# Analysis of automotive paint and glass samples by combined LIBS and Raman spectroscopy

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## Motivation

- Laser-induced Breakdown Spectroscopy (LIBS) and Raman spectroscopy give complementary (elemental and molecular) information of a sample.
- Here, we will show that the combination of LIBS and Raman can lead to a better classification and discrimination of forensic samples.
- The data were obtained with our newly developed LIBS-Raman-instrument CORALIS which allows us to measure LIBS and Raman spectra at the same sample spot.

## Differentiation of glass samples

LIBS and Raman spectra of sixteen different glass samples were measured on twenty different spots on each sample.

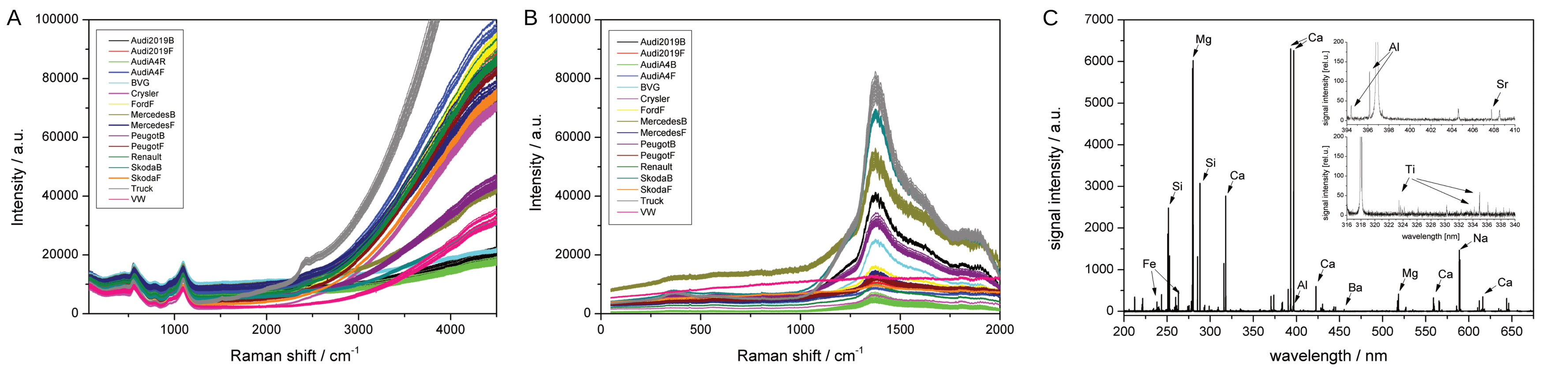


Figure 1: A, B) Raman spectra excited at A) 532 nm (I = 5·10$^4$ W·cm$^{-2}$, 50 x 1 s) and B) 785 nm ((I = 2·10$^4$ W·cm$^{-2}$, 50 x 2 s) and C) LIBS spectra (5 mJ, 10x5 pulses, delay: 1.8 µs) of the sixteen different glass samples.

Differentiation of samples was tested using a principal component analysis (PCA). For that the spectra were vector normalized. For LIBS, instead of the whole spectrum integral values of selected lines were used (Table 2). The integral values were then transformed to a standard normal distribution.

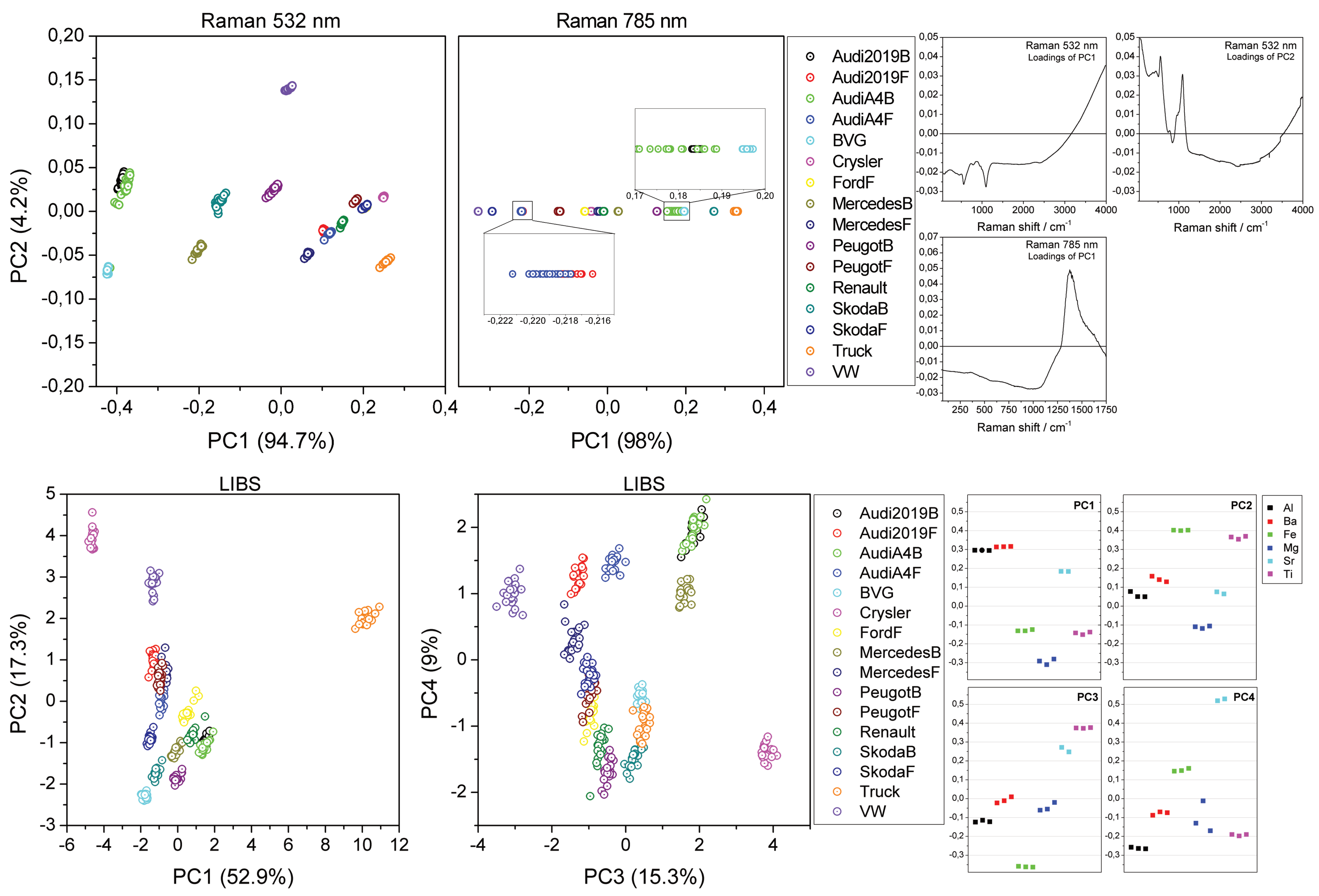


Figure 2: Scores and loadings resulting from the principal component analysis performed on the Raman spectra excited at 532 nm and 785 nm and the LIBS spectra, respectively.

In a next step we fused the score values of the individual PCAs and checked the differentiation in the newly developed multidimensional space. We defined two clusters as seperated when the minimal squared Mahalanobis distance between the points of two clusters is grater than the $X^2$-value for 99.99 % confidence interval and the number of chosen principal components as the degrees of freedom (decisive Mahalanobis distance).

| Method | No. differentiated samples |
|---|---|
| Raman 532 nm | 11 |
| Raman 532 nm | 12 |
| LIBS | 14 |
| LIBS-Raman | 14 |

Table 1: Number of samples that could be distinguished using the above mentioned criterion when using only the Raman data obtained with excitation at 532 nm and 785 nm, respectively or the LIBS data alone and with the combination of the scores of the individual PCAs (LIBS-Raman).

| Element | Center wavelength of selected lines / nm |
|---|---|
| Aluminum (Al) | 308.215, 394.401, 396.152 |
| Barium (Ba) | 455.403, 493.408, 614.171 |
| Iron (Fe) | 238.204, 259.939, 260.708 |
| Magnesium (Mg) | 277.983, 285.213, 518.360 |
| Strontium (Sr) | 407.771, 421.552 |
| Titanium (Ti) | 323.452, 336.121, 337.280 |

Table 2: Center wavelength of the LIBS lines used for the multivariate analysis.

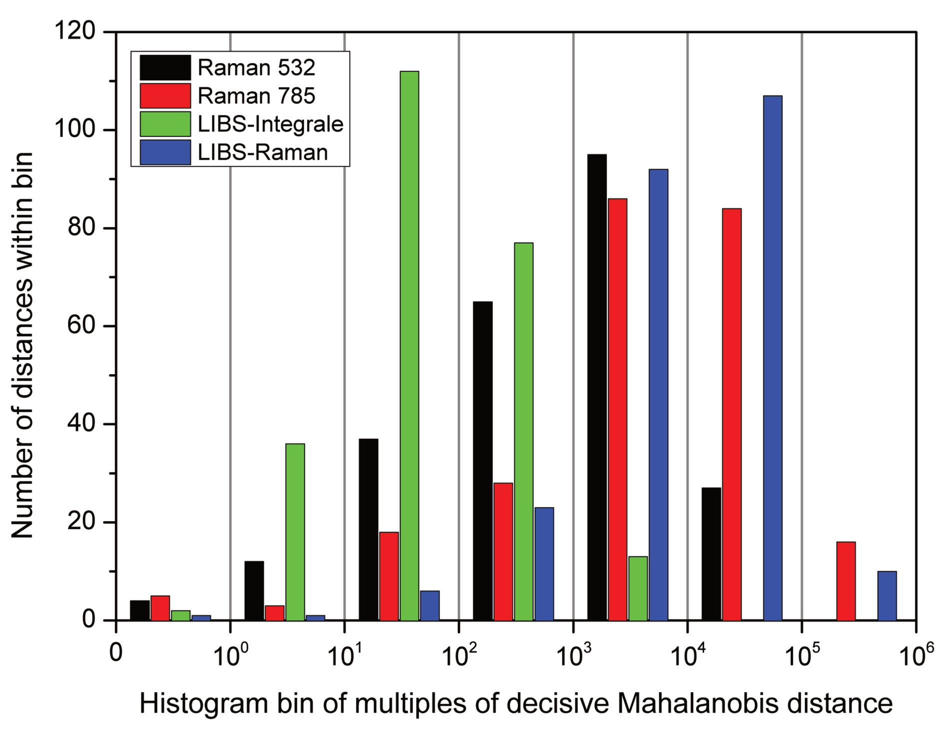


Figure 3: Distribution of distances in means of multiples of decisive Mahalanobis distance.

The results show that with LIBS as well as the combination of both methods 14 out of 16 samples can be distinguished. In comparison to LIBS alone the Mahalanobis distances becomes higher by combining both methods which means that we get a better differentiation (Figure 3).

## Analysis of automotive paint samples

Automotive paint samples consist of different layers which are visible in the cross section (Figure 4 C, D). LIBS and Raman measurements were performed on four lines across the sample (Figure 4 E). Until now we investigated eight different paint samples. For two of them the results are presented here.

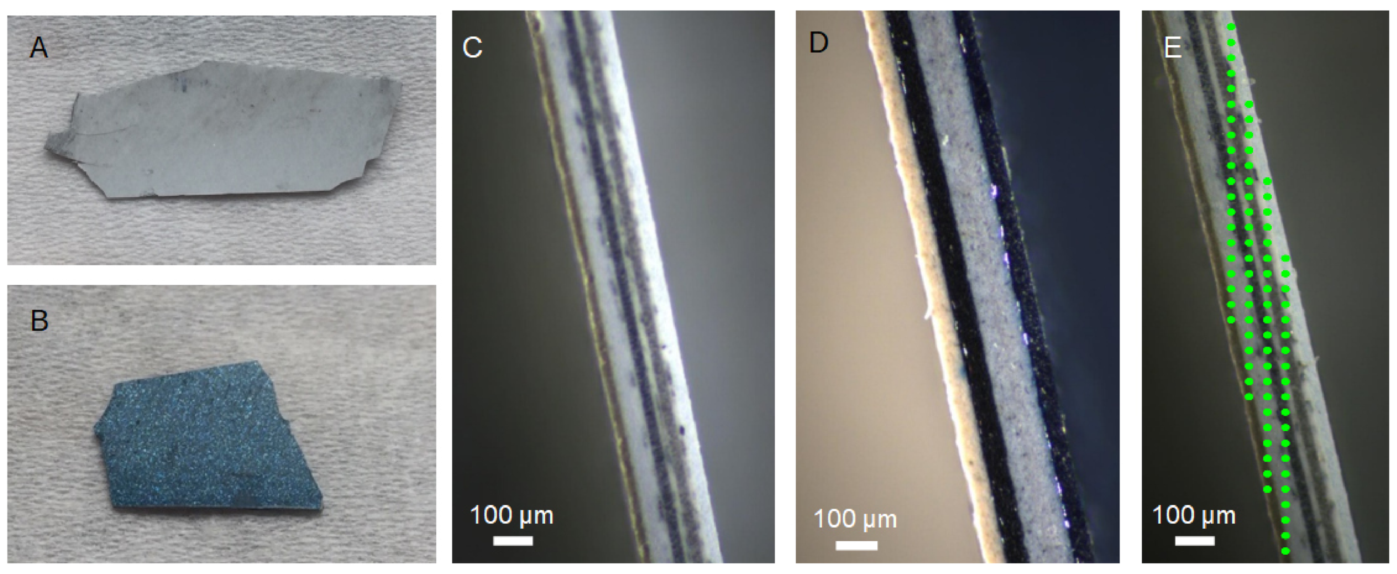


Figure 4: A, B) Photographs of two exemplary automotive paint samples c. D) Micrographs of the crosssections of the samples in A and B, respectively. E) Exemplary measurement grid (sample was measured with a tilt of eleven degree and the point distance was 50 µm).

With LIBS a variety of elements was found in the different paint samples. Among them Aluminum, Barium, Carbon, Calcium, Iron, Magnesium, Silicon, Sodium, Titanium and Zink were found in nearly all of the samples. Furthermore Bismuth, Copper, Chromium, Lead, Lithium, Maganese, Nickel, Phosporous, and Tin were found in some of the samples. The amount as well as the distribution of the elements in the different layers was found to be different among the samples (Figure 4).

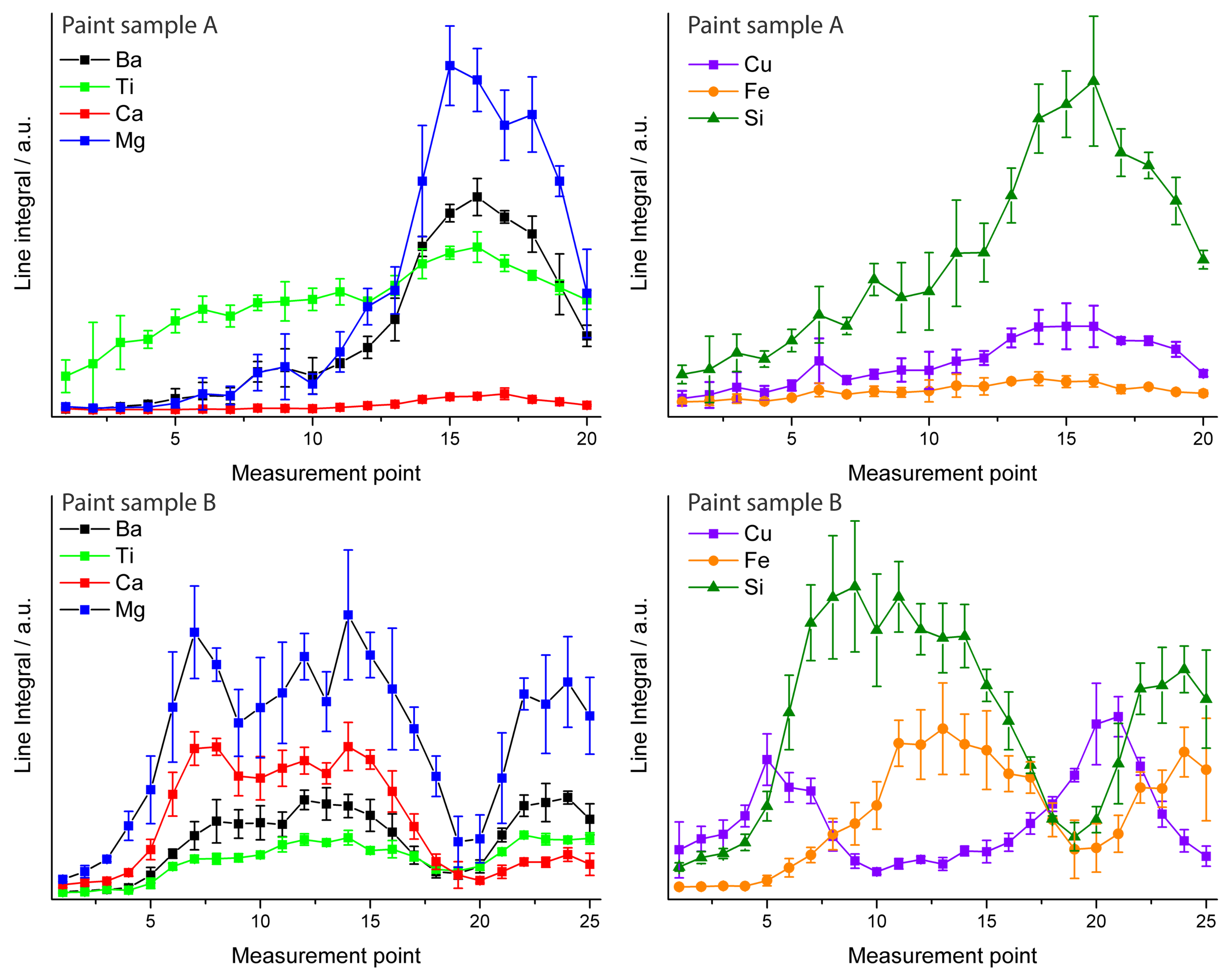


Figure 5: Distribution of line integrals of selected elements along the measurement points on the cross sections of the samples shown in Figure 4.

The Raman spectra show bands of polymers, pigments and filler material as well as fluorescence. The existence and intensity of the Raman bands is individual for the different samples and layers as shown in Figure 6 for the bands of titanium dioxide at 444 cm$^{-1}$, polystyrene at 1003 cm$^{-1}$ and copperphtalocyanine at 1525 cm$^{-1}$.

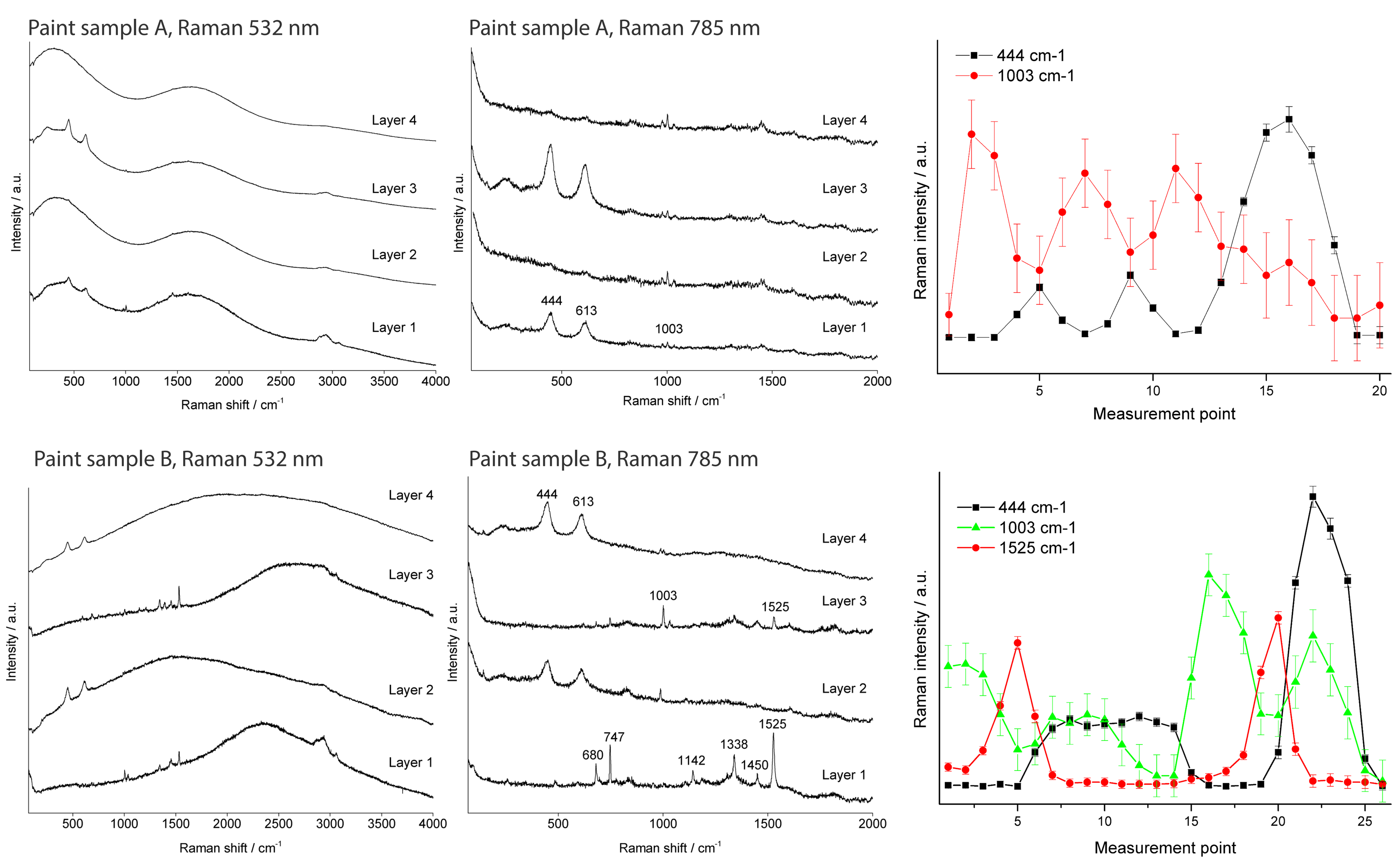


Figure 6: Examplary Raman spectra obtained with excitation at 532 nm and 785 nm, respectively and the Raman intensity of selected bands in dependence of the measurement point.

## Conclusions

- The combination of LIBS and Raman shows to be benificial for the analysis of glass and automotive paint samples.
- 14 out of 16 glass samples could be distinguished in a principal component analysis by combining LIBS and Raman data.
- With the CORALIS instrument we are able to obtain different data, e.g. number of layer, layer thickness, as well as space-resolved elemental and chemical composition of automotive paint samples within one measurement. That might lead to an improved and faster identification and comparison of such samples.

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