Chemometric methods in plasma spectrometry

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Plasma spectrometry is frequently used mechanism of multiple analytical methods focusing on elemental analysis and imaging. It includes, in particular, mass spectrometry with inductively coupled plasma (ICP-MS), ICP-MS with laser ablation (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS). The goal of this study is to explore different approaches for data processing and statistical analysis of these multivariate data. This work is split into 3 parts; data reduction for bulk analysis and imaging, image enhancement by convolutional neural networks and classification of samples.

A data reduction software Ilaps was developed for fast processing and visualisation of mass spectrometric data. After loading the acquired data, the time-resolved analysis is visualised in an interactive graph and the peaks and background are automatically selected using a threshold value or timestamps from the laser ablation system. The program offers multiple processes of analysis, including despiking, background subtraction, calibration, quantification, data correction and elemental imaging. To use the software for elemental imaging of LIBS data, a short script was created to allow import.

Second part of this study focuses on elemental imaging enhancement using fast.ai library [1]. With destructive methods, such as LA-ICP-MS or LIBS, the sample is ablated by laser beam, resulting in a pixelated image, where the resolution is dependent among other things, on the beam size. Decreasing the beam size infinitely is not possible, which leads to the image enhancement by computers. A ResNet34 model was trained on a dataset of brain images and cellular images. The training set consisted of original high-resolution images and their low-quality version created by virtual ablation [2] developed at the National institute of chemistry in Ljubljana. The results were compared by normalised mean squared error (NRMSE), structural similarity index (SSIM) and peak signal to noise ratio (PSNR), and for both models, the predicted image ranked better on all 3 metrics in comparison to the ablated image and the image enhanced by bicubic interpolation. The whole project is open-source and published on GitHub [3].

The last part concentrate on the classification of wine samples using advanced statistical methods and finding an algorithm for this classification with the best performance. Wines from four different European countries were analysed using fluorescence spectrometry. The dataset contains 441 samples from Austria, Czech, Serbia and Slovakia. Using their emission spectra, multiple models were trained and validated: random forest algorithm, k nearest neighbours, linear neural network and convolutional neural network (CNN). Best performance (97%) was achieved using CNN after converting spectra to images using gramian angular field.

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