



## Strategies for trace metal quantification in polymer samples with an unknown matrix using Laser-Induced Breakdown Spectroscopy

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### ABSTRACT

Providing unique advantages, laser-based analytical techniques such as LIBS have gained more and more popularity for quantitative elemental analysis in the last few years. However, to obtain reliable quantitative results, matrix-matched standards are required. A particular material of interest for quantitative trace metal analysis is synthetic polymers, which is among the most widely used materials in our modern world. As the exact composition of a polymer under investigation (polymer type and applied additives) is often not known, the selection of an appropriate matrix-matched standard is difficult. In this work, we investigate and assess different approaches for quantifying potassium in unknown polymer types or polymers with an unknown composition where matrix-matched standards cannot be employed. This is of great interest in the semiconductor industry where monitoring of mobile ions in applied polymers is crucial, and the composition of the polymer is often not known due to confidentiality. We use the unique capabilities of LIBS, providing adequate sensitivity for potassium, and additionally delivering polymer-specific emission signals. Two different multivariate approaches (Random Decision Forest classification combined with conventional univariate calibration and a Partial Least Squares model) are developed and applied. Therefore, an in-house prepared library of standards of 8 different polymer types (Acrylic, PAN, PI, PMMA, PSU, PVA, PVC and PVP) is prepared. The errors obtained from the multivariate approaches are compared with conventional matrix-matched as well as non-matrix-matched quantification. With our developed approaches, for some samples quantitative determination of potassium in the low  $\mu\text{g/g}$  range in unknown polymer types is achieved with a relative error less than 20% which is comparable to conventional matrix-matched quantification. For all other samples, relative errors in the range of 30%–90% are obtained, which offers a precision adequate for many applications. E.g. in the food-packaging- or semiconductor-industry in many cases it is sufficient to determine if the contamination level of a sample with an unknown matrix is below or above a certain threshold. In this case, the developed approach poses a significant improvement compared to non-matrix-matched quantification which often leads to deviations up to a factor 10 or more from the nominal concentration.

### 1. Introduction

Besides different physical properties such as hardness, strength, durability, and resilience, trace metal content is one of the most critical polymers' characteristics influencing their applications [1]. In the semiconductor industry, the employment of high purity materials, such as polymers, is crucial, as contaminants of mobile ions can affect

electronic devices' performance and lifetime [2,3]. In sectors such as the food packaging industry, the content of trace metals in the polymers used is monitored because of the possible migration of toxic species into the food [4,5]. Investigating trace metals in microplastics is also of significant interest as these contaminants may cause an additional ecological impact on exposed environments [6,7]. Therefore, the determination of trace metal contents in wide ranges of different

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polymer applications is of great interest and poses a challenge for analytical chemistry.

Conventional analytical approaches for the determination of the trace metal content in polymers include microwave-assisted digestion [8], dry ashing [9] or microwave-induced combustion [10] of the sample for conversion into solutions with subsequent liquid Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measurement [11]. All these approaches have in common an easier path to quantification based on the availability of certified liquid standards. Nevertheless, certain drawbacks must be considered: harsh and hazardous chemicals must be employed to ensure complete digestion of the sample, including manual sample handling which is laborious, time-consuming, and susceptible to contamination. When using digestion protocols to determine trace metal content in polymers, incomplete digestion or volatilization of analytes may underestimate the actual trace metal content. At the same time, contamination by manual sample handling may cause an overestimation. Additionally, the samples are usually diluted, limiting the analysis's sensitivity, and only bulk information is available.

For these reasons, direct solid sampling approaches such as X-ray fluorescence spectroscopy (XRF) to detect metal traces in polymers have recently been reported in the literature [12,13]. Laser-based techniques such as Laser-Induced Breakdown Spectroscopy (LIBS) [14,15] and Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry LA-ICP-MS [16–18] have also been applied successfully for metal analysis in polymers. These direct-solid sampling techniques all benefit from eliminating the sample preparation steps, thus reducing the chemicals and time required for the analysis. Additionally, the risk of contaminants is reduced significantly as less manual sample handling is required. Besides advantages regarding the lack of sample preparation, direct solid-sampling techniques can provide information about the spatial distribution in the form of images or depth profiles [19–21], which is not accessible with conventional liquid analysis.

Nevertheless, direct-solid sampling techniques come with one significant drawback: quantification is a challenging task. Due to matrix effects occurring during the measurement, matrix-matched standards are necessary to obtain reliable quantitative results [22–24]. Besides the availability of matrix-matched standards being limited for some materials, also information about the exact matrix of the sample under investigation is necessary for proper selection and application. The matrix-matched requirement is especially problematic for polymers. This type of material usually exhibits a wide variety of chemical structures and properties, such as optical absorption behavior, and hardness influencing the ablation process. Different additives, which are often used in the polymer industry to adjust material properties [25], can also lead to varying matrix-effects. When analyzing polymer samples used in industrial applications, due to confidentiality, often the exact sample composition (polymer type and applied additives) is not known. Additionally, in the field of microplastics analysis, information on the polymer type of individual particles is also not known a priori. Therefore, the selection of suitable matrix-matched standards is difficult, hampering quantification with conventional calibration approaches without prior comprehensive sample characterization.

In contrast to XRF and LA-ICP-MS, which are focused on conventional elemental analysis, LIBS provides not only information about the main constituents of the polymer (the elements C, H, O, N), but also characteristic molecular features (e.g. C<sub>2</sub> Swan band, CN violet band) from the organic material under investigation [26]. In the LIBS literature, the use of these molecular emission signals is widely reported for the classification and discrimination of polymers [27–29]. Other applications of LIBS signals originating from organic materials include e.g. characterization of degradation [30,31], or investigation of molecular structures [32,33]. In this work, we investigate a novel application of polymer-specific signals with the idea to circumvent the need for matrix-matched standards for quantitative analysis of trace metals in polymers.

The presented work focuses on demonstrating the advantages of LIBS

concerning quantifying the potassium content in unknown polymer types or polymers with an unknown composition using polymer-specific LIBS signals combined with multivariate statistics. Potassium was selected as the analyte of interest because the contamination of polymers with mobile ions is of great interest in the semiconductor industry [35,36]. Therefore, a library consisting of in-house prepared standards of 8 different polymer types was prepared, and broadband LIBS spectra were recorded. We applied and evaluated two different multivariate data evaluation strategies based on a Random Decision Forest (RDF) classification model and a Partial Least Squares (PLS) model. To assess the performance of the applied procedures, benchmarks are required. Therefore, conventional matrix-matched and non-matrix-matched quantification is evaluated.

## 2. Experimental

### 2.1. Chemicals

High-purity silicon wafers (n-doped) used as substrate materials were provided by Infineon Austria AG (Villach, Austria). Polyimide (PI) P84 in powder form (>98% purity) was obtained by HP Polymer GmbH (Lenzing, Austria). Polyacrylonitrile (PAN), Poly (methyl methacrylate) (PMMA), Polysulfone (PSU), Polyvinyl acetate (PVA), Polyvinyl chloride (PVC), and Polyvinyl pyrrolidone (PVP) in powder form were obtained from Arcos Organics, Geel, Belgium. Acrylic varnishes (TerraGloss UV) were obtained from ACTEGA Terra GmbH, Lehrte, Germany. Surface additives used for the preparation of acrylic standards were obtained from BYK-Gardner GmbH, Geretsried, Germany. Conostan, SPS Science, Quebec, Canada, provided oil-based standards for spiking acrylic varnish. A polyester film used as a substrate material for acrylic standards was obtained from BYK-Gardner GmbH, Geretsried, Germany. N-Methyl-2-pyrrolidone (NMP) with p.a. grade quality was obtained from Merck (Darmstadt, Germany). Potassium trifluoromethane sulfonate (98%) soluble in NMP used to prepare spiked solutions were acquired from Sigma-Aldrich, Buchs, Switzerland.

### 2.2. Preparation of polymer standards

For the preparation of PAN, PI, PMMA, PSU, PVA, PVC, and PVP standards, polymer powders were dissolved in NMP, obtaining solutions with concentrations ranging from 10 to 20 wt% depending on the polymer type. A stock solution for spiking was prepared by dissolving Potassium trifluoromethane sulfonate in NMP. Different concentration levels of K were prepared by diluting the prepared stock solutions using NMP. NMP standards were used to spike the prepared polymer solutions, and the obtained mixtures were thoroughly homogenized using a vortex mixer. Thin films of spiked polymer were prepared by applying 50 µl of the mixtures to cut high purity Si wafer with 10 mm × 10 mm using a pipette and cured at 80 °C for 12 h. The thickness of produced polymer thin films was 10 µm, determined by a Dektak XT Profilometer (Bruker Corporation, USA). A more detailed description of these standards' preparation is given by Bonta et al [14]

For acrylic standards, a 1:1 mixture of two different acrylic varnishes, varying in viscosity, was used. An anti-foaming agent and a surface additive were added. Potassium was added in the form of a certified oil-based standard. The mixture was dispersed thoroughly using an Ultra Turrax® by IKA Werke GmbH & CO. KG, Staufen, Germany. Thin films of varnish were applied onto a 100 µm thick polyester substrate with uniform layer thickness with the help of wire-wound rods and an automatic film applicator (Automatic Film Applicator S by BYK-Gardner GmbH, Geretsried, Germany). A layer thickness of 25 µm was chosen. The varnish was put into a UV-chamber (Dinies Technologies GmbH, Villingendorf, Germany) and hardened under UV-light for a few minutes. To prevent inhibition of the radical polymerization by oxygen, the UV-chamber was flushed with nitrogen.

Potassium concentrations of the prepared standards were in the

range of 0–70  $\mu\text{g/g}$ . For each polymer type, between 4 and 8 standards were prepared. A Table containing the concentration of each standard is provided in the supplementary material.

### 2.3. LIBS instrumentation and data evaluation

A LIBS system (Model J200) equipped with a 266 nm Nd: YAG laser by Applied Spectra, Inc. (West Sacramento, California) was used for LIBS measurements. The light emitted by the laser-induced plasma was collected and was transferred to a Czerny-Turner spectrometer covering a wavelength range from 186 to 1048 nm and detected using a CCD detector. Samples were placed in a sealed chamber mounted on an XY stage continuously flushed with Ar. Each polymer standard was analyzed using a pattern consisting of 10 parallel line scans with a total length of 1.8 mm. With a distance of 0.15 mm between each laser-shot, a total number of 120 spectra were recorded per standard. To improve signal-to-noise ratios and reduce the amount of data, sets of 6 shots were accumulated, resulting in 20 spectra per standard. The accumulated spectra were normalized to the Euclidean norm to reduce shot-to-shot variations which is commonly used in LIBS analysis [34]. This normalization approach reduced the Relative Standard Deviation (RSD) of the 20 LIBS spectra per standard on average from 11% to 7%. The RSD of the potassium signal of the standard with the highest nominal concentration for each polymer type was in a range of 7% (PVA) to 12% (PVC), confirming the homogeneity of the standards.

Each laser-shot was performed with a separation distance of 0.15 mm to the previous measurement, avoiding previous measurements' influences (cross-contamination). LIBS parameters (laser energy and gate delay) were optimized in preliminary experiments to fulfil three main requirements: no penetration of the polymer films, sufficient sensitivity to detect the standard with the lowest potassium concentration of each polymer type, and a high signal-to-base ratio of elemental and molecular emission signals originating from the polymer. The laser energy was optimized to a maximum value before penetration of any of the polymer films occurred to avoid the presence of signals originating from the substrate in the spectra which may cause problems in further multivariate data evaluation. The data acquisition starting time, or gate delay, was set to a compromised value between using a short gate delay (<1  $\mu\text{s}$ ), where atomic emission signals (e.g., K, C, H, O) usually show a higher signal-to-base ratio and a longer gate delay (>1  $\mu\text{s}$ ) where molecular emission signals (e.g., CN violet band, C<sub>2</sub> swan band) show a higher signal-to-base ratio and a more stable background is observed. A signal-to-base-ratio of at least 3 of the potassium signal at 766.49 nm was selected as a requirement for sufficient sensitivity and was achieved for all polymer standards. Used LIBS parameters are summarized in Table 1. Crater depths after LIBS measurements were measured using a Dektak XT Profilometer (Bruker Corporation, USA) and were used to determine ablation rates. LIBS data were collected using Axiom 2.0 software provided by the manufacturer. Univariate and multivariate data evaluation was carried out using Epina ImageLab 3.34 (Retz, Austria).

## 3. Results and discussion

In this work, different approaches for quantifying the potassium

**Table 1**  
LIBS parameters used for the analysis of polymer standards.

LIBS parameters	
Laser wavelength (nm)	266
Laser energy (mJ)	3.12
Spot size ( $\mu\text{m}$ )	100
Repetition rate (Hz)	10
Gate delay ( $\mu\text{s}$ )	1
Gate width (ms)	1.05
Atmosphere	Ar

content in unknown polymer types or polymers with an unknown composition are investigated and evaluated.

LIBS spectra were obtained from in-house prepared standards of 8 different investigated polymer types (Acrylic, PAN, PI, PMMA, PSU, PVA, PVC, and PVP) containing potassium levels in the range of 0–70  $\mu\text{g/g}$ . Fig. 1 shows an overview of the different data evaluation approaches followed in this work. In a first step, univariate calibration curves are calculated for all investigated polymer types. Errors obtained from matrix-matched quantification are calculated and used as a best-case benchmark. In a second step, quantification of unknown polymer types is considered where matrix-matched quantification is not feasible. Therefore, non-matrix-matched quantification is investigated where each of the investigated polymer types is evaluated using the univariate calibration functions of all remaining polymer types. Next, two multivariate data evaluation strategies are presented based on a Random Decision Forest (RDF) classification model and a Partial Least Squares (PLS) model where each investigated polymer type is considered as unknown one after the other. The idea behind the RDF approach is a matching of the unknown polymer type to the closest-matching polymer from the dataset to minimize the error from non-matrix-matched quantification. The PLS approach is based on building a statistical model estimating the potassium concentration using the LIBS data from the different polymer types.

### 3.1. Matrix-matched univariate calibrations

The first step in this study involved the performance evaluation of the classical univariate calibration approach for each polymer type. Therefore, the emission signal of potassium (766.14 nm - 766.90 nm) is integrated after normalization of the spectra to the Euclidean norm. A background correction was performed by averaging and subtracting the background signal at 765.60 nm - 766.04 nm and 767.01 nm - 767.55 nm next to the potassium emission line.

Univariate calibration models with correlation coefficients (R [2]) ranging from 0.971 (PAN) to 0.998 (PSU) are obtained for all polymer types confirming the applicability of the in-house prepared standards. Limits of quantification (LOQ) are determined for each polymer type according to DIN 32645 [37] and are in the range of 0.3  $\mu\text{g/g}$  (PSU) to 1.4  $\mu\text{g/g}$  (PMMA). The standard with the lowest potassium concentration of each polymer type is at least 4.3 times higher than the LOQ, also confirming the standards' applicability.

Different slopes of different polymer types' calibration curves are observed, ranging from 0.0018 a.u./ $\mu\text{g}\cdot\text{g}^{-1}$  (PI) to 0.0440 a.u./ $\mu\text{g}\cdot\text{g}^{-1}$  (PVA). The slopes of the remaining 6 polymer types lie in-between forming two groups of similar slopes (Group 1: Acrylic, PMMA, PVC; Group 2: PAN, PSU, PVP). Table 2 gives an overview of the figures of merit of the obtained univariate calibration functions as well as the ablation rate and carbon content for each polymer type. The carbon content was calculated from the nominal composition of each polymer type.

The variability in the observed slopes of the univariate calibration curves can be explained by matrix-effects that occur when analyzing different polymer types with LIBS. Different polymer types show different absorption behavior resulting in different ablation rates and different fluctuating plasma energies, leading to different atomization and excitation efficiency of the analyte within the laser-induced plasma.

We investigate two different normalization strategies to reduce the variability of observed slopes: normalization to the ablation rate, which is already reported in the literature [38,39], and normalization to the carbon content of the polymer. Comparing the ablation rate and the carbon content of each polymer type with the slope of the univariate calibration curve (Table 2), no correlation is observed. For example, PAN and PI exhibit identical ablation rates and comparable carbon contents but the slopes of the calibration are significantly different. Acrylic and PVC show similar slopes although the carbon content and the ablation rate are significantly different. Therefore, slope variations

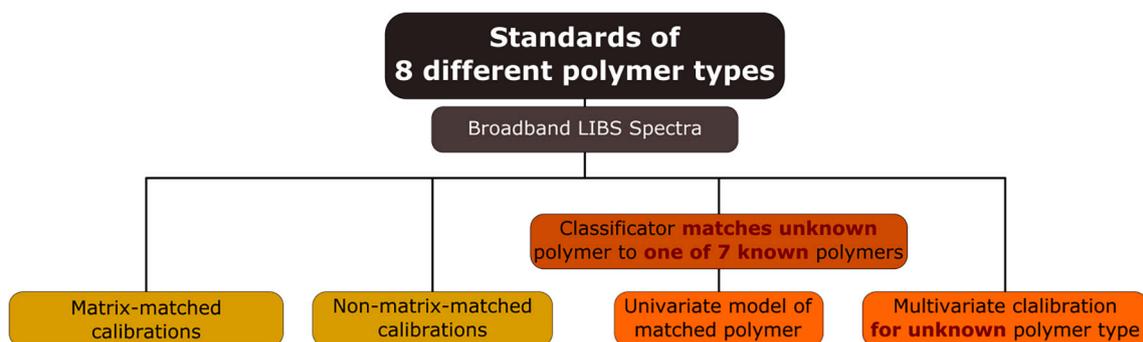


Fig. 1. Overview of all different data evaluation approaches presented in this work.

Table 2

Figures of merit of observed univariate calibration functions and properties of the investigated polymer types.

	R <sup>2</sup>	LOQ (µg/g)	wt% C (%)	Ablation rate (µm/shot)	Slope (a.u./µg·g <sup>-1</sup> )
Acrylic	0.992	0.7	68	0.7	0.0221
PAN	0.971	1.2	68	0.6	0.0052
PI	0.990	0.6	72	0.6	0.0018
PMMA	0.956	1.4	60	1.1	0.0223
PSU	0.998	0.3	73	1.3	0.0056
PVA	0.976	1.1	53	5.7	0.0400
PVC	0.992	0.5	38	1.8	0.0197
PVP	0.974	1.0	65	0.5	0.0060

cannot be explained by different ablation rates or carbon content. Thus for potential reduction of matrix effects additional material properties must be considered, or other more sophisticated approaches for data evaluation are needed.

In the next step errors for matrix-matched quantification are estimated. These errors will be used as best-case benchmark values to assess the performance of the proposed multivariate models for the quantification in unknown polymer types. Therefore, the potassium concentration of the standards in the concentration range of 8–25 µg/g of all polymer types are evaluated by the corresponding univariate calibration of the same polymer type using a leave-one-out (LOO) cross-validation. Relative errors are calculated according to

$$\text{Relative Error} = \left| \frac{c_{\text{estimated}} - c_{\text{nominal}}}{c_{\text{nominal}}} \right| \cdot 100 \quad (1)$$

where  $c_{\text{estimated}}$  is the estimated potassium concentration of the evaluated standard and  $c_{\text{nominal}}$  is the nominal concentration of the evaluated standard. The obtained relative errors are averaged for each polymer type. Relative errors shown in the diagonal of Table 3 correspond to matrix-matched quantification. Derived values range from 7% (Acrylic)

Table 3

Relative errors obtained when evaluating the potassium content in standards with a concentration range of 8–25 µg/g of all polymer types by the different univariate calibration curves of all polymer types. The cells in the diagonal correspond to matrix-matched quantification, whereas all the other cells represent non-matrix-matched quantification.

		Relative error (%)							
		Applied univariate calibration							
		Acrylic	PAN	PI	PMMA	PSU	PVA	PVC	PVP
Evaluated polymer type	Acrylic	7	538	1815	22	523	23	29	452
	PAN	118	11	279	94	19	75	140	28
	PI	157	105	17	125	76	83	190	129
	PMMA	38	466	1602	17	454	16	52	365
	PSU	155	37	216	116	9	71	194	76
	PVA	19	479	1634	11	464	9	31	377
	PVC	18	643	2105	47	619	10	9	517
	PVP	121	79	528	86	98	59	154	12

to 17% (PI and PMMA), resulting in an averaged relative error of 11% ( $n = 8$ ) for all polymers. The order of magnitude of the observed error is in good agreement with relative errors reported in the field of LIBS and other direct-solid sampling techniques such as LA-ICP-MS using matrix-matched standards for quantification [40–43]. All other cells in Table 3 correspond to non-matrix-matched quantification when a polymer type is evaluated by the univariate calibration of a different polymer type and will be discussed in the next chapter.

### 3.2. Quantification strategies for unknown polymer types

#### 3.2.1. Non-matrix-matched quantification

When performing quantitative analysis of unknown polymer types or polymers with an unknown composition, non-matrix-matched quantification is the only conventional approach available. In this case, the potassium content of an unknown polymer type is assessed using the univariate calibration functions of a different polymer type. In this chapter, the expected errors from non-matrix-matched quantification are evaluated. Therefore, the standards in the concentration range of 8–25 µg/g of each polymer type are evaluated by the univariate calibration functions of the other polymer types within our dataset and relative errors are calculated. The results are shown in Table 3.

In this case, a high variability of the relative errors is observed. In some cases, low relative errors are obtained for non-matrix-matched quantification (e.g. evaluating PVA using the univariate calibration of PMMA results in a relative error of 11%), in other cases large errors are obtained (e.g. evaluating PVC using the univariate calibration of PI results in a relative error of 2105%). Interpreting the results presented in Table 3 with the perspective of quantification of the potassium content in unknown polymer types it can be concluded that non-matrix-matched calibration can provide reliable quantification in some cases. Nevertheless, choosing a random calibration curve for the quantification of an unknown polymer type is not a feasible approach as expected errors cannot be estimated and may result in deviations more than a factor of

10 from the nominal content. For example, only 3 out of the 56 possible standard and unknown polymer combinations results in errors comparable to matrix-matched calibrations whereas 31 combinations show a relative error > 100% and 10 combinations show a relative error > 500%. To improve the performance of quantification of unknown polymer types, multivariate data evaluation strategies are investigated in the next part of this work.

### 3.2.2. Multivariate evaluation strategies

To evaluate the performance of multivariate data evaluation models for the quantitative determination of the potassium content in unknown polymer types, each of the 8 investigated polymer types will be considered an unknown polymer type and is evaluated by a multivariate model based on the remaining 7 known polymer types. For the multivariate models we use not only the emission signal of potassium for quantification but also polymer-specific signals from the LIBS spectrum, including atomic emission signals of the main components of the investigated polymers (C, H, and O) and molecular signals (CN violet band and C<sub>2</sub> swan band) A representative LIBS spectrum with marked emission signals used for multivariate models is shown in Fig. 2.

**3.2.2.1. Multivariate classification (RDF) combined with univariate calibration.** The first multivariate approach for the quantification of the potassium content in unknown polymer types is based on a Random Decision Forest (RDF) classification model, commonly used in LIBS data analysis [44,45]. In this study, we use the RDF analysis to select the appropriate calibration model for a particular unknown polymer type. For example, we use the RDF analysis to find the closest match to the unknown polymer type among the 7 known polymer types. Then, we apply the univariate calibration model corresponding to the matched standard material to evaluate the unknown polymer type. Assuming that the similarity in the broadband LIBS spectra is indicative for the matrix-effects observed in univariate calibration models, in the best-case scenario the polymer type yielding the lowest non-matrix-matched error is selected by the RDF for the corresponding unknown polymer type.

The RDF uses all intensities of the marked regions of the obtained LIBS spectra (Fig. 2) as input variables. The model is built with 75 trees and a resampling factor of 0.5. 8 different RDFs were calculated, each excluding one of the polymer types. Therefore, e.g., PI will not be classified as PI because PI was not part of the training set for this respective RDF. Instead, the built RDF will find the polymer type out of the remaining 7 types with the closest matching LIBS spectrum to PI. A majority vote on the classification is used to determine the matched

polymer type.

To evaluate the described approach, each polymer type from our sample set is considered an unknown polymer type, and relative errors for the standards within the concentration range 8–25 µg/g are calculated and shown in Table 4. Evaluating the polymer types PI, PMMA, and PVA, the best-case result with the lowest possible relative error is obtained by this approach. PAN and PVP are matched to the second-best-case. The other polymer types are not matched to the best-case scenario by the RDF resulting in non-optimal results. Nevertheless, the worst-case scenario is only selected for PSU. These results indicate the benefit of the application of a classification model for subsequent non-matrix-matched quantification of unknown polymer types. Compared to the random selection of non-matrix-matched standards, which delivers useful results only in a limited number of cases, the RDF approach provides significant advances. Nevertheless, for some polymer types the results are still not satisfying, thus further improvements are necessary.

**3.2.2.2. Multivariate calibration (PLS).** The second multivariate approach for quantifying the potassium content in unknown polymer types is based on a PLS regression model, which is also commonly used in the field of LIBS [46,47]. In this study, PLS models are built using data of 7 of the 8 polymer types. The obtained PLS model is used to quantify the omitted polymer type. The same regions of the broadband LIBS spectra (Fig. 2) used for the RDF are used as input variables for the PLS model. Moreover, the corresponding element-specific signals for potassium (766.10 nm - 766.91 nm and 769.44 nm - 770.41 nm) were added to the polymer specific emission signals as input variables. Similar to the RDF approach, 8 different PLS models are calculated, each excluding one of the 8 polymer types treated as an unknown polymer type for this model. The number of factors for each PLS model was optimized by calculating a cross-validation and choosing the number of factors with the lowest Root Mean Square Error of Prediction (RMSEP).

Relative errors for the standards within a concentration range 8–25 µg/g obtained from this approach are shown in Table 4. The PLS approach employed for the quantification of unknown polymer types shows promising results with adequate relative errors in the two-digit range for all polymer types. PI, PMMA, and PVP yield even lower relative errors compared to the best-case non-matrix-matched quantification within our dataset. PVC shows the highest relative error. One reason for this may be that PVC is the only polymer type within our dataset containing a halogen. This might have an influence on polymer-specific signals observed in the LIBS spectrum due to different interactions within the laser-induced plasma resulting in a significant influence on the performance of the PLS approach. Nevertheless, the PLS approach applied for the quantification of unknown polymers enables a reliable estimation of the potassium concentration in all investigated polymer types. Compared to the RDF approach, the PLS approach provides a more universal application.

To sum up the performance of all evaluated data evaluation strategies, relative errors for each polymer type are shown in Fig. 3.

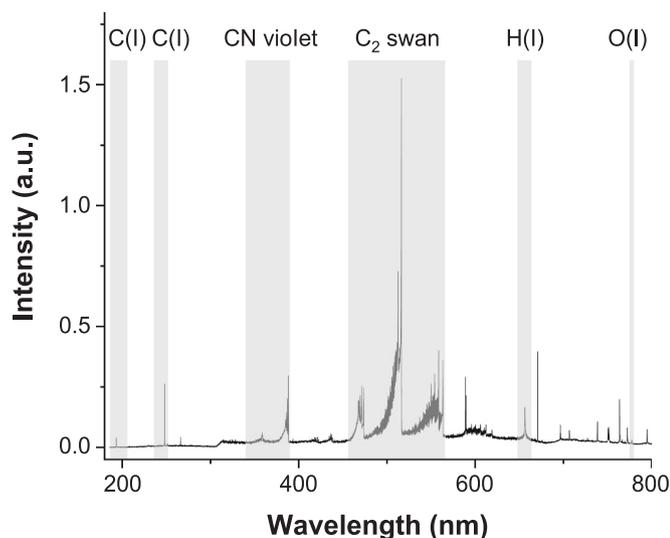


Fig. 2. Exemplary broadband LIBS spectrum of PI with marked polymer-specific emission signals used for multivariate data processing.

Table 4

Results of the multivariate approaches for the quantification of unknown polymer types where each of the 8 investigated polymer type was considered unknown.

Polymer type considered unknown	RDF Approach		PLS Approach
	Matched polymer type	Relative error (%)	Relative error (%)
Acrylic	PVP	425	38
PAN	PVP	28	30
PI	PSU	76	54
PMMA	PVA	16	16
PSU	PI	216	74
PVA	PMMA	11	19
PVC	PVP	517	90
PVP	PAN	79	45

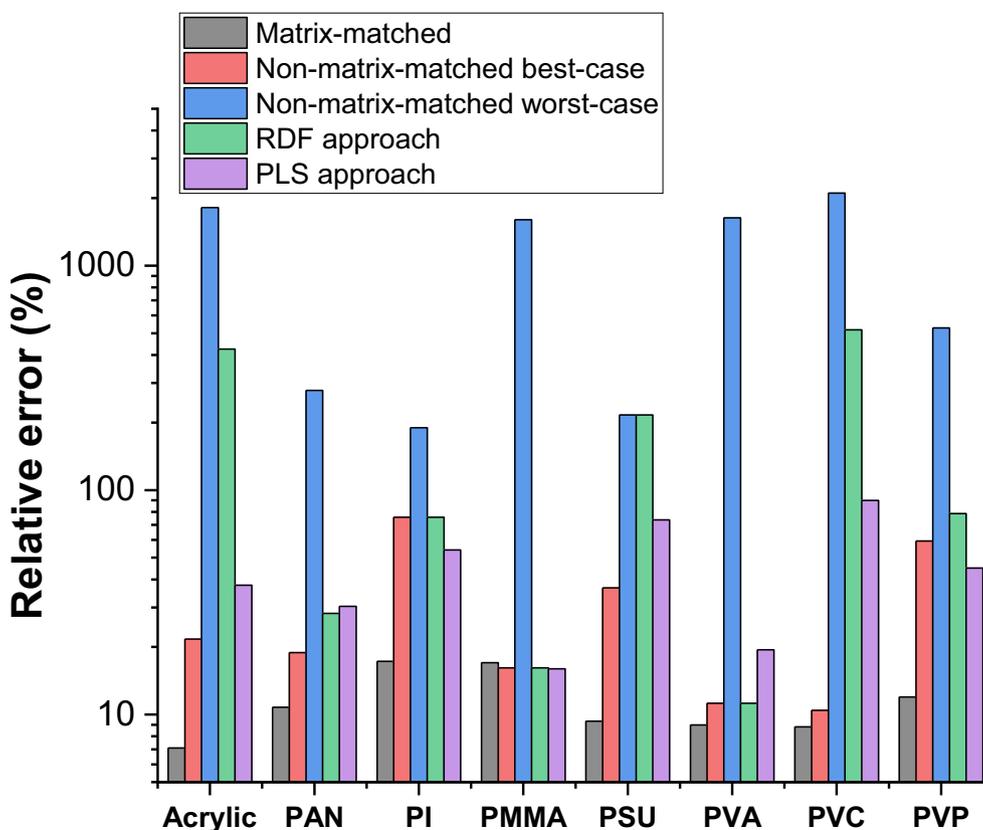


Fig. 3. Overview of the relative errors obtained for the different data evaluation strategies for the quantification of unknown polymers presented in this work.

#### 4. Conclusion

In this work we investigate the possibility of using LIBS for the quantitative analysis of potassium in unknown polymer types where matrix-matched standards cannot be used. In a first step we evaluated univariate calibration curves of 8 different polymer types where significant matrix-effects were observed. Relative errors of matrix-matched quantification and non-matrix-matched quantification were calculated and used as benchmark values to assess the performance of multivariate approaches for the quantification in unknown polymer types. Fig. 3 Shows the errors obtained from presented data evaluation approaches. The selected standards for the evaluation of relative errors are in a concentration range of 8–25  $\mu\text{g/g}$  which is only one order of magnitude higher compared to the obtained LOQs.

Naturally, matrix-matched quantification yields the lowest relative errors ranging from 7% to 17%. As for the quantification of polymer samples where the exact composition is not known, matrix-matched quantification cannot be employed, conventionally only non-matrix-matched quantification can be used. Since different polymer types come with a wide range of physical and chemical properties, the relative errors obtained from non-matrix-matched quantification heavily depend on the polymer type selected for quantification. The presented results show that conventional non-matrix-matched quantification using a random polymer type as a reference material for an unknown polymer type is not feasible, as the expected error cannot be estimated. By chance, an appropriate polymer type can be selected for non-matrix-matched quantification resulting in relative errors of 20% or less. However, in most of the cases relative errors resulting from non-matrix-matched quantification can result in deviations more than a factor 10 from the nominal concentration which is not suitable for research tasks or industrial/environmental routine analysis. Considering polymer-specific signals provided by LIBS broadband spectra significantly improved the quality of the analysis. The two developed multivariate

approaches based on a RDF- and a PLS-model for the quantitative analysis of the potassium content in unknown polymer types yield relative errors ranging from 11% to 517% and 16% to 90% respectively. Comparing the findings for these two multivariate approaches, the RDF approach delivers inadequate results for some polymers (e.g. Acrylic or PVC), whereas the PLS-model allows a universal application for all polymer types. Considering that the quantification of the multivariate models is carried out without the use of matrix-matched standards, precise quantification cannot be expected. Nevertheless, the presented approaches enable a reliable estimate of the potassium content in the low  $\mu\text{g/g}$  range. Thus applications are enabled which do not need an accurate quantification but rather the evaluation of prevailing concentration levels, e.g. compliance with given material specifications can be controlled. For example in many industrial applications (e.g. in the semiconductor-industry) it is important that contaminations are below a certain threshold value to ensure the aspired product properties. An analytical research task which could be accomplished so far only with the use of matrix-matched standards.

In further works, more elements will be added to the standards for a broader range of applications. Additionally, the influence of an increase in the number of polymer types available in the library on the obtained errors will be investigated.

#### Declaration of Competing Interest

There are no competing interests to declare.

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## Appendix A. Supplementary data

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