# MATRIX EFFECTS IN QUANTITATIVE POLYMER ANALYSIS: A COMPARISON OF ns AND fs LASER SYSTEMS

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## 1. INTRODUCTION

As synthetic polymers are becoming more and more important in our daily lives, the need for comprehensive characterization and analysis arises. Besides various physical properties, also the metal content is crucial for many applications. In the food packaging industry, toxic metals must be monitored to avoid migration into the food [Whitt 2013], whereas contaminations of mobile ions in polymers used in the semiconductor industry may cause devices failures [Atkinson 2018]. Conventionally, digestion or combustion protocols with a consecutive liquid ICP-MS or ICP-OES analysis is used to determine the metal content of polymers [Pereira 2011]. As this approach comes with many disadvantages, recently direct-solid sampling techniques such as LIBS have been used for this task. Even though, LIBS can provide many advantages in polymer analysis, obtaining reliable quantitative results is still challenging as matrix-effects occurring during the ablation and excitation of the sample highly influence the signal response. As the use of fs-laser systems has proven to be useful to decrease matrix-effects in LA-ICP-MS analysis compared to ns-laser systems [Koch 2007], in this work we investigate this influence in LIBS analysis. Therefore, a set of in-house prepared polymer standards of 7 different polymer types is analyzed using a ns and a fs LIBS setup and matrix-effects are assessed and compared.

## 2. EXPERIMENTAL

### 2.1. Materials

Polymer solutions of seven different polymer types (Polyacrylonitrile (PAN), Polyimide (PI), Poly(methyl methacrylate) (PMMA), Polysulfones (PSU), Polyvinylacetate (PVA), Polyvinylchloride (PVC) and Polyvinylpyrrolidone (PVP) were prepared by dissolving polymer granulates obtained from HP Polymer GmbH (Lenzing, Austria) and Arcos Organics, Geel, Belgium in N-Methyl-2-pyrrolidon (NMP) with p.a. grade quality obtained from Merck (Darmstadt, Germany). NMP standards containing various levels of

lithium were prepared by dissolving Lithium trifluoromethanesulfonate (98%) (Sigma-Aldrich, Buchs, Switzerland) in NMP. Prepared polymer solutions were spiked with the corresponding NMP standards and applied to high purity Si-wafer (10 mm x 10 mm) (Infineon Austria AG, Villach, Austria) via a spin-coating procedure. Samples were cured at 80°C for 12 h to ensure complete evaporation of NMP.

## 2.2. Instrumentation

LIBS experiments were carried out using a commercially available LIBS J200 system equipped with a Nd:YAG laser operating at 266 nm and a pulse duration in the ns range and a commercially available LIBS J200 Femto iX system equipped with a Yb:YAG laser operating at 1030 nm with a pulse duration in the fs range. In each system, a collection optic was used to collect the light emitted by the laser-induced plasma. Emitted light is transported to an ICCD detection system using optical fibers detecting the Li-emission line at 670.78 nm. Instrumental parameters are summarized in **Table 1**.

| LIBS J200 Applied Spectra (West Sacramento, CA) | | |
|:---:|:---:|:---:|
| **Wavelength (nm)** | 266 | 1030 |
| **Pulse duration** | ns | fs |
| **Spot size (µm)** | 100 | |
| **Repetition rate (Hz)** | 10 | |
| **Gate delay (µs)** | 1 | 0.1 |
| **Accumulated spectra** | 35 | |
| **Measurement spots/sample** | 6 | |
| **Atmosphere** | Ar | |

**Table 1:** LIBS measurement parameters

## 3. RESULTS AND DISCUSSION

The main goal of this work is to investigate the occurrence of matrix-effects during quantitative ns- and fs-LIBS analysis of polymer samples. Therefore, in-house prepared standards of 7 different polymer types were investigated with two different LIBS systems. In a first step, homogeneity of the prepared standards was investigated by assessing Li signal variations over the analyzed area. Different data normalization methods were investigated to improve the quality of the obtained calibration curves (normalization to signal background and normalization to the nominal carbon content). Additionally, the overall quality of the univariate calibration models is assessed and compared between ns- and fs-LIBS. Matrix-effects of different polymer types are observed in different polymer types, as different slopes of the calibration curves. The variation of the obtained slopes was used as a reference value for the occurrence of

matrix-effects. If matrix-effects are reduced, the variation of the obtained slopes of the calibration curves of different polymer types should decrease.

With the different investigated data evaluation strategies, univariate calibration models of adequate quality were obtained for each polymer type and each laser system even though the Li signal response was observed to be highly dependent on the polymer type as well as the employed laser system. Besides PVC showing the highest slope for both laser systems, no systematic trend was observed regarding the signal response between the ns- and fs-LIBS analysis. Additionally, no significant reduction of matrix effects (represented by the variation of the observed slopes of the univariate calibration models) was observed by the use of a fs-LIBS system compared to a ns-LIBS system.

## 4. CONCLUSIONS

Matrix-effects occurring during quantitative polymer analysis for fs- and ns-LIBS is assessed and compared in this work. No reduction of the severity of matrix-effects was observed for fs-LIBS. The different polymer types showed a highly varying signal response depending not only on the polymer type but also the employed laser system. Therefore, we conclude, that fs-LIBS does not offer any advantages by a reduction of matrix-effects for quantitative polymer analysis compared to ns-LIBS.

## 5. ACKNOWLEDGMENTS

## 6. REFERENCES

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