



A versatile approach for the preparation of matrix-matched standards for LA-ICP-MS analysis – Standard addition by the spraying of liquid standards

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ABSTRACT

In the last years, LA-ICP-MS has become an attractive technique for analyzing solid samples from various research fields. However, application in material science is often hampered by the limited availability of appropriate certified reference materials, which are a precondition for accurate quantification. Thus, frequently in-house prepared standards are used, which match the sample's composition and include all elements of interest at the required concentration levels. However, preparing and characterizing such standards is often labor-intensive and time-consuming.

This work proposes a new approach for the fabrication of matrix-matched standards based on the concept of standard addition. In the first step, the analytes of interest are homogeneously deposited onto the sample surface using liquid standards and a spraying device. For analysis, the generated thin layer is ablated simultaneously with the underlying sample. Thereby deviations in the ablation process and particle transport can be avoided. It could be shown that the developed method is highly versatile and could be easily adapted to the actual needs. Using silicon, silicon carbide, copper, aluminum, and glass as a matrix, excellent linear correlations between observed signal intensities and deposited amounts were found for the elements Zn, Ag, In, and Pb (R^2 - values greater than 0.99).

The method was applied to determine the content of sulfur, zinc, silver, indium, and lead in a commercial Kapton® polyimide film. The obtained results could be verified based on the homogeneously distributed sulfur by conventional liquid ICP-MS analysis after sample digestion, showing similar precision and accuracy. Lead was found to show a very inhomogeneous distribution in the Kapton® film, with concentration below the LOD at most measured locations and irregularly occurring spots with significantly higher concentrations. Finally, a quantitative depth profile of sulfur in a Kapton® film has been measured to assess the uptake of SO₂ after a weathering experiment.

1. Introduction

The development of analytical techniques and instruments is always pushed further to meet the increasing demands for technological advances in all kinds of industries and research fields. Nevertheless, aside from instrumental improvements, the development of suitable methods is essential to enable the extraction of the desired information for the respective question with the necessary confidence. These methods require thorough adjustment and optimization to the utilized instrument and the investigated material.

Polymers are nowadays used in a large variety of industries and

products. In many applications, polymers contain additives such as pigments, stabilizers, plasticizers, anti-oxidizing agents, flame retardants, and antistatic agents to tune their physical and chemical properties [1]. These polymer additives cover a wide range of organic and inorganic substances and must be monitored in production regarding their content and distribution to ensure the desired product properties [2]. Not only deliberately added substances but also unintended contaminations must be monitored, as they could negatively impact product quality or must not exceed certain limits specified by legal authorities [3]. In addition to these necessities in production, some applications also require analysis of the interaction of a polymer product

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with the environment (e.g., uptake, accumulation, or emission of substances [4,5], stability, aging, and degradation characteristics [6]), which can be essential either from a technological or an environmental point of view. Thus, polymer analysis is an important area in Analytical Chemistry. The applications of polymer materials cover relatively trivial uses like (one-way) packaging materials for consumer goods and construction materials [7]. Yet nowadays, they also have found their way into more demanding fields, such as the electronic and semiconductor industries [8]. There, polymers are often employed as an encapsulation material or protective layer to prevent devices from the influence of light and atmosphere. While operational conditions in an average home or office environment are not as critical, device protection is of high importance in harsh environments, e.g., in devices used in industrial- or automotive applications, where usually gases such as hydrogen sulfide or sulfur dioxide are present at higher concentrations [9,10]. Development and capability studies of such coatings require sensitive determination of sulfur levels.

Conventional approaches for elemental analysis in polymers are based on sample digestion or combustion, followed by liquid ICP-MS/OES analysis [11,12]. While offering reliable quantitative results, these approaches come with certain drawbacks. They usually result in a substantial dilution of the sample, which might become a problem regarding the required sensitivity of analysis, and they provide only bulk information. Further, time-consuming sample preparation, which also increases contamination risk, and the need for hazardous and expensive reagents, make direct solid sampling techniques such as LIBS and LA-ICP-MS more attractive.

Since more than 30 years ago, LA-ICP-MS has been used to determine natural and synthetic specimens' elemental composition [13]. This analytical method offers vast applicability for direct solid sampling analysis with minimal sample preparation in analyzing major, minor, and trace constituents over a wide elemental range and performing laterally- and depth-resolved microanalysis without requiring vacuum or conducting samples [14]. With a linear dynamic range of up to 10 orders of magnitude, excellent limits of detection, and high sample throughput, LA-ICP-MS finds application in various research fields (e.g., for analyzing biological, medical, geological, and technological samples [14–20]). Additionally, LA-ICP-MS has already been successfully applied for elemental analysis of polymer materials several times [21–24].

Despite all mentioned advantages, LA-ICP-MS is constrained by limitations in performing quantitative analysis. Because of matrix effects occurring in the ablation process, size- and shape-dependent efficiency of the particle aerosol transport from the ablation chamber to the mass spectrometer, and the atomization and ionization efficiency in the ICP, the measured signal intensities are not exactly representative of the original sample composition. The particle formation (size, shape, and size distribution) depends on the laser wavelength and pulse duration used in the ablation process, as well as the properties of the sample material, like morphology, absorption, reflectivity, and thermal conductivity [14]. Transport and atomization efficiency depend on the size and shape of the generated particles, as smaller particles are transported more efficiently. In comparison, larger particles might not get fully atomized in the ICP [25,26]. The ionization efficiency depends on the plasma conditions. A high matrix load with certain species can suppress or enhance the ion yield of other species in the plasma and, thereby, the obtained signal intensity of the investigated analytes [27]. The consequences of these matrix effects have already been reported for polymer samples, showing significant deviations in the slope of the calibration function of different polymer types (polyimide, polymethylmethacrylate, polyvinylpyrrolidone) spiked with platinum [24, 28]. Modern laser ablation systems using pulsed UV radiation (e.g., ArF 193 nm, Nd:YAG 213 nm) or femtosecond pulse lengths minimize these matrix effects in ablation but cannot eliminate them entirely [25,29]. For these reasons, reliable quantification can only be achieved using calibration standards representing the same matrix composition as the

sample under investigation.

The best and most straightforward way to achieve reliable quantitative data is by using certified reference materials (CRM) with identical compositions. However, their availability is limited to specific sample matrices, making this approach impossible for many research questions, especially if newly developed materials are investigated. To compensate for these limitations, several new approaches have been developed in the past, using in-house prepared matrix-matched standards [14,30–33] or different concepts of standard addition [14,34,35]. However, the production and characterization of such standards are usually work-intensive and time demanding.

A possible method for preparing matrix-matched standards of polymer samples is by spiking polymer solutions with different amounts of the elements of interest and subsequently evaporating the solvent after shaping via casting or spin-coating [24]. However, this requires some *a priori* knowledge about the composition of the investigated polymer, and it further must be assumed that the properties of the prepared standards are still similar to those of the original sample. A method that allows standard addition directly onto solid samples is dried droplet quantification, where a defined volume of liquid standard with known concentration is deposited on the sample surface. After solvent evaporation, the residue is analyzed simultaneously with the sample substrate. Thus, deviations in the ablation process between sample and standard could be avoided. Using multiple droplets with different concentration levels results in a calibration function. Although the dried droplet approach represents an attractive method for matrix-matched calibration, this method bears some disadvantageous aspects. In the drying process, the “coffee ring” effect and size discrimination [36,37] lead to inhomogeneous deposition of residue on the surface. This can be compensated by complete ablation of the entire residue. Considering the size of the droplet residues, which can be up to several mm² depending on the applied volume and the hydrophobicity of the substrate, the ablation can be rather time-consuming. Additionally, prepared dried droplet standards can only be analyzed once, which is undesirable, as LA-ICP-MS needs to be calibrated for each analysis.

This work presents a new approach for matrix-matched standard calibration with LA-ICP-MS, circumventing significant drawbacks of conventional dried droplet quantification or standard addition techniques that use sample spiking. For this purpose, a commercial spraying device is used to homogeneously deposit thin layers of standards with different concentration levels onto the sample surface. The applicability of the proposed procedure is demonstrated by the analysis of selected elements in polymer films. Further, it is shown that the developed method can also be applied to other sample materials.

2. Experimental

2.1. Preparation of spraying standard solutions

All sample intake and dilution steps were performed gravimetrically. Certified single-element ICP-MS standards (1 mg/ml) of indium, europium, gadolinium, sulfur, zinc, silver, and lead were acquired from Merck Millipore. 30% isopropanol (v/v) was prepared using MilliQ water (18.2 MΩ•cm) freshly dispensed from a Barnstead EASYPURE II water system from ThermoFisher Scientific (Marietta, OH, USA) and isopropanol (p.a.) from Merck (Darmstadt, Germany). The spraying standard solutions were prepared by combining two stock solutions and 30% isopropanol in the respective ratios, where stock A contained the matrix and internal standard, and stock B the elements of interest. Stock A was prepared by dissolving 1 g of polyethylene glycol (PEG) with an average molecular weight of 10,000 Da (Honeywell Fluka™, ≥99%) and addition of 1 g of a 1 mg/g europium ICP standard into 98 g of the 30% isopropanol, resulting in an approximately 30% isopropanol solution with 1% PEG and 10 µg/g europium. Stock B was prepared by addition of 2.5 g of an advance prepared ICP-MS standard mix, containing the elements of interest with the desired concentrations, into 97.5 g of the

30% isopropanol. For each experiment, 5 g of Stock A was mixed with varying amounts of stock B and 30% isopropanol to obtain 10 g of each spraying standard solution, ultimately containing approximately 30% isopropanol, 0.5% PEG, 5 $\mu\text{g/g}$ Eu, and the desired concentration of the target elements.

For the initial experiments for the optimization of the spraying parameters on Kapton® as well as the preparation of sulfur standards on Kapton®, the element mix added to Stock B contained 345 mg of 2,2'-Dithio-dipyridine (Sigma-Aldrich, $\geq 99\%$), 2 g of a 1,000 $\mu\text{g/g}$ indium ICP standard and 155 mg of 30% isopropanol, resulting in a solution with 1 mg/g sulfur and 3 $\mu\text{g/g}$ indium. The prepared spraying standards (Stock A + Stock B + 30% IP) resulted in 5 different levels of S from 10 to 150 $\mu\text{g/g}$ and In from 0.2 to 3 $\mu\text{g/g}$. For the determination of the deposited mass per sample area via sample digestion and liquid ICP-MS determination, Stock B was prepared containing 20 $\mu\text{g/g}$ indium, resulting in a spraying standard with 10 $\mu\text{g/g}$ In. For the multielement spraying standards on Kapton® and on different other substrate materials, Stock B was prepared with 50 $\mu\text{g/g}$ of zinc, silver, indium, and lead, resulting in spraying standards with concentration levels from 0.01 to 25 $\mu\text{g/g}$.

2.2. Preparation of sprayed standards by aerosol deposition

A TM-Sprayer from HTX Technologies LCC (Chapel Hill, NC, USA) was used for applying liquid standards on surfaces. The spraying parameters for aerosol deposition were optimized using a Kapton® - polyimide film roll with a thickness of 13 μm , purchased from Goodfellow GmbH. (Hamburg, Germany, manufacturer: DuPont). A piece of 150 \times 40 mm^2 was fixed onto a silicon wafer and covered with a 3D-printed mask. The mask left squared areas of 7 \times 7 mm^2 with rounded corners uncovered, one for each standard level. The uncovered regions were sprayed, each with a different standard concentration level, while all other areas were covered to prevent cross-contamination. The TM-Sprayer was operated under ambient conditions with a flow rate of 30 $\mu\text{l}/\text{min}$, a nozzle velocity of 1,000 mm/min , and a nozzle temperature of 45 $^\circ\text{C}$ for all experiments. The nozzle moving pattern was a meander with a 1 mm line distance and was performed for two cycles with a 90° rotation of the spraying pattern. The resulting Kapton® film then contained separate locations with thin layers of different standard addition levels. The spraying process applied to the Kapton® film is schematically depicted in Fig. 1.

In addition to the Kapton® films, five other substrate materials have been chosen for spraying tests with multielement standards. Eight different concentration levels from 0.01 to 25 $\mu\text{g/g}$ and 5 $\mu\text{g/g}$ Eu internal standard were applied on silicon, silicon carbide, glass, copper, and aluminum.

To determine the deposited standard mass per area, 12 pieces of 10 \times 10 mm^2 high-purity silicon wafer from Infineon Technologies Austria (Villach, Austria) were used as a substrate. They were masked and sprayed analogously, using a standard solution with 10 $\mu\text{g/g}$ indium.

2.3. Weathering experiment

The weathering treatment of Kapton® films with corrosive gases at a defined temperature and relative humidity (r.h.) was performed in an in-house developed mixed-flowing gas (MFG) setup. The test gas (1,000 ppm SO_2 , (v/v)) is mixed with synthetic air to the desired concentration using mass flow controllers. The relative humidity is adjusted by mixing a dry (0% r. h.) with a humidified (100% r. h.) synthetic air stream. The set gas mixture enters a weathering cell positioned inside a laboratory oven to adjust the temperature between room temperature and 300 $^\circ\text{C}$. A 20 \times 20 mm^2 Kapton® film was attached to the edge of a glass slide with adhesive tape ensuring both sides of the film were exposed to the surrounding atmosphere and placed in the weathering cell. The sample was weathered for 72 h using 100 ppm (v/v) SO_2 at 22 $^\circ\text{C}$ and 90% relative humidity with a gas exchange rate of 4 h^{-1} . For LA-ICP-MS measurement, the film was fixed onto a silicon wafer substrate using adhesive tape.

2.4. LA-ICP-MS measurements

LA-ICP-MS measurements were performed with an "imageGEO193" laser ablation system from Elemental Scientific Lasers (Bozeman, MT, USA) coupled with an "iCAP Q" ICP-MS system from ThermoFisher Scientific (Bremen, Germany) using PTFE tubing and a helium flow rate of 800 ml/min . The instrument was tuned daily for a maximum ^{115}In signal while ablating NIST SRM 612 reference material. Spraying parameters were optimized iteratively to ensure a homogeneous application of the standards. Images of 1.5 \times 1.5 mm^2 were recorded on the substrates silicon and glass, using a 10 \times 10 μm^2 square-shaped spot, a fluence of 1 J/cm^2 , 100 Hz repetition rate, and 100 $\mu\text{m}/\text{s}$ scan speed. For the calibrations on different substrate materials, the sample regions prepared with varying levels of In, Ag, Zn, and Pb were analyzed with five line scans (each 6 mm in length) on each standard. The ICP-MS parameters are shown in Table 1.

Measurements of sulfur in Kapton® samples were carried out in reaction mode to overcome spectral interferences. Using oxygen as reaction gas, sulfur was determined as $^{32}\text{S}^{16}\text{O}$ at m/z 48 and carbon as a marker for the ablated polymer mass as $^{13}\text{C}^{16}\text{O}$ at m/z 29. Before the analysis, the mass spectrometer was tuned for a maximum signal at m/z 48 while measuring the native Kapton® film with a laser pulse frequency of 200 Hz. For analysis of calibration standards, each concentration level was measured using 20 individual spots. Measurements were performed in burst mode, enabling a complete penetration of the polymer film in approximately 2 s, resulting in one transient signal per sample location. A sample location without any added standard was used for blank measurements. The laser fluence of 1 J/cm^2 was below the ablation threshold of the silicon wafer to ensure no contribution of the substrate to the m/z 29 signal. The multielement calibration of Zn, Ag, In, and Pb on Kapton® was performed using the same laser ablation procedure as for the sulfur determination, but the ICP-MS parameters as for the spray standards on different substrates (Table 1) with additional acquiring ^{13}C

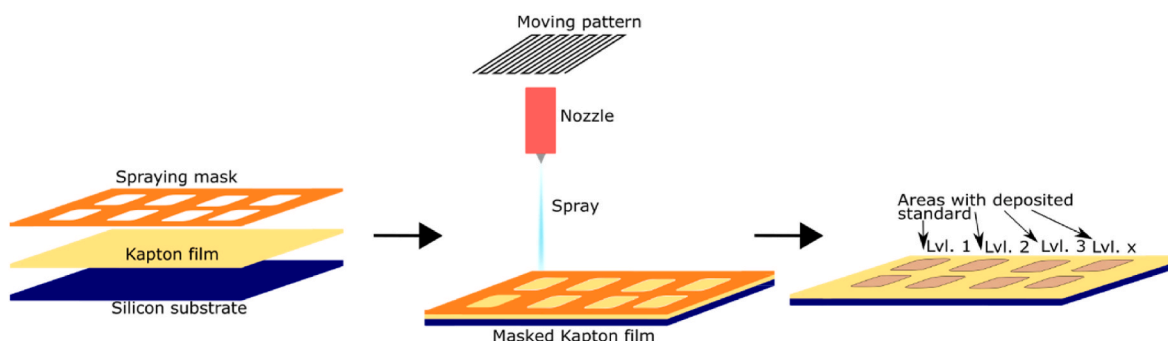


Fig. 1. Schematic depiction of the standard preparation via spray application on Kapton®.

Table 1
LA-ICP-MS instrumental parameters.

ICP-MS		
Plasma power	1,400 W	
Auxiliary gas flow rate	0.8 l/min (Ar)	
Cooling gas flow rate	13.8 l/min (Ar)	
Make-up gas flow rate	0.8 ml/min (Ar)	
Experiment	Spray standards on different materials	Kapton® sulfur spray standard calibration
Measurement mode	Standard	Reaction
Reaction gas flow rate	–	3 ml/min (10% O ₂ /He)
Measured isotopes	⁶⁶ Zn, ¹⁰⁹ Ag, ¹¹⁵ In, ²⁰⁸ Pb, ¹⁵³ Eu	(¹³ C ¹⁶ O), (³² S ¹⁶ O), ¹⁵³ Eu
Dwell times	10 ms for all isotopes	10 ms (29, 153), 20 ms (48)
LA		
Experiment	Spray standards on different materials	Spray standard calibration
Scan type	Line scan	Spot scan
Spot size	40 μm (square shape)	200 μm (circular shape)
Sample fluence	1.0 J/cm ²	1.0 J/cm ²
Repetition rate	50 Hz	40 Hz

for normalization. For evaluation, the obtained transient signals of each spot were integrated using the software OriginPro 2022 (version 9.9.0.225, OriginLab Corp.). The measurement was repeated at five different locations. Instrumental parameters are shown in Table 1.

2.5. Microwave-assisted acid digestion and liquid ICP-MS measurements

For conventional liquid ICP-MS analysis, the samples were converted into measurement solutions by performing microwave-assisted acid digestion and subsequent sample dilution. The digestion was performed with a “Multiwave 5000” with “20SVT50” rotor and PTFE-TFM vessels by Anton Paar GmbH (Graz, Austria), using a mixture of 2.85 ml of concentrated nitric acid (EMSURE®, p. a., MERK) and 0.15 ml of 30% hydrogen peroxide (Suprapur®, p. a., MERK). The digestion routine consisted of a linear heating ramp from 20 °C to 185 °C in 25 min, followed by a holding time of 20 min at 185 °C and a final cooling step down to 60 °C at the maximum rate. After digestion, the content of each vessel was transferred into a 15 ml centrifuge vial. Each digestion vessel was rinsed with 2 ml of MilliQ water, and the wash solution was added to the centrifuge vials. The vials were then filled to 15 ml with MilliQ water, resulting in pre-diluted sample solutions.

To determine the area-specific deposited mass of the spraying method, the silicon wafers with indium standard applied to the surface were used for digestion. Since the used digestion reagents deliberately did not contain any hydrofluoric acid, only the deposited standard residues were digested and transferred into the solution, while the silicon wafers remained unaffected. For analysis, the obtained sample solutions were further diluted with MilliQ water by a factor of 20 and spiked with gadolinium, resulting in solutions containing 1% HNO₃ and 1 ng/g Gd as internal standard. External calibration standards were prepared using indium ICP standard diluted with 1% HNO₃ and addition of Gd as internal standard, resulting in calibration standards with levels of 0.1, 0.5, 2, and 10 ng/g In, and 1 ng/g Gd.

For the reference measurement of the bulk concentrations of the Kapton® film, twelve replicates, with a sample intake of 50 mg Kapton® each, were used for digestion. Before ICP-MS analysis, the pre-diluted sample solutions were further diluted with MilliQ water by a factor of two and spiked with gadolinium ICP-MS standard, resulting in measurement solutions containing 10% HNO₃ and 1 ng/g Gd. For the sulfur determination in reaction mode, external calibration standards were prepared using sulfur ICP-MS standard diluted with 10% HNO₃ adding

again Gd as internal standard. For the determination of Zn, Ag, In, and Pb in standard measurement mode, the named single-element ICP-MS standards were combined into a multielement stock solution and diluted, analogous to the sulfur standards.

For liquid ICP-MS measurements, the instrument was tuned daily to a maximum ¹¹⁵In signal intensity using the instrument tuning solution from ThermoFisher Scientific. Sample introduction was carried out with a self-aspirating PFA nebulizer from Elemental Scientific Inc. (Omaha, NE, USA), providing a sample intake of 400 μl/min. For the coverage determination of the spraying method, the external indium standards and sample solutions were measured conventionally in standard mode by acquiring ¹¹⁵In and ¹⁵⁷Gd signals with dwell times of 10 ms. The nebulizer gas flow rate was 1.0 l/min for all liquid ICP-MS measurements. Analysis of zinc, silver, indium, and lead standards, as well as of the Kapton® sample solutions, was performed using the same remaining instrumental parameters as shown in Table 1. To determine the sulfur content of the Kapton® films, the prepared sulfur standards, and the sample solutions were measured in reaction mode with a reaction gas flow rate of 3 ml/min (10% O₂/He) after tuning the instrument for a maximum signal at an *m/z* of 48 (³²S¹⁶O) using a 100 ng/g sulfur ICP-MS standard. The dwell times were 20 ms for *m/z* 48 and 10 ms for *m/z* 157. The remaining instrumental parameters were the same as with the LA-ICP-MS measurements (Table 1).

3. Results and discussion

3.1. Method development and optimization

In the first step, the spraying standard solution composition and the parameters of the spraying instrument were optimized. The primary goal was a satisfying thin layer deposition regarding adhesion and homogeneity. This was achieved by varying the organic solvent content and the content of PEG, the latter facilitating film formation and inhibiting inhomogeneous crystal formation and aggregation. The solutions were applied to the Kapton® polymer surface, varying the spraying instrument's flow rate, nozzle temperature, nozzle velocity, and line distance of the nozzle moving pattern. The dried residues were studied by optical microscopy using a VHX 5000 from Keyence (Mechelen, Belgium) and measured with LA-ICP-MS to evaluate the homogeneity of the deposited residues.

To investigate the applicability of the optimized spraying method regarding various target elements and other substrate materials, standards containing levels of 0.01–25 μg/g of Zn, Ag, In, Pb, and 5 μg/g Eu were sprayed onto silicon, silicon carbide, copper, aluminum and glass. To indicate the variant characteristic of the residual film deposited on different materials, which could be observed on the microscopic images, 1.5 × 1.5 mm² LA-ICP-MS maps were measured on the substrates silicon and glass with 5 μg/g of all elements in the applied spraying solution. The elemental maps were co-registered and fused with the previously recorded microscopic images using the software ImageLab (version 4.21, Epina GmbH), resulting in the hyperspectral images shown in Fig. 2. The intensities of ¹⁵³Eu (internal standard) are displayed in blue. It can be observed that the deposited film on Si is more uniform, with some locations where no standard residues are present, whereas, on glass, the residues are shaped in the form of separated islets.

To test the homogeneity of the standards on both substrates, the images (150 × 150 pixels) were sub-divided into ten equally sized horizontal stripes, and the ¹⁵³Eu-normalized intensities of the measured elements in the resulting groups were compared with a one-way ANOVA. With a significance level of 0.05, the null hypothesis cannot be rejected, indicating no significant difference between the group means and, thus, a homogeneous distribution of the standard residues by the applied spraying procedure. Each ANOVA group is equivalent to a measured area of 0.225 mm². Therefore, sampling an area of at least that size should be representative of the respective standard concentration with the present standard homogeneity. This implies that despite the

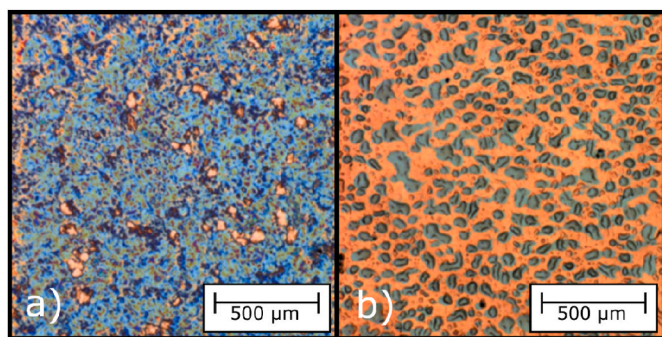


Fig. 2. Hyperspectral images of silicon (a) and glass (b) after spray deposition of standards. ^{153}Eu signal intensities above a threshold of 10^5 cps are overlaid in blue.

different behavior in the shaping of the residues during the rapid drying of the solvent on different materials, a reliable and reproducible calibration can be achieved simply by sampling a sufficiently large area by either using multiple spot measurements or line scans.

3.2. Determination of absolute analyte mass in fabricated standards

The $10 \times 10 \text{ mm}^2$ silicon wafer pieces, which were spray coated using a $10 \mu\text{g/g}$ indium spraying standard solution with optimized conditions solely to an unmasked area of 45.86 mm^2 , were digested and analyzed for their indium content using conventional liquid ICP-MS. Derived findings were used to calculate the masses of each element deposited per area as a function of the concentration in the applied standard solution. The determination of indium resulted in an absolute mass of $19.2 \pm 0.4 \text{ ng}$ per sample. Consequently, the deposited mass of In after spraying a standard solution with $10 \mu\text{g/g}$ is equivalent to $418 \pm 9 \text{ pg/mm}^2$. For all the other sprayed standards, the absolute mass of each added element per area is calculated by multiplication of $41.8 \pm 0.9 \text{ pg/mm}^2$ with the respective concentration in the applied standard solution in $\mu\text{g/g}$.

Hence, the calculated coverage of the multielement standards on different substrates corresponds to approximately 418 fg/mm^2 for the lowest concentrated solution (10 ng/g) and 1.045 ng/mm^2 for the highest ($25 \mu\text{g/g}$). For the fabricated standards on Kapton®, the applied solution concentrations from 10 to $150 \mu\text{g/g}$ of sulfur correspond to a coverage of 0.41 – 6.27 ng/mm^2 . For zinc, silver, indium, and lead, the applied solution concentrations from 0.01 to $25 \mu\text{g/g}$ correspond to a coverage of 418 fg/mm^2 – 1.04 ng/mm^2 for each of the individual elements.

3.3. LA-ICP-MS calibration of the multielement standards on different substrates

The average intensities for In, Ag, Zn, and Pb of five line scans (6 mm) on each standard show an excellent linear correlation with the concentration of the applied standard solution on all investigated substrates. Correlation coefficients go from $R^2 = 0.994$ to 0.99999 with F -values from 1495 to $645,961$, with one exception for Zn on the substrate aluminum ($R^2 = 0.973$, $F = 251$). These results provide evidence for the applicability of the spraying deposition method for multielement calibration over more than three orders of magnitude on different sample materials. As a prerequisite for the presented approach, it was assumed that by using constant spraying parameters, the deposited mass of the target element per area is directly proportional to its concentration in the applied solution, provided that the concentration is negligibly low compared to the main solution constituent (50 mg/g PEG). This was now confirmed by the calibrations measured for In, Ag, Zn, and Pb on various substrates with deposited analyte masses going as low as 418 fg/mm^2 (10 ng/g in applied solution), where a single line scan (0.3 mm^2 ablated

area) corresponds to a sampled mass of 125.4 fg . Relative standard deviations between 5 repetitive line scans were from 0.5 to 5% for concentrations higher than $0.5 \mu\text{g/g}$ (in applied solution) and 1 – 10% for concentrations from 10 to 500 ng/g (in applied solution). A quintuplicate measurement of one standard only took 30 s , corresponding to a sampled area of 1.5 mm^2 . This is beneficial compared to conventional dried droplet ablation, which requires total ablation of the area of the droplet, which can be up to 20 mm^2 and more, for only one replicate. Further, each standard can be reused multiple times, which is a considerable advantage, as LA-ICP-MS requires calibration for each analysis and after regular time intervals.

Table 2 shows the slopes of the calibration functions and the limit of detection (LOD) calculated as the absolute mass required for detection normalized to one mm^2 . The LODs were calculated using the calibration approach and reach from 0.17 fg/mm^2 (In on glass substrate) to 8.7 fg/mm^2 (Zn on Al substrate). The variation of the slopes of each element on the different substrates (i.e., matrices) indicates differences in the sensitivity, which derive from matrix effects in ablation, transport, and ionization efficiency. Blank measurements indicated the presence of Zn and Pb in the glass and the aluminum substrate and the presence of Ag in the copper substrate. In contrast, in silicon and silicon carbide, which are ultrapure materials in semiconductor manufacturing quality, none of the measured elements could be detected in the blank substrates.

The results in this chapter demonstrate the general applicability of the spraying procedure on different material types. For quantitative analysis resulting in concentration values, the ablated sample mass or the analyzed volume must be known or determined, which is demonstrated for the Kapton® film in chapter 3.4.

3.4. Quantification of selected trace elements in Kapton® and method validation

Each ablation event completely penetrated the Kapton® film. Therefore, the sample mass ablated with each spot is calculated from the diameter of the laser spot ($200 \mu\text{m}$), the material density (1.38 g/cm^3), and the film thickness ($13 \mu\text{m}$). The deposited masses of sulfur, zinc, silver, indium, and lead for each ablation event and each standard level were calculated from the laser spot area, the area-specific mass deposition, and the respective concentrations in the applied solutions. The resulting standard addition levels are listed in Table 3. The measured signal intensities accountable to each element are generated from the native content of the Kapton® film plus the masses deposited on the surface of the respective standard level.

The transient signals of each ablation event were baseline subtracted and integrated. To account for the spot-to-spot variability, the obtained $^{32}\text{S}^{16}\text{O}$ signals of each measured spot were corrected with the internal standard signals of ^{153}Eu after previous blank correction. Subsequently, the signal derived from sulfur was normalized to the corresponding

Table 2

Slopes and LODs (5 measurements per concentration level) of Zn, Ag, In, and Pb on different substrate materials.

		Substrate material				
		Si	SiC	Cu	Al	Glass
Zn	Slope ^a	0.79	0.77	2.23	1.42	1.61
	LOD ^b	2.06	3.57	1.22	8.70	0.63
Ag	Slope ^a	8.00	7.74	7.70	10.48	11.29
	LOD ^b	1.93	2.97	2.39	2.09	0.49
In	Slope ^a	26.63	28.64	31.37	32.98	39.20
	LOD ^b	0.64	2.19	1.02	0.17	0.40
Pb	Slope ^a	26.82	29.37	32.23	29.91	38.47
	LOD ^b	1.22	0.61	0.60	1.09	1.26

^a In $10^3 \text{ cts}/(\text{fg/mm}^2)$.

^b Absolute mass required for detection in fg/mm^2 . Calculated according to the calibration approach from 3.3 times the standard error of the regression divided by the slope.

Table 3
Added concentrations of the prepared Kapton® standards.

Kapton® standard level ^a	Concentration in applied solutions [µg/g]	Added element masses per area	Additional concentration of resulting standard [µg/g] ^b
1	0.01	0.42 pg/mm	0.023
2	0.05	2.09 pg/mm	0.117
3	0.25	10.45 pg/mm	0.583
4	0.50	20.90 pg/mm	1.165
5	1.50	62.70 pg/mm	3.495
6	5.00	209.00 pg/mm	11.650
7	10.00	0.42 ng/mm	23.300
8	25.00	1.04 ng/mm	58.300
9	50.00	2.09 ng/mm	116.500
10	100.00	4.18 ng/mm	233.000
11	150.00	6.27 ng/mm	349.000

^a The standard levels 1 to 8 were measured for the determination of Zn, Ag, In, and Pb. For the determination of sulfur, the standard levels 7 to 11 were measured.

^b Calculated from absolute element masses in relation to the polymer mass (564 ng) ablated per spot burst measurement with an area of 0.0314 mm² and complete ablation of the 13 µm thick film with a density of 1.38 g/cm³. The calculated concentration is added additionally to the unknown native concentration of the Kapton® film.

¹³C¹⁶O signal, representing a marker of the amount of carbon ablated from the polymer. The linear regression of the received calibration points showed a correlation coefficient of $R^2 = 0.993$ ($F = 812$). Calculating the bulk concentration of the Kapton® film from the calibration function using the slope and the intercept, with the error derived from the slope error, results in 32.4 ± 1.2 µg/g of sulfur. Alternatively, by calculating it from the native Kapton® measurements and the slope of the calibration function, with the error representing the standard deviation of the 20 consecutive blank measurements, the bulk sulfur concentration of the Kapton® film is 35.5 ± 2.3 µg/g. The reached limit of detection of 0.116 µg/g is excellent compared to reported literature for the quantitative determination of sulfur via LA-ICP-MS (10–100 µg/g in glasses, minerals, and melt inclusions [38,39]). To the best of the author's knowledge, no LOD for the determination of sulfur in polymers using laser ablation in combination with quadrupole ICP-MS has been reported so far.

The results were verified by applying sample digestion and liquid ICP-MS determination of sulfur in the Kapton® film as a reference method. The average sulfur concentration in 12 diluted sample digests resulted in 43.7 ± 3.6 ng/g, being well above the limit of quantification (6.3 ng/g) calculated from ten times the standard deviation of 10 blank measurements divided by the slope of the external calibration curve. After accounting for the sample intake and the dilution by the digestion reagents and MilliQ water prior to the measurement of each sample, the average sulfur concentration of the Kapton® film was 31.6 ± 2.0 µg/g. This result is in good agreement with the results derived from LA-ICP-MS using the newly developed spray standard addition method for quantification. To statistically support this statement, the uncertainty was calculated for both determination methods by multiplying the standard deviation with the respective factor of the student t distribution for a 95% confidence level, $n = 20$ for the LA method ($t = 2.09$) and $n = 12$ for the reference method ($t = 2.20$). The resulting average values and uncertainties of 35.5 ± 4.7 and 31.6 ± 4.1 overlap. Therefore, the values cannot be significantly distinguished. This provides proof of concept for the developed method and confident evidence of validity and reliability through agreement with the results of a well-established reference method.

The transient signals of Zn, Ag, In, and Pb were determined in a second analysis in standard measurement mode. The evaluation was analogous to sulfur, including Eu correction and normalization to carbon. The measurements of the fabricated standards resulted in an

excellent linear signal response with the concentration of the respective standard. The received calibration functions had correlation coefficients from $R^2 = 0.996$ to 0.999 ($F = 1563$ to 14,810). Table 4 shows the calculated LODs, and the determined concentrations in the blank Kapton® film. No signals for Zn, Ag and In could be measured in the blank Kapton® film, indicating the absence of measurable amounts of these elements. For Pb, it was observed that no signal was detected at most measured spots, whereas some delivered comparably higher Pb signals. Therefore, 180 additional spots were measured and included in the evaluation of Pb. Of the total of 200 measured spots, 112 spots delivered signals below the limit of detection (0.023 µg/g), while the maximum value was as high as 0.943 µg/g. This indicates a highly inhomogeneous distribution of Pb in the Kapton® film, which is also reflected in the relative standard deviation of 183%.

For liquid ICP-MS reference measurements of Zn, Ag, In, and Pb, the solutions of the digested samples and external calibration standards were also measured in a second run in standard measurement mode. The obtained results match those acquired using LA-ICP-MS, regarding that the signals for Zn, Ag, and In in the digested sample solutions were not different from those of the acid blank measurements (10% HNO₃). Results for Pb show a substantial variation between the digested samples, ranging from 0.063 to 1.499 µg/g with an RSD of 76% ($n = 12$). Contamination during the sample digestion and dilution can be excluded, as the procedure was additionally performed with acid blanks, which consistently resulted in values below the limit of detection in the ICP-MS analysis. Since the RSDs of repeated measurement of the same digested sample ($n = 3$) were below 1.5% for each element, it is indicated that the variations in the Pb concentration are derived from the sample's contents rather than from contamination or errors in the measurement. To further investigate the strong scattering and inconsistent results for Pb of the LA-ICP-MS method (0.056 ± 0.103 µg/g) and the reference method (0.726 ± 0.553 µg/g), the distribution of Pb was analyzed by measuring four large elemental mappings on the blank Kapton® film via LA-ICP-MS. For each image, an area of 2×2 mm² was measured using a 50×50 µm² square-shaped spot with 97% overlapping shots, a fluence of 1.5 J/cm², 200 Hz repetition rate, and ICP-MS parameters as used for the spot measurements of the standards via LA-ICP-MS (Table 1). The chosen overlap enabled nearly complete penetration of the Kapton® film during the measurement. Therefore, the concentrations obtained for each pixel can be considered good estimates for the locally occurring bulk content. Fig. 3 shows the derived distribution images, indicating that most of the area contains Pb concentrations lower than the LOD (0.023 µg/g). In contrast, "hot spots" of Pb with concentrations of approximately 0.5 µg/g and higher occur irregularly. The visualization in Fig. 3 confirms the inhomogeneous distributions of Pb in the Kapton® film, which was already suggested after the evaluation of the LA-ICP-MS spot measurements and the reference measurements of the digested samples. Compared to the sample mass that was used for one sample digestion (50 mg), the calculated total sampled mass of all four images of approximately 290 µg is more than a factor of 170 less, and thus still not sufficient for the determination of representative bulk contents. For these reasons, no match of the results of the developed LA-ICP-MS method and the reference method can be achieved for the determined Pb bulk concentration.

The shown results of the different lead determination methods

Table 4
LODs and determined concentrations ($n = 20$) of selected trace elements in Kapton®.

	S ¹	Zn	Ag	In	Pb
LOD ^a [µg/g]	0.126	0.050	0.083	0.046	0.023
c _{blank} [µg/g]	35.5 ± 2.3	< LOD	< LOD	< LOD	0.056 ± 0.103 ^b

^a Calculated according to the calibration approach from 3.3 times the standard error of the regression divided by the slope.

^b Average over 200 measured spots.

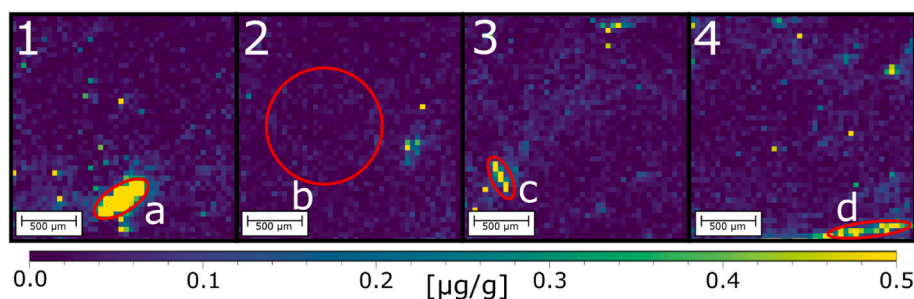


Fig. 3. Elemental mapping of Pb in Kapton®. Each of the four images corresponds to an area of 4 mm². The average Pb concentrations of the regions that are marked with red circles were calculated as 2.399 µg/g (a), < LOD (b), 0.495 µg/g (c), and 0.304 µg/g (d).

demonstrate that a homogeneous distribution of the element of interest in the analyzed sample is crucial when determining the bulk concentration is desired, and a spatially resolved technique such as LA-ICP-MS is applied. This was verified in the case of homogeneously distributed sulfur, where the developed method and the reference method delivered well-agreeing results, and in the case of inhomogeneously distributed lead, where no satisfying agreement could be received. Nevertheless, the proposed approach allows quantitatively assessing the Pb distribution in the analyzed Kapton® film – information that is not accessible with conventional liquid sample analysis.

3.5. Application: quantitative sulfur depth profile of a weathered Kapton® film

As polymers are known to have a finite permeability for gases [40], an uptake of SO₂ is expected as a consequence of the weathering experiment. Conventional digestion and liquid analysis of this sample would deliver only bulk information. Aside from that, it is also possible that measured concentrations would be below the limit of quantification if the absorbed amount were too low when averaged to the total sample mass. To emphasize a main advantage of LA-ICP-MS, which is the capability of spatially resolved analysis, the developed quantification strategy was applied to perform quantitative depth-resolved measurements of a weathered Kapton® film. The depth profile was recorded using repetitive line scans (6 mm) with a 40 × 40 µm² square-shaped spot, 75% overlapping shots, 200 Hz repetition rate, and a slightly increased laser fluence of 1.5 J/cm². ICP-MS parameters were analogous to the sulfur calibration (Table 1). Fig. 4 shows the results of the

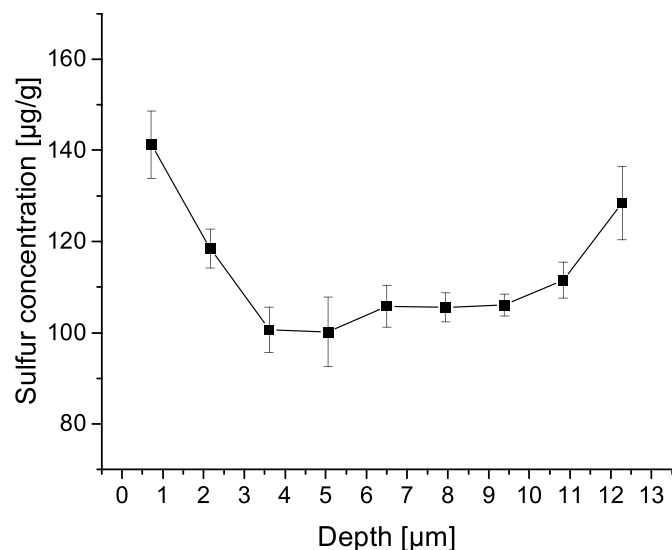


Fig. 4. Depth profile of the sulfur concentration of the weathered Kapton® film.

measurements, with each data point representing the average concentration of the respective ablation layer at five different sample locations and the standard deviation of the five measurements displayed as error bars. The quantification was performed using integrated sulfur signals (³²S¹⁶O) normalized to carbon signals (¹³C¹⁶O) for each line scan. For calibration, the native Kapton® film with the deposited sulfur standard was used the way described in section 3.4. As carbon is a main constituent of the polymer backbone, it can be assumed to be evenly distributed within the polymer, and the measured signal is representative of the ablated sample mass. Thus, normalization to carbon enables the possibility to apply the calibration measured on bulk Kapton® for the quantification of a spatially resolved analysis. Crater depth measurements using a profile meter showed a linear relationship between the total ablation depth and the number of ablated layers in previous experiments with the 193 nm excimer laser (having a flat-top beam profile), up to a total ablation depth of more than 20 µm. Therefore, the ablation depth of the 9 layers until complete penetration of the 13 µm Kapton® film was assumed to be equal for each layer and calculated as 1.5 µm. As shown in Fig. 4, it can be observed that the sulfur concentration significantly increased compared to the previously determined bulk sulfur concentration of the native Kapton® film (35.5 ± 2.3 µg/g). The sulfur concentration is higher at the surfaces (120–140 µg/g) compared to the middle of the film, with approximately 100–110 µg/g sulfur. This depicts the uptake of SO₂ at the interface to the atmosphere and the diffusion of SO₂ into the polymer, driven by the concentration gradient, until an equilibrium would be reached.

The measured depth profile gives an example for investigations of the diffusion of gaseous species in polymers. Systematic weathering experiments with varying temperatures, relative humidity, gas concentration, and time of exposure will give insight into the polymer properties regarding the applicability as protective layers for corrosion-sensitive components. Studies similar to these also play an important role in packaging materials for, e.g., food [41] and other industrial or consumer products [42,43]. Quantitative depth profiles can further be used, e.g., to evaluate diffusion coefficients and compare the influence of various weathering conditions and the behavior of different materials to one another.

4. Conclusions

This work presents a new approach for the fabrication of matrix-matched standards required for quantitative LA-ICP-MS analysis of thin films or coatings. The procedure is based on the homogeneous deposition of a defined amount of standard on the sample surface. The derived thin layer is measured simultaneously with the underlying sample, enabling quantitative determination of the analyte contents in the sample on the principle of standard addition.

The method was applied to measure the native contents of S, Zn, Ag, In, and Pb in a commercial Kapton® polyimide film. The sulfur content of the polymer film was found to be homogeneously distributed with a mean value of 35.5 ± 2.3 µg/g, while no measurable content for zinc,

silver, and indium content could be detected. Method validation could be achieved by a reference determination using liquid ICP-MS analysis after sample digestion, showing well-agreeing results for sulfur. For lead, distinct deviations between individual sample measurements and, thus, high relative standard deviations were observed for both methods. Further investigation confirmed the inhomogeneous distribution of lead in the Kapton® film, which was concentrated in irregularly occurring hot spots. Thus, the determination of a representative bulk content was not possible with the developed LA-ICP-MS procedure. However, valuable information about the occurring concentration ranges of Pb in the Kapton® film could be obtained.

The method shows great potential for universal applicability to other materials. It was demonstrated that multielement calibration is feasible on different materials and that a homogeneous deposition of the standard residues can be achieved. A sufficiently large sprayed area can be used multiple times for calibration. Generally speaking, the suitability of the proposed procedure is not limited to polymer analysis, and the method can also be applied to other scientific questions where spatially resolved and quantitative analysis is required, e.g., in material science, life sciences, or geology.

Compared to matrix-matched standard preparation via pressing of pellets, an advantage is that no powdered samples are required. Thus, related consequences such as pressability and insufficient pellet stability or homogeneity are not limiting. Nevertheless, there are certain requirements and limitations. As with dried droplet quantification, it is mandatory to determine the mass of ablated sample to calculate the concentration of the standard. In this work, this is achieved by complete penetration of the Kapton® film with a known thickness and density, as previously reported in other work [44]. Without a known film thickness but a known material density, the ablated sample mass can be derived from the ablation volume after measuring the depth of the obtained ablation craters. It would also be possible to achieve absolute quantification if a homogeneously distributed main or minor constituent with known concentration is present in the sample of interest, using the respective signal for normalization.

Credit author statement

Jakob Willner: Conceptualization, Methodology, Investigation, Writing – Original Draft, Writing – Review and Editing, Visualization, Validation, Formal analysis. Lukas Brunnbauer: Conceptualization, Methodology. Silvia Larisegger: Conceptualization, Funding acquisition. Michael Nelhiebel: Conceptualization, Funding acquisition. Martina Marchetti-Deschmann: Resources. Andreas Limbeck: Conceptualization, Methodology, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- [1] J.C.J. Bart, *ADDITIVES IN POLYMERS Industrial Analysis and Applications*, John Wiley & Sons, Ltd, 2005.
- [2] V. Marturano, P. Cerruti, V. Ambrogio, *Polymer additives*, *Phys. Sci. Rev. 2* (2019), https://doi.org/10.1515/PSR-2016-0130/ASSET/GRAPHIC/J_PSR-2016-0130_FIG_013.JPG.
- [3] A. Turner, M. Filella, *Hazardous metal additives in plastics and their environmental impacts*, *Environ. Int.* 156 (2021), 106622, <https://doi.org/10.1016/j.envint.2021.106622>.
- [4] R. Javed, L.A. Shah, M. Sayed, M.S. Khan, *Uptake of heavy metal ions from aqueous media by hydrogels and their conversion to nanoparticles for generation of a catalyst system: two-fold application study*, *RSC Adv.* 8 (2018) 14787–14797, <https://doi.org/10.1039/C8RA00578H>.
- [5] C.M. Rochman, *Plastics and priority pollutants: a multiple stressor in aquatic habitats*, *Environ. Sci. Technol.* 47 (2013) 2439–2440, <https://doi.org/10.1021/ES400748B>.
- [6] H. Moeller, *Progress in Polymer Degradation and Stability Research*, 2008 (accessed March 7, 2022), https://books.google.at/books?hl=de&lr=&id=Xh2x1-50VeYC&oi=fnd&pg=PR7&dq=polymer+degradation+and+stability&ots=h2ZyHJzT92&sig=mUx-PbqZwXvtZH_1eWxBlwkwHi8.
- [7] G. Akovali, *Polymers in Construction*, Rapra Technology Limited, Shawbury, 2005.
- [8] H. Sasajima, I. Watanabe, M. Takamoto, K. Dakede, S. Itoh, Y. Nishitani, J. Tabei, T. Mori, *Materials for Advanced Packaging*, Springer International Publishing, Cham, 2017, https://doi.org/10.1007/978-3-319-45098-8_1.
- [9] J.J. Licari, *Functions and requirements of coatings for electronic applications*, *Coat. Mater. Electron. Appl.* (2003) 1–63, <https://doi.org/10.1016/B978-081551492-3.50003-9>.
- [10] C.P. Wong, *Application of polymer in encapsulation of electronic parts*, *Electron. Appl.* (2005) 63–83, <https://doi.org/10.1007/BFB0025903>.
- [11] J.S.F. Pereira, C.L. Knorr, L.S.F. Pereira, D.P. Moraes, J.N.G. Paniz, E.M.M. Flores, G. Knapp, *Evaluation of sample preparation methods for polymer digestion and trace elements determination by ICPMS and ICP-OES*, *J. Anal. At. Spectrom.* 26 (2011) 1849–1857, <https://doi.org/10.1039/C1JA10050E>.
- [12] E.M.M. Flores, E.I. Müller, F.A. Duarte, P. Grinberg, R.E. Sturgeon, *Determination of trace elements in fluoropolymers after microwave-induced combustion (JPEG)*, *Anal. Chem.* 85 (2013) 374–380, https://doi.org/10.1021/AC3029213/ASSET/IMAGES/LARGE/AC-2012-029213_0003.
- [13] P.J. Sylvester, S.E. Jackson, *A brief history of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)*, *Elements* 12 (2016) 307–310, <https://doi.org/10.2113/gselements.12.5.307>.
- [14] A. Limbeck, P. Galler, M. Bonta, G. Bauer, W. Nischkauer, F. Vanhaecke, *Recent advances in quantitative LA-ICP-MS analysis: challenges and solutions in the life sciences and environmental chemistry ABC Highlights: authored by Rising Stars and Top Experts*, *Anal. Bioanal. Chem.* 407 (2015) 6593–6617, <https://doi.org/10.1007/s00216-015-8858-0>.
- [15] R.E. Russo, X. Mao, O.V. Borisov, *Laser ablation sampling*, *TrAC, Trends Anal. Chem.* 17 (1998) 461–469, [https://doi.org/10.1016/S0165-9936\(98\)00047-8](https://doi.org/10.1016/S0165-9936(98)00047-8).
- [16] D. Günther, B. Hattendorf, *Solid sample analysis using laser ablation inductively coupled plasma mass spectrometry*, *TrAC, Trends Anal. Chem.* 24 (2005) 255–265, <https://doi.org/10.1016/J.TRAC.2004.11.017>.
- [17] S.F. Durrant, *Laser ablation inductively coupled plasma mass spectrometry: achievements, problems, prospects*, *J. Anal. At. Spectrom.* 14 (1999) 1385–1403, <https://doi.org/10.1039/A901765H>.
- [18] S. Sindern, *Analysis of rare earth elements in rock and mineral samples by ICP-MS and LA-ICP-MS*, *Phys. Sci. Rev. 2* (2017), https://doi.org/10.1515/PSR-2016-0066/ASSET/GRAPHIC/J_PSR-2016-0066_FIG_004.JPG.
- [19] A. Sussulini, J.S. Becker, J.S. Becker, *Laser ablation ICP-MS: application in biomedical research*, *Mass Spectrom. Rev.* 36 (2017) 47–57, <https://doi.org/10.1002/MAS.21481>.
- [20] A. Limbeck, M. Bonta, W. Nischkauer, *Improvements in the direct analysis of advanced materials using ICP-based measurement techniques*, *J. Anal. At. Spectrom.* 32 (2017) 212–232, <https://doi.org/10.1039/C6JA00335D>.
- [21] M. Voss, M.A.G. Nunes, G. Corazza, E.M.M. Flores, E.I. Müller, V.L. Dressler, *A new approach to calibration and determination of selected trace elements in food contact polymers by LA-ICP-MS*, *Talanta* 170 (2017) 488–495, <https://doi.org/10.1016/j.talanta.2017.04.048>.
- [22] Á. Villaseñor, M. Bocconcelli, J.L. Todolí, *Quantitative elemental analysis of polymers through laser ablation – inductively coupled plasma by using a dried droplet calibration approach*, *DDCA, J. Anal. At. Spectrom.* 33 (2018) 1173–1183, <https://doi.org/10.1039/C8JA00055G>.
- [23] Á. Villaseñor, R. Sánchez, M. Bocconcelli, J.L. Todolí, *Localized quantitative analysis of polymeric films through laser ablation–inductively coupled plasma mass spectrometry*, *Polymers* 13 (2021) 345, <https://doi.org/10.3390/POLY13030345>.
- [24] M. Bonta, A. Limbeck, *Metal analysis in polymers using tandem LA-ICP-MS/LIBS: eliminating matrix effects using multivariate calibration*, *J. Anal. At. Spectrom.* 33 (2018) 1631–1637, <https://doi.org/10.1039/c8ja00161h>.

- [25] D. Günther, C.A. Heinrich, Comparison of the ablation behaviour of 266 nm Nd: YAG and 193 nm ArF excimer lasers for LA-ICP-MS analysis, *J. Anal. At. Spectrom.* 14 (1999) 1369–1374, <https://doi.org/10.1039/A901649J>.
- [26] I. Krosalakova, D. Günther, Elemental fractionation in laser ablation-inductively coupled plasma-mass spectrometry: evidence for mass load induced matrix effects in the ICP during ablation of a silicate glass, *J. Anal. At. Spectrom.* 22 (2006) 51–62, <https://doi.org/10.1039/B606522H>.
- [27] J. Fietzke, M. Frische, Experimental evaluation of elemental behavior during LA-ICP-MS: influences of plasma conditions and limits of plasma robustness, *J. Anal. At. Spectrom.* 31 (2015) 234–244, <https://doi.org/10.1039/C5JA00253B>.
- [28] L. Brunnbauer, J. Gonzalez, H. Lohninger, J. Bode, C. Vogt, M. Nelhiebel, S. Larissegger, A. Limbeck, Strategies for trace metal quantification in polymer samples with an unknown matrix using Laser-Induced Breakdown Spectroscopy, *Spectrochim. Acta Part B At. Spectrosc.* 183 (2021), 106272, <https://doi.org/10.1016/J.SAB.2021.106272>.
- [29] P.K. Diwakar, S.S. Harilal, N.L. Lahaye, A. Hassanein, P. Kulkarni, The influence of laser pulse duration and energy on ICP-MS signal intensity, elemental fractionation, and particle size distribution in NIR fs-LA-ICP-MS, *J. Anal. At. Spectrom.* 28 (2013) 1420–1429, <https://doi.org/10.1039/C3JA50088H>.
- [30] N. Miliszkiewicz, S. Walas, A. Tobiasz, Current approaches to calibration of LA-ICP-MS analysis, *J. Anal. At. Spectrom.* 30 (2015) 327–338, <https://doi.org/10.1039/C4JA00325J>.
- [31] D.J. Sinclair, L.P.J. Kinsley, M.T. McCulloch, High resolution analysis of trace elements in corals by laser ablation ICP-MS, *Geochem. Cosmochim. Acta* 62 (1998) 1889–1901, [https://doi.org/10.1016/S0016-7037\(98\)00112-4](https://doi.org/10.1016/S0016-7037(98)00112-4).
- [32] W.T. Perkins, R. Fuge, N.J.G. Pearce, Quantitative analysis of trace elements in carbonates using laser ablation inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 6 (1991) 445–449, <https://doi.org/10.1039/JA9910600445>.
- [33] A.J. Fitzpatrick, T. Kurtis Kyser, D. Chipley, D. Beauchemin, Fabrication of solid calibration standards by a sol-gel process and use in laser ablation ICPMS, *J. Anal. At. Spectrom.* 23 (2008) 244–248, <https://doi.org/10.1039/B712366C>.
- [34] J. Lin, Y. Liu, Y. Yang, Z. Hu, Calibration and correction of LA-ICP-MS and LA-MC-ICP-MS analyses for element contents and isotopic ratios, *Solid Earth Sci* 1 (2016) 5–27, <https://doi.org/10.1016/J.SESCI.2016.04.002>.
- [35] F. Kuczelinis, J.H. Petersen, P. Weis, N.H. Bings, Calibration of LA-ICP-MS via standard addition using dried picoliter droplets, *J. Anal. At. Spectrom.* 35 (2020) 1922–1931, <https://doi.org/10.1039/D0JA00184H>.
- [36] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A. Witten, Capillary flow as the cause of ring stains from dried liquid drops, 3896653. *Natalia* 389 (1997) (1997) 827–829, <https://doi.org/10.1038/39827>.
- [37] R.D. Deegan, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, T.A. Witten, Contact line deposits in an evaporating drop, *Phys. Rev. E* 62 (2000) 756, <https://doi.org/10.1103/PhysRevE.62.756>.
- [38] B. Rottier, A. Audétat, In-situ quantification of chlorine and sulfur in glasses, minerals and melt inclusions by LA-ICP-MS, *Chem. Geol.* 504 (2019) 1–13, <https://doi.org/10.1016/J.CHEMGEO.2018.11.012>.
- [39] M. Guillong, C. Latkoczy, J.H. Seo, D. Günther, C.A. Heinrich, Determination of sulfur in fluid inclusions by laser ablation ICP-MS, *J. Anal. At. Spectrom.* 23 (2008) 1581–1589, <https://doi.org/10.1039/B807383J>.
- [40] S.A. Stern, J.R. Fried, Permeability of polymers to gases and vapors, *Phys. Prop. Polym. Handb.* (2007) 1033–1047, https://doi.org/10.1007/978-0-387-69002-5_61.
- [41] M. Giacinti Baschetti, M. Minelli, Test methods for the characterization of gas and vapor permeability in polymers for food packaging application: a review, *Polym. Test.* 89 (2020), 106606, <https://doi.org/10.1016/J.POLYMERTESTING.2020.106606>.
- [42] A. Gerlach, W. Keller, J. Schulz, K. Schumacher, Gas permeability of adhesives and their application for hermetic packaging of microcomponents, *Microsyst. Technol.* 71 (7) (2001) 17–22, <https://doi.org/10.1007/S005420000056>.
- [43] N.S. Sangaj, V.C. Malshe, Permeability of polymers in protective organic coatings, *Prog. Org. Coating* 50 (2004) 28–39, <https://doi.org/10.1016/J.PORGCOAT.2003.09.015>.
- [44] F. Kuczelinis, J.H. Petersen, P. Weis, N.H. Bings, Calibration of LA-ICP-MS via standard addition using dried picoliter droplets, *J. Anal. At. Spectrom.* 35 (2020) 1922–1931, <https://doi.org/10.1039/D0JA00184H>.