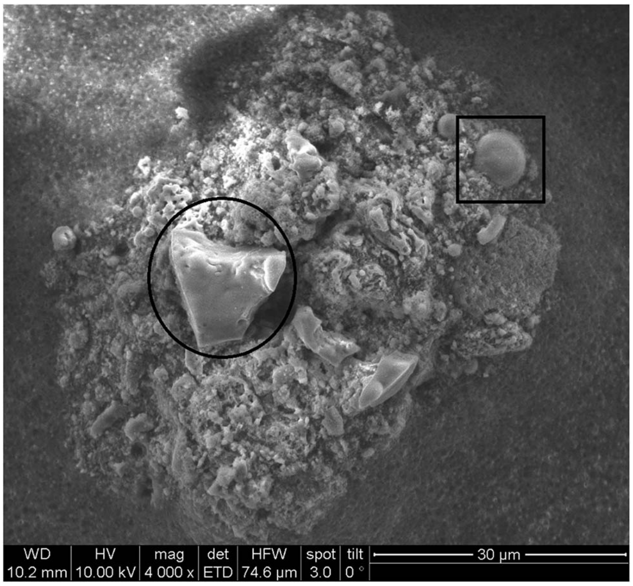


Fig. 3 SEM image of fly ash sample cross-section.

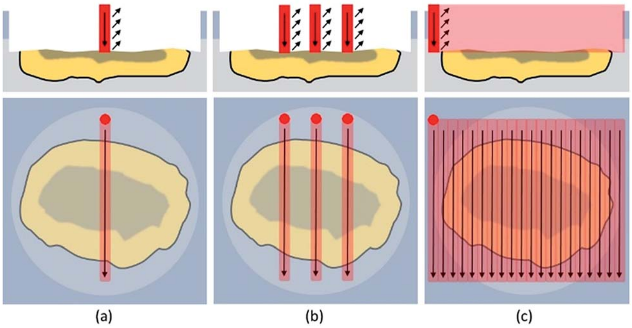


Fig. 4 Schematic description of the analysis of the cross section by one single (a), three parallel line scans (b) and by covering the whole particle surface with a pattern of adjacent line scans (c).

and fast analysis of the exposed cross sections. Scan speed (5–40 μm s^{-1}), ablation rate (1–10 Hz), and laser output energy were set to ensure best lateral resolution, depending on the dimensions of each individual particle. The fluence varied between 5 and 18 J cm^{-2} resulting in much harsher ablation conditions than used for accessing the cross-section.

When analyzing particles with these parameters, a transient signal with the following course was expected: at first, background levels for target analytes, during ablation of the embedding medium. When reaching the exposed particle cross-section, analyte signals should increase based on the analytes present in the particle. Relative amounts as well as distributions could be derived from these scans. Finally, intensities should drop to background level when again ablating just the embedding material. Exemplary analysis results for one particle are shown in Fig. 5.

68 particles were investigated with this cross-section approach. Three types of expected signal courses were found in the analyzed particles: homogeneous analyte distribution, completely inhomogeneous analyte distribution, as well as a core–shell-type signal pattern. Al was found to be evenly distributed in all measurements with a rather constant

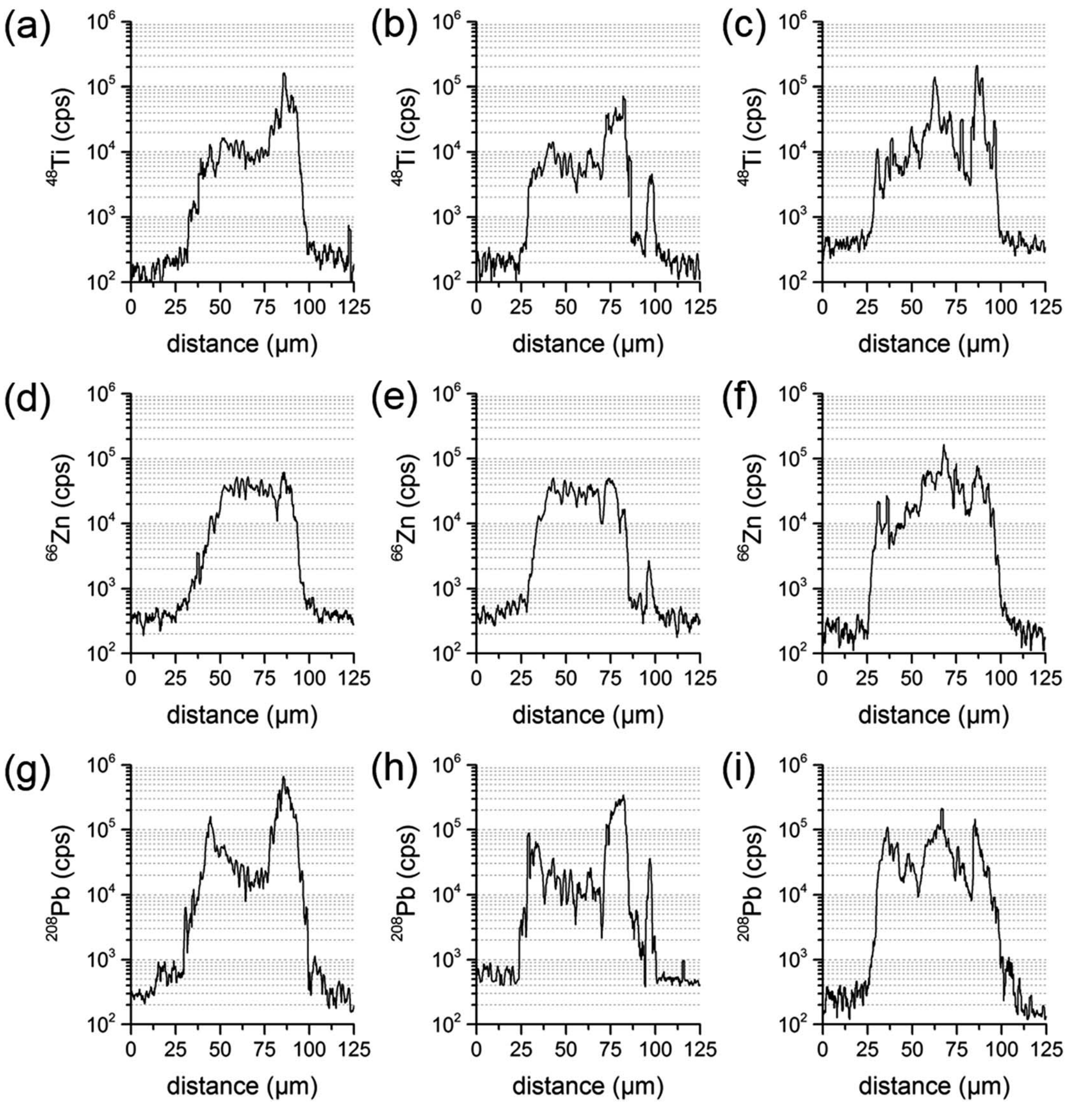


Fig. 5 Transient signal courses of three parallel line scans of the same sample particle for the elements Ti (a–c), Zn (d–f) and Pb (g–i).

transient signal over the whole cross-section diameter. In some cases, Ti, Zn, Cu and Pb were significantly enriched in the shell and showed higher intensities in the transient signal (by a factor of 15 to 30) at the edges than at the centre. However, for these elements also signal courses without a specific pattern were achieved. Some particles were found with higher intensities at the edges and some even had maximum intensity values in the centre. Again others were evenly distributed for the named analytes.

Since LA-ICP-MS results are depending on the location analyzed at the sample particle cross-section, one line scan could be insufficient to derive the elemental composition of the whole particle. To investigate the influence of the actual line scan location, three parallel line scans were performed at one and the same particle cross-section. Distance between the central axes of the line scans was set to 15 μm. A particle where an inhomogeneous distribution has already been identified was chosen for that purpose. Transient signal courses differed distinctly for the three scans. The first measurement showed varying concentrations for Pb and Ti, with a higher Ti signal intensity at one edge of the particle, and an increase in Pb at both edges. The second measurement displayed similar signal courses for all analytes and a third line scan showed varying concentrations for Ti, Zn and Pb and signal courses not similar to the ones already measured. All line three scans are presented in Fig. 5.

These investigations were repeated with several other particles, always yielding comparable results. The conclusion is that the enrichment of some elements, especially at the shell, is a highly variable process. Real sample particles are not perfect spheres. Moreover, surface deposits during their formation may not be homogeneous. Most likely, due to condensation processes during the MWI ash generation, some elements coagulate at the particle surface in unevenly distributed areas of the particle. Assuming that analyte enrichment at the surface is not even in the whole shell, these differences are most likely not identified when using only one single line scan per target particle. Thus, single line scans are not suited for representative analysis of the particle composition.

Sample analysis using a line scan pattern – imaging

A different approach is required to investigate the whole cross-section in a comprehensive manner. One way is to completely ablate the particle cross-section with consecutive, adjacent line scans. The data can be further processed to generate a 2D image, showing elemental distributions on the analyzed particle cross section in a two-dimensional manner. A schematic sketch is shown in Fig. 4.

For imaging purposes, the ablation parameters were modified to achieve optimum conditions. Scan speed and laser repetition rate were carefully optimized to achieve sufficient lateral resolution in one direction. The spot diameters were decreased to 5 μm (5–6 J cm^{-2}) at first and later on to 3 μm (17–18 J cm^{-2}) with consecutively increasing laser output to maintain a fluence of 10 J cm^{-2} for guaranteeing optimum resolution (*i.e.*, minimal sample carry-over) between the consecutive line scans. Under optimized conditions, several particles with diameters ranging from 25 μm to 100 μm were analyzed. Results indicate that the analyzed particle pool is highly heterogeneous, consisting of numerous different particle types. Still, some trends could be observed. Al and Si were found to be evenly distributed not only along one lateral line but over most of the cross-section, depending on the nature of the particle. Sometimes higher concentrations (up to two orders of magnitude) were observed in areas with distinct geometrical shapes with regards to a corresponding SEM image. However, in some cases neither Al nor Si were found in the particle bulk. These particles were believed to be carbon-based, a theory which unfortunately cannot be tested with LA-ICP-MS due to sensitivity issues, but was later on confirmed by EDX analysis.

Cu, Pb and Zn were found in different distributions. These elements could be identified in locally enriched sites as well as spread over the whole cross-section. When spread, Cu, Pb and Zn were absent in the particle centre and distributed throughout the outer cross-section ring. Ti was only found in locally enriched, mostly central positioned sites when comparing the elemental distribution image to the SEM image (see Fig. 3 & 6). These 4 elements were found only in the crumb-like cross-section parts and were absent in all more confined and dense-appearing structures.

These findings show that particles with a difference in shell/core composition can be identified using the presented approach. To validate the found elemental distribution images, matching results with an established comparative analysis technique are required.

Method validation

Since SEM analysis has already been employed, the SEM-EDX elemental mapping feature was applied. With a sub-μm lateral resolution, this technique would be a perfect choice for high-resolution comparative measurements. A representative choice of particles was visually selected. The particles cross-sections were exposed using Laser Ablation, as previously described. Since EDX-analysis is a non-destructive analysis technique, SEM pictures and an EDX-mapping of the particles were done prior to LA-ICP-MS imaging. SEM-EDX analysis was conducted under high vacuum conditions with an operating distance of approximately 10 mm. The accelerating voltage was set to 10 kV. After completing the SEM-EDX measurements, the samples were transferred to LA-ICP-MS and ablated with imaging conditions. SEM-EDX as well as LA-ICP-MS signal data were both exported to the ImageLab software which was used to compare the obtained laterally resolved element information (see Fig. 7).

The analyte choice for method validation was limited to elements with a sufficient concentration for EDX-mapping (sensitivities in the low %-range) and was restricted to those elements accessible with LA-ICP-MS; Al, Si, Ti and Zn met these requirements. When comparing LA-ICP-MS imaging and EDX-mapping of these elements, a very good agreement was found, as indicated in (Fig. 7). Some smaller discrepancies can be explained by the method differences between LA-ICP-MS and

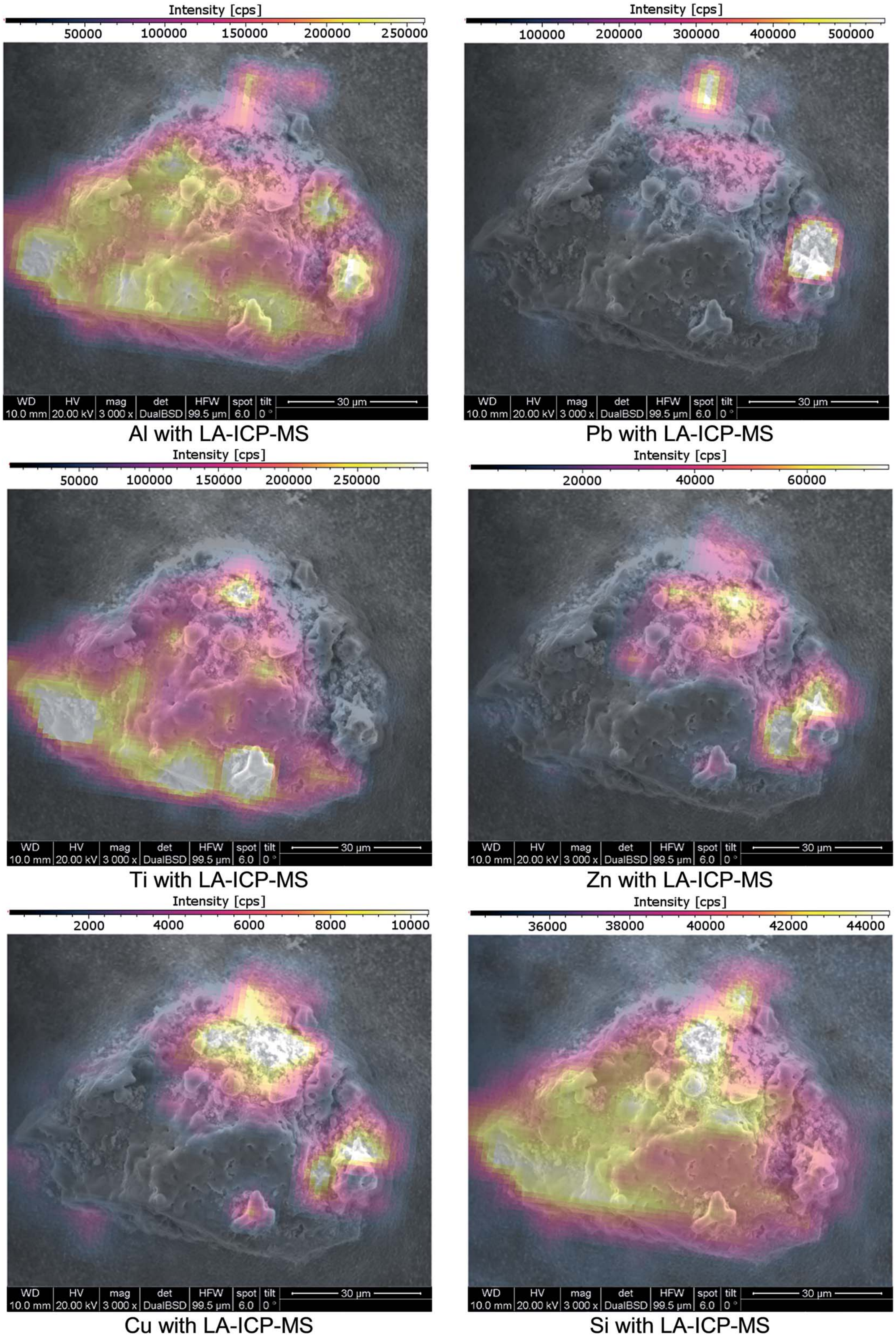
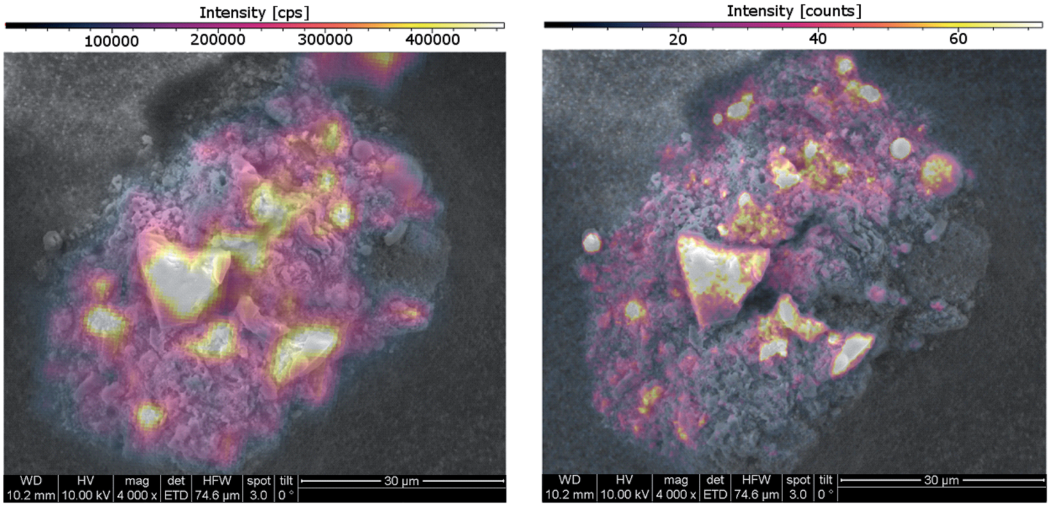
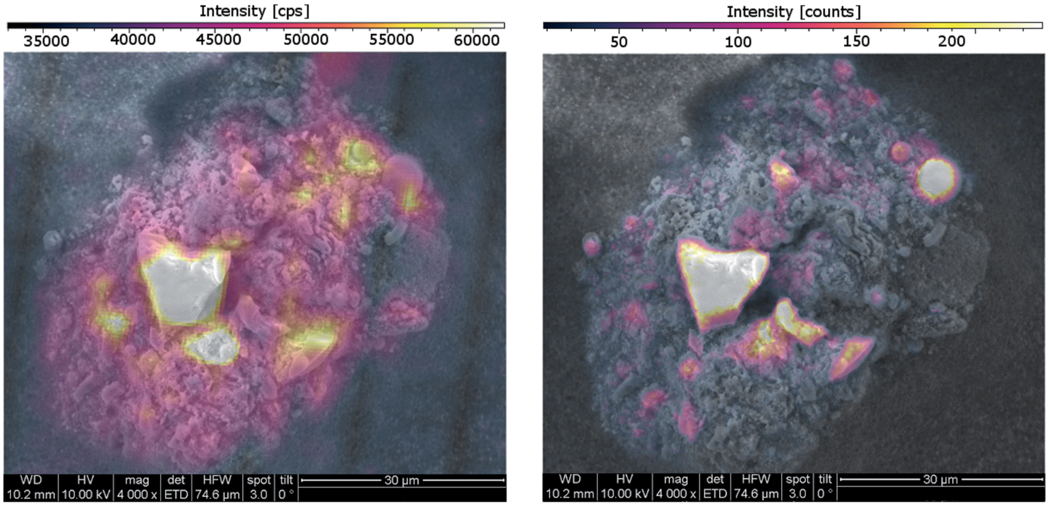


Fig. 6 SEM images of a cross-section of a fly ash particle; imaging provided by ImageLab, calculated from transient signal ICP-MS data.

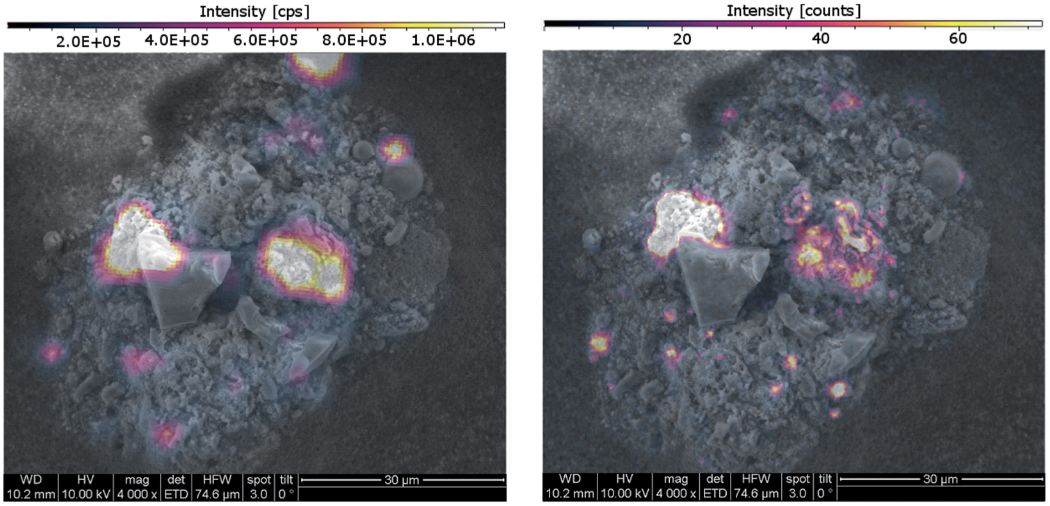
SEM-EDX. On the one hand LA-ICP-MS is a very sensitive technique but compared to SEM-EDX, lateral resolution is weaker, making the distribution images appear a bit blurrier. For example, when comparing Al the wider dynamic range of LA-ICP-MS measurements is obvious: even though the colour scale is proportional, EDX shows only areas with elevated



Al with LA-ICP-MS Al with SEM-EDX



Si with LA-ICP-MS Si with SEM-EDX



Ti with LA-ICP-MS Ti with SEM-EDX

Fig. 7 SEM images of a cross-section of a fly ash particle; imaging provided by ImageLab, calculated from transient signal ICP-MS data or EDX-mapping output data.

concentrations whereas with LA-ICP-MS also minor amounts could be detected. On the other hand, SEM-EDX is able to resolve the lateral information to a much finer extent than LA-ICP-MS with a beam diameter of 3 µm. Therefore, average information from fine structures is sometimes compiled in single pixels of the LA images whereas local enrichments are rather resolved in the EDX images. Concerning carbon, valuable information was provided by EDX analysis which could not be covered by LA-ICP-MS. Furthermore, SEM-EDX also allows the analysis of oxygen, providing additional information about the prevailing general nature of the existing elements – metallic form, oxides or carbonates.

Conclusions

In this paper a method for achieving spatial information from particulate environmental samples by LA-ICP-MS imaging is presented. Sample preparation to finally exhibit cross-sections turned out to be a viable approach. In a first step, particles were cross-sectioned using mild laser ablation conditions followed by the ablation of adjacent consecutive line scans to generate 2D images of target analytes. Thereby, information about the lateral distribution of major and minor metallic constituents of fly ash particles could be obtained. The preparation process is adaptable and can be adjusted to the means necessary for complementary analysis techniques (*e.g.*, SEM-EDX). With this method, particle sizes from 25 μm to 100 μm were investigated regarding their differences in elemental composition. The method was validated by comparison with SEM-EDX analysis. Al, Si, Ti and Zn were found in good agreement between both techniques considering analytical differences and limitations especially in sensitivity.

A fly ash sample originating from MWI, was used for method development and validation. Even though more than 60 comparable particles were analyzed, no definitive trends regarding the particle composition and structure were found. Some particles revealed a rather homogeneous analyte distribution, for some particles a core–shell-type signal pattern was observed, and some particles showed a completely inhomogeneous analyte distribution. The investigated particles consisted either of a silicate or a carbon core. Elements like Cu and Pb were often enriched at the particle surfaces whereas Al, Si, and Zn were found to be evenly distributed as well as locally enriched. Ti was mostly found in confined sites inside the particle. As initially stated these results can be used to develop recycling approaches for the element(s) of interest. Derived from these results Cu and Pb can be easily accessed with surface recycling techniques (*e.g.* leaching). To recover Al, Si, and Zn, recycling needs to process the whole particle. For Ti no surface techniques are applicable because it is only found at the particles interior.

The method may also be suitable to assess toxicity and health risks originating from environmental particles. For that purpose, knowledge about surface composition is crucial. In this case the presence of Pb at the surface could be of interest. For further work in this field the choice of analytes needs to be amended regarding specific interests and a suitable approach for signal quantification has to be developed.

For future development, smaller particles may be accessible with further optimisation of the instrument configuration, considering wash-out cell volume and transfer line arrangement. The preparation approach could also be easily adapted to all kinds of substrates, depending on requirements of the particular analysis technique like transparency or conductivity.

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POSTER 4 (POSTER AWARD WINNER)

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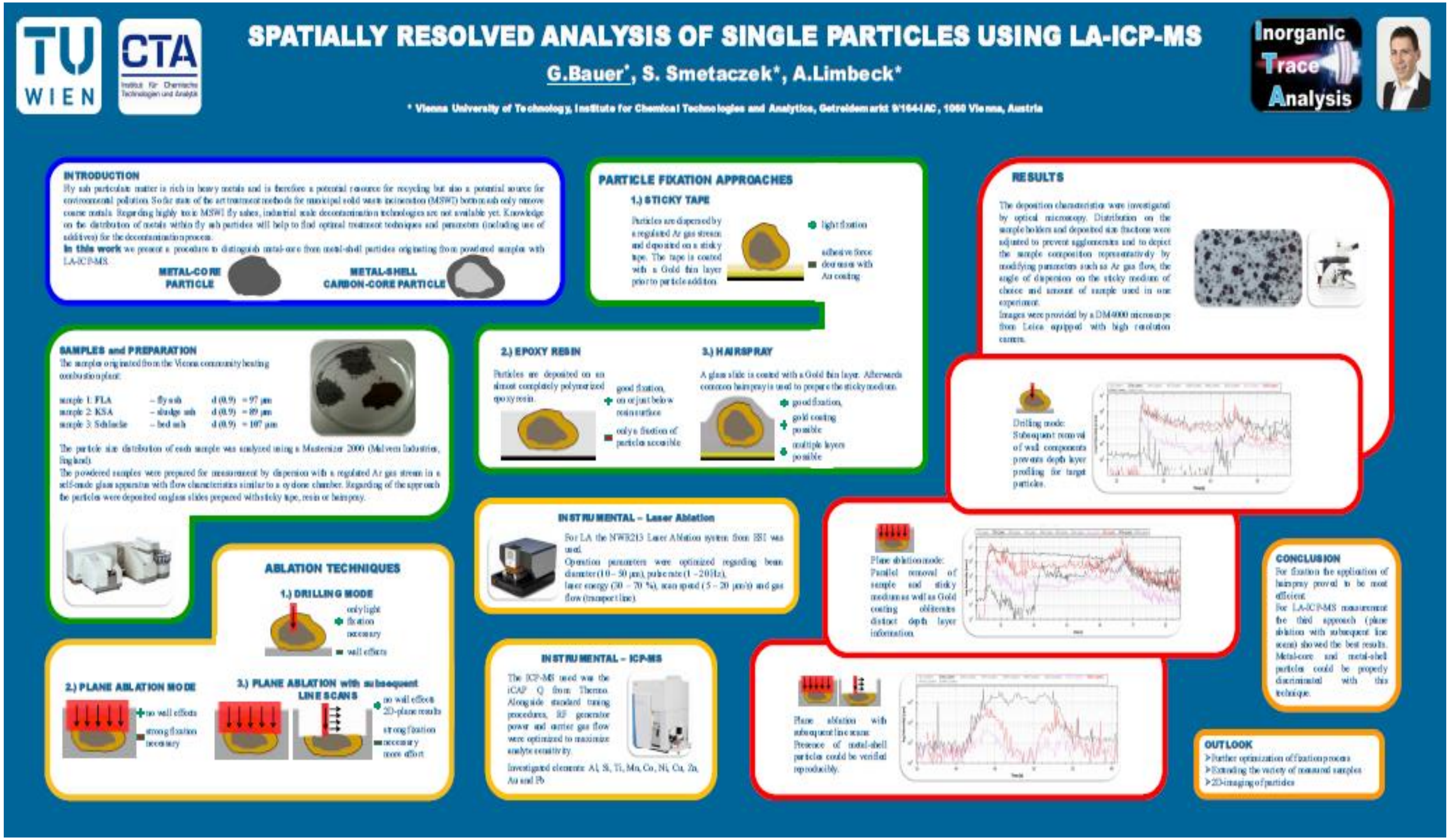

SPATIALLY RESOLVED ANALYSIS OF SINGLE PARTICLES USING LA-ICP-MS

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INTRODUCTION

Fly ash particulate matter is rich in heavy metals and is therefore a potential resource for recycling but also a potential source for environmental pollution. So far state of the art treatment methods for municipal solid waste incineration (MSWI) bottom ash only remove coarse metals. Regarding highly toxic MSWI fly ashes, industrial scale decontamination technologies are not available yet. Knowledge on the distribution of metals within fly ash particles will help to find optimal treatment techniques and parameters (including use of additives) for the decontamination process.

In this work we present a procedure to distinguish metal-core from metal-shell particles originating from powdered samples with LA-ICP-MS.

METAL-CORE PARTICLE

METAL-SHELL CARBON-CORE PARTICLE

SAMPLES and PREPARATION

The samples originated from the Vienna community heating combustion plant:

sample 1: FLA	– fly ash	d (0.9) = 97 µm
sample 2: KSA	– sludge ash	d (0.9) = 89 µm
sample 3: Schlacke	– bed ash	d (0.9) = 107 µm

The particle size distribution of each sample was analyzed using a Mastersizer 2000 (Malvern Industries, England).

The powdered samples were prepared for measurement by dispersion with a regulated Ar gas stream in a self-made glass apparatus with flow characteristics similar to a cyclone chamber. Regarding of the approach the particles were deposited on glass slides prepared with sticky tape, resin or hairspray.

PARTICLE FIXATION APPROACHES

1.) STICKY TAPE

Particles are dispersed by a regulated Ar gas stream and deposited on a sticky tape. The tape is coated with a Gold thin layer prior to particle addition.

- \+ light fixation
- – adhesive force decreases with Au coating

2.) EPOXY RESIN

Particles are deposited on an almost completely polymerized epoxy resin.

- \+ good fixation, on or just below resin surface
- – only a fraction of particles accessible

3.) HAIRSPRAY

A glass slide is coated with a Gold thin layer. Afterwards common hairspray is used to prepare the sticky medium.

- \+ good fixation,
- \+ gold coating possible
- \+ multiple layers possible

ABLATION TECHNIQUES

1.) DRILLING MODE

- \+ only light fixation necessary
- – wall effects

2.) PLANE ABLATION MODE

- \+ no wall effects
- – strong fixation necessary

3.) PLANE ABLATION with subsequent LINE SCANS

- \+ no wall effects 2D-plane results
- – strong fixation necessary more effort

INSTRUMENTAL – Laser Ablation

For LA the NWR213 Laser Ablation system from ESI was used.

Operation parameters were optimized regarding beam diameter (10 – 50 µm), pulse rate (1 – 20 Hz), laser energy (30 – 70 %), scan speed (5 – 20 µm/s) and gas flow (transport line).

INSTRUMENTAL – ICP-MS

The ICP-MS used was the iCAP Q from Thermo. Alongside standard tuning procedures, RF generator power and carrier gas flow were optimized to maximize analyte sensitivity.

Investigated elements: Al, Si, Ti, Mn, Co, Ni, Cu, Zn, Au and Pb

RESULTS

The deposition characteristics were investigated by optical microscopy. Distribution on the sample holders and deposited size fractions were adjusted to prevent agglomerates and to depict the sample composition representatively by modifying parameters such as Ar gas flow, the angle of dispersion on the sticky medium of choice and amount of sample used in one experiment.

Images were provided by a DM4000 microscope from Leica equipped with high resolution camera.

Drilling mode: Subsequent removal of wall components prevents depth layer profiling for target particles.

Plane ablation mode: Parallel removal of sample and sticky medium as well as Gold coating obliterates distinct depth layer information.

Plane ablation with subsequent line scans: Presence of metal-shell particles could be verified reproducibly.

CONCLUSION

For fixation the application of hairspray proved to be most efficient.

For LA-ICP-MS measurement the third approach (plane ablation with subsequent line scans) showed the best results. Metal-core and metal-shell particles could be properly discriminated with this technique.

OUTLOOK

- ➢Further optimization of fixation process
- ➢Extending the variety of measured samples
- ➢2D-imaging of particles

6. LIST OF PUBLICATIONS

6.1. PEER REVIEWED ARTICLES

Sol–gel films with polymodal porosity by surfactant-assisted breath figure templating
Marina Lomoschitz, Stefan Edinger, **Gerald Bauer**, Gernot Friedbacher and Ulrich Schubert.
Journal of Materials Chemistry, 11 (2010) 2075-2078.
http://dx.doi.org/10.1039/B927433B

Dispersed particle extraction—A new procedure for trace element enrichment from natural aqueous samples with subsequent ICP-OES analysis
Gerald Bauer, Marie-Alexandra Neouze and Andreas Limbeck.
Talanta, 103 (2013) 145 – 152.

http://dx.doi.org/10.1016/j.talanta.2012.10.023

Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry. Review Article.
Andreas Limbeck, Patrick Galler, Maximilian Bonta, **Gerald Bauer**, Winfried Nischkauer and Frank Vanhaecke.
Analytical and Bioanalytical Chemistry, 407 (2015) 6593 – 6617.
http://dx.doi.org/10.1007/s00216-015-8858-0

Quantitative analysis of trace elements in environmental powders with laser ablation inductively coupled mass spectrometry using non-sample-corresponding reference materials for signal evaluation.
Gerald Bauer and Andreas Limbeck.
Spectrochimica Acta Part B, 113 (2015) 63-69.
http://dx.doi.org/10.1016/j.sab.2015.09.007

Analysis of single fly ash particles using laser ablation ICP-MS – an approach achieving lateral elemental distribution information via imaging
Gerald Bauer, Birgit Achleitner, Maximilian Bonta, Gernot Friedbacher and Andreas Limbeck.
RSC Advances, 7 (2017) 20510-20519.
http://dx.doi.org/10.1039/c7ra00975e

ETV-ICP-OES analysis of trace elements in fly-ash samples - A fast and easy way for simplified routine determination.
Gerald Bauer and Andreas Limbeck.
Microchemical Journal, 137 (2018) 496-501.
https://doi.org/10.1016/j.microc.2017.12.017

6.2. ORAL PRESENTATIONS AT CONFERENCES

Presenting author is marked in bold.

G. Bauer, A. Limbeck:
"A new trace metal enrichment procedure for ICP-OES-analysis based on the renewable surfaces approach";
2012 Winter Conference on Plasma Spectrochemistry, Tucson, Arizona, US; 09.01.2012 - 14.01.2012; in: "2012 Winter Conference Program and Abstracts", (2012), ISSN: 0161-6951; p. 107

G. Bauer, A. Limbeck:
"Sample preparation for powder analysis by LA-ICP-MS - pelletizing, embedding and their applicability for "in-house" standard preparation";
23. ICP-MS Anwendertreffen, Tulln, Austria; 10.09.2012 - 12.09.2012; in: "Band of Abstracts", (2012), p. 13.

G. Bauer, A. Limbeck:
"Combining in-house standard preparation and plasma stabilization techniques to enable LA-ICP-MS quantification for a wide range of environmental matrices";
2014 Winter Conference on Plasma Spectrochemistry, Amelia Island, Florida, US; 06.01.2014 - 11.01.2014; in: "2014 Winter Conference Program and Abstracts", (2014), ISSN: 0161-6951; p. 148

6.3. POSTER PRESENTATIONS AT CONFERENCES

Presenting author is marked in bold.

G. Bauer, A. Limbeck:
"Postfunctionalized nanoparticles for enrichment of trace metals in environmental liquids";
2010 Junior Scientist Conference, Vienna, Austria; 07.04.2010 – 09.04.2010; in: "Proceedings of the Junior Scientist Conference 2010"; p. 409-410

G. Bauer, A. Limbeck:
"Fast and accurate ETV-ICP-OES analysis of trace metals in fly ash origination from waste combustion";
2012 Winter Conference on Plasma Spectrochemistry, Tucson, Arizona, US; 09.01.2012 - 14.01.2012; in: "2012 Winter Conference Program and Abstracts", (2012), ISSN: 0161-6951; p. 346

G. Bauer, A. Limbeck:
"Accurate analysis of trace metals in fly ash using electro-thermal-vaporisation in combination with ICP-MS detection";
Euroanalysis 17, Warsaw, Poland; 25.08.2013 - 29.08.2013; in: "Book of Abstracts", (2013), p. 338.

G. Bauer, A. Limbeck:
"Development of a LA-ICP-MS procedure for accurate quantification of solid environmental samples without matrix matched standards";
Euroanalysis 17, Warsaw, Poland; 25.08.2013 - 29.08.2013; in: "Book of Abstracts", (2013), p. 339.

G. Bauer, A. Limbeck: (Poster Award Winner)
"Spatially resolved analysis of single particles using LA-ICP-MS";
2014 Winter Conference on Plasma Spectrochemistry, Amelia Island, Florida, US; 06.01.2014 - 11.01.2014; in: "2014 Winter Conference Program and Abstracts", (2014), ISSN: 0161-6951; p. 124

G. Bauer
" On Site Detection of Chemical Contamination on Surfaces via HAPSITE® by Combining SIM with Provisional Swipe Analysis";
3rd International Symposium on Development of CBRN Defence Capabilities, Berlin, Germany; 19.10.2015 – 21.10.2015; in “Conference Magazine 2015”: p. 51

G. Bauer
" Stabilization of potable water containers with silver ions in emergency situations - challenges for sampling and analysis";
2017 European Winter Conference on Plasma Spectrochemistry, Sankt Anton, Arlberg, Austria; 19.02.2017 – 24.02.2017; in: "EWCPS2017 book of abstracts", p. 306

7. CURRICULUM VITAE

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2100 Korneuburg

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Personal data

Date of birth:	March 8th, 1986
Place of birth:	Vienna
Citizenship:	Austria
Military rank:	Captain

Education

10/2015 – 06/2016	**United Nations Youth and Students Association of Austria - Academic forum for foreign affairs Vienna** Global Advancement Program
03/2011 -	**Vienna University of Technology, 1040 Vienna** **PhD studies - Chemistry** Topic: laser ablation mass spectrometry with inductively coupled plasma
10/2005 - 12/2010	**Vienna University of Technology, 1040 Vienna** **Master studies - technical Chemistry** Focus: chemistry and technology of materials Master thesis „Development of enrichment procedures for accurate determination of trace metals in complex matrices (formation water)" in cooperation with OMV
10/2004 – 10/2005	**Military service**
09/1996 – 06/2004	**Secondary School - GRG21, 1210 Wien** Focus: political education

Work experience

05/2014 - 07/2014	**humanitarian aid mission in Bosnia & Herzegovina** AUTHUM/AFDRU-BiH, Head of laboratory
03/2011 -	**Austrian Armed Forces** (full time) Expert for chemical weapons, industrial hazards and water analysis Set-up, development and leading a technical responder team
11/2009 - 12/2009	**Vienna University of Technology** Tutor for analytical chemistry
01/2006 - 02/2011	**doctors practice, Bauer Birgit, MD** Blood analysis and IT services (part time)
Summer 2009	**Vienna University of Technology, institute for materials chemistry** (Internship)
Summer 2008	**Military support mission - AssE/Sche** in "Bruck an der Leitha" Deputy squad leader
Summer 2007	**Vienna University of Technology, institute for chemical technologies and analytics** (Internship)

Voluntary engagement

2005 -	ITF-Austria (vice president since 2016, club president since 2017) V. degree black belt, trainer, chairman of national tournament & umpire committee
2000 - 2010	Gymnastic club "Turnverein Langenzersdorf" Caregiver in two gym lessons (weekly) camp supervisor/caregiver 2006, 2007, 2009 and 2010

Language skills

German: Mother tongue
English: fluently spoken and written

IT skills

Programming: VBA, Delphi, php, Latex
Microsoft Office: ECDL - Word, Excel, Access, PowerPoint, Outlook

Additional skills

- Sports manager basic license (2008)
- Mediator in secondary school (2001-2004)
- IATA DGR packing license

Military education

- Courses: leadership to level of company commander, political education, communication skills
- external communications officer (since 2013)

Taekwon-do (International Taekwon-do Federation)

- Participation at International Instructor Courses: 2007, 2009, 2010, 2012, 2013, 2014, 2015
- local champion, EC and WC-participation in Germany 2005, Canada 2007, Argentina 2009, Slovakia 2011, Slovenia 2012, Spain 2013, Hungary 2014, Italy 2015, Hungary 2016 and Ireland 2017
- Umpire courses (International 2009, chairman of national umpire committee)

Extra curricula activities & Hobbies

- participation Talents@Alpbach 2014, TUTalents 4 Siemens 2013, TUtheTOP 2011/12
- sports, reading

Awards

- poster award for the best poster at the Winter Conference on Plasma Spectrochemistry 2014, Amelia Island, Florida, US: "Spatially resolved analysis of single particles using LA-ICP-MS"

Gerald Bauer

Vienna, 4th of February 2018 signature (Gerald Bauer)