CLASSIFICATION OF PLASTICS USING LIBS AND RAMAN SPECTROSCOPY DATA FUSION

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1. INTRODUCTION

Not all materials can be classified using singular spectroscopic methods without tedious pretreatment and data mining. Such materials pose a challenge for usage of spectroscopic methods in automatized industrial processes. Laser Induced Breakdown Spectroscopy (LIBS) gained much attention in recent years thanks to its robustness, low or none material preparation needs and possible usage in remote areas without human presence among other benefits. On the other hand, the Raman spectroscopy method is used regularly in various fields for approximately last 50 years. Its benefits and limitations are well known. Both these methods need little to none sample preparation and can be used remotely. Moreover, these two methods are complementary, because LIBS yields atomic information and Raman spectroscopy provides molecular information. In addition to similar instruments, this duo is a great candidate for combination of acquired data.

In this work, the combination is done via data fusion. This method was already demonstrated by several academic teams and seems to bring better classification results when compared to separately used methods. In work of Hoehse et al. this data fusion was used for classification of inks and pigments. It was demonstrated, that by using LIBS + Raman data fusion, one can recognize similar inks, which form non-recognizable clusters in separate data sets [Hoehse 2012]. Similar results were also provided by Prochazka et al., who used similar data fusion for classification of bacteria [Prochazka 2018].

The aim of this work is to use referenced data fusion method to distinguish spectroscopically challenging material types with as little pretreatment and data mining as possible. For this, several (12) types of plastic were used. Different plastic types were used because of their similar chemical composition and possible industrial utilization. This project should lead to unified way of data treatment for LIBS and Raman spectroscopy data fusion. Now we present results of classification using basic chemometric methods such as PCA and SIMCA. Most important concerns with this type of data fusion are also presented.

2. Experimental

The measurement consisted of LIBS and Raman spectroscopy parts. Samples were chosen from semiproduced materials. All samples except one (PVC) were uncolored. Plastics types are similar to each other chemically due to their chemical composition. All plastics are polymers. They are built by connecting many identical base elements – mers. These mers usually consist of Carbon base and additives. Differences between plastic types are induced by differences between these additives and their connection to base Carbon skeleton.

Raman measurements were done at Institute of Scientific Instruments of Czech Academy of Sciences in Brno. Raman instrument used was Renishaw inVia Raman Spectrometer, Renishaw plc., Wotton-under-Edge, UK. Laser wavelength was 785 nm, objective used had 20x magnification, illumination time was 1 s which was accumulated 10 times for final spectra. Each sample was measured 5 times at 1300 cm^{-1} central Raman shift.

LIBS measurements were done at LIBS laboratory of Department of Physical Engineering of Brno University of Technology. Laboratory system LIBS Discovery was used. Laser wavelength was 532 nm, laser energy was 22 mJ, each spectrum was a result of 5 accumulated shots at the same location. Spectrometer used was EMU Catalina Scientific with an Echelle type grating. Each sample was measured 25 times.

3. Results and discussion

3.1. LIBS data analysis

Chemical similarities of different plastic types lead to similar chemical footprint and difficult classification in LIBS. Plastic type classification via LIBS was done several times by various scientific groups. To reach satisfactory accuracy, tedious pretreatment of data mining had to be used. By using Argon atmosphere, line selection and several other data treatments, scientific team from Wuhan (China) reached accuracy over 90% in classification of 11 kinds of plastic [Yu 2014].

Before analysis took place, some data treatment was needed. LIBS spectra were cut to contain only relevant part of wavelength range. Resulting range is 300-800 nm. Lines important for plastic analysis were pinpointed in previous works on plastic identification in LIBS, so these lines were highlighted in our spectra. In attempt to minimize data treatment, this was concluded LIBS data treatment before analysis.

LIBS spectra were then introduced to Principal Component Analysis algorithm. Main goal for this part was to show the need for data fusion. We expect poor classification by LIBS without tedious data treatment. By using first two Principal Components (PCs) more than 95% of data set variance was depicted. Score plot for PC1 and PC2 can be seen in **Figure 1**. One of the plastic types is separated from others in the PC space. This is PVC, which was pointed out in the Experiment section as the only colored sample. The difference is highly likely caused by the color additives present in the PVC sample, which are absent in the rest of the samples.

If the data is automatically clustered using k-means clustering, only 3 clusters are formed, which is not surprising. Additional LIBS data analysis is not aim of this work. The expectation that LIBS is not able to properly classify plastic types without complex data treatment was confirmed.

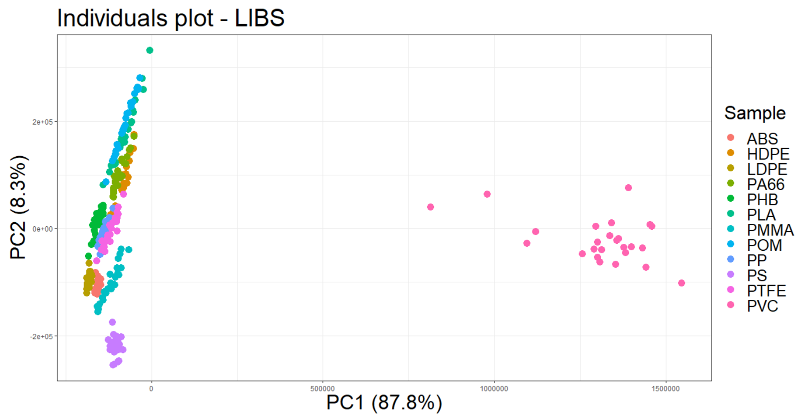

Figure 1. Score plot of separate LIBS measurement.

3.2. Raman spectroscopy data analysis

While LIBS can hardly distinguish plastic types due to similarities in chemical composition, Raman spectroscopy should be more suitable to this task. As plastic types differ in molecular composition, Raman should be able to identify these differences and be more successful in plastic type classification. This was repeatedly confirmed by several papers in past years. For example, in one paper by a scientific team based in Idaho (USA) it was found that 6 types of plastic cound be classified using PCA with an accuracy exceeding 80% [Allen 1999].

Raman spectroscopy data used in this work are of lower resolution in comparison to LIBS data. Before PCA analysis of the data, we tried to pinpoint interesting lines for further usage. This leads us to various papers on Raman spectroscopy of various plastic types. This was needed, because due to molecular differences, no Raman transition was present in every plastic type. Moreover, when the Raman transition was present in multiple plastic types, its Raman shift was different. This leads to different behavior of Raman data in further analysis.

Raman data was then analyzed by PCA in the same way as LIBS data. Again, first two PCs were used to form a scores plot. First two PCs depicted 82.7% of total data variance. Lower percentage of variance depicted by the first two PCs is due to higher number of differences in Raman data of different plastic types. The score plot can be seen in **Figure 2**. It is evident, that the plastic types are more distinguished than in separate LIBS PC space. Again, the colored PVC sample seems farthest from other plastic types. Nevertheless, using k-means clustering, only 8 clusters were formed, as some of the plastic types cannot be distinguished from each other in this PC space.

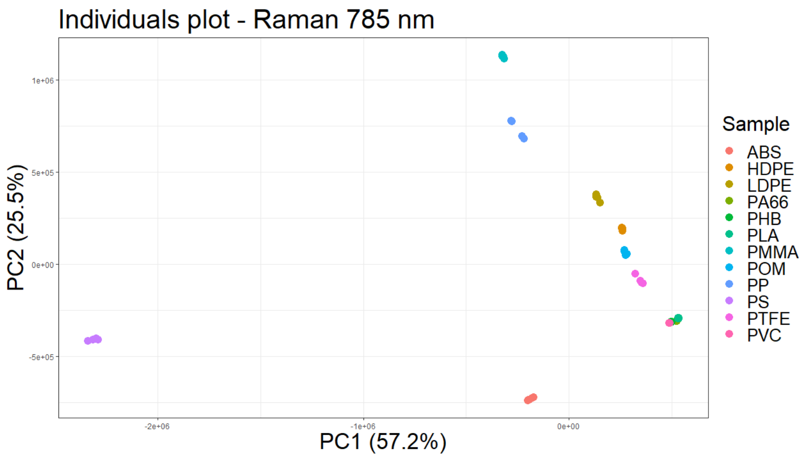

Figure 2. Score plot of separate Raman measurement.

3.3. Fused data analysis

After data fusion, the date set is analyzed by PCA and SIMCA. PCA analysis was done again by analyzing score plot of first two PCs, which depicted 61.4% of data variance. The score plot is in **Figure 3**. It is evident, that data fusion helped with distinction between plastic types in PC space. The data now form 12 separate groups, which is corresponding with the number of plastic types measured. By introducing k-means algorithm, 12 clusters were formed with minimal errors.

To confirm these results, SIMCA algorithm was used. For the training of the algorithm, 35 random pseudo-spectra from every sample were used. The rest of data was used as test set. From 1500 pseudo-spectra, 1370 were correctly classified, the rest was not assigned to any plastic type. This result in accuracy of 91.3%, which is a significant increase in comparison to separately used methods. The results confirmed our expectations.

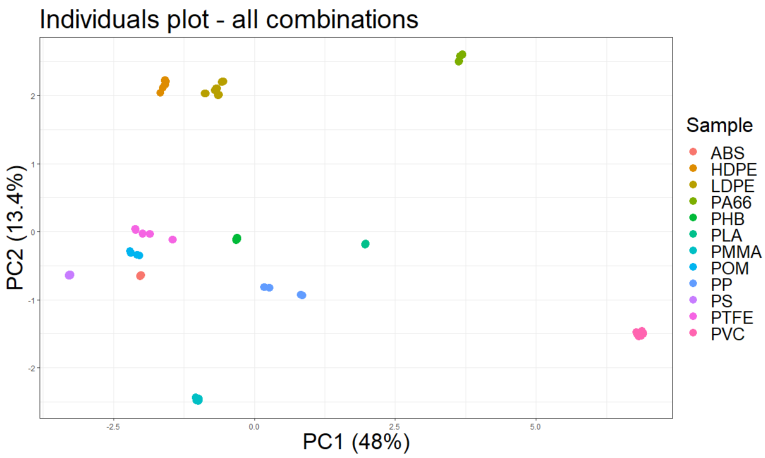

Figure 3. Score plot of fused data sets.

4. Conclusions

This work was aimed at confirmation of viability of data fusion of LIBS and Raman spectroscopy. 12 different plastic types were chosen as samples. Plastic types classification has also an industrial value. We demonstrated that with minimal data preparation, accuracy of classification using basic methods as PCA and SIMCA increased with usage of fused data. The resulting accuracy using fused data set was 91.3%. This could be used as a stepping stone for automatization of plastic classification.

5. Acknowledgements

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