Application Note - Forensics 3

Investigation of Automotive Glass with the Combined Raman/fluorescence and LIBS System, CORALIS

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Introduction

In this application note we focus on the analysis of automotive glass via Raman and fluorescence combined with laser-induced breakdown spectroscopy (LIBS). Glass can be an important source of evidence in forensics, i.e. for identification and comparison of glass samples, as well as determination of their origin. For example, this may be important for identifying cars after hit-and-run accidents.

So far various analytical techniques – e.g. X-ray microfluorescence and laser ablation, inductively coupled plasma, and mass spectrometry – have been used for glass analysis. Both LIBS and Raman spectroscopy have been successfully applied for forensic analysis. [1], [2]

The aim of this paper is to demonstrate the potential of our CORALIS system for analyzing automotive glass using its capability to perform Raman and fluorescence spectroscopy in conjunction with LIBS at the same measuring point. Furthermore, principal component analysis (PCA) for differentiation of the different samples is applied.

Instrument

The CORALIS allows simultaneous detection of Raman, fluorescence and LIBS spectra at the same sample point. It is also capable of raster scanning over larger areas and acquiring spectra of a multitude of sample points by laying a grid of raster scan points over the sample. In this way, the user receives complementary information about the molecular and elemental composition. Typically, Raman detects only major sample components. In contrast, fluorescence can be very sensitive for detection of minor additives. LIBS complements these methods with its sensitivity to atomic quantities down to the ppm range. For the analysis of the spectra different tools are implemented in the software of the system.

A detailed description of the technical features with all hardware and software components can be found in the already published application notes “Car paint coatings” [3] and “Depth scan multi-layer” [4].

Materials and Methods

The samples analyzed in this study were collected from broken car windows, either as remains from car accidents or as pieces chipped from discarded windows. The samples were analyzed without any treatments such as cleaning or burnishing. Table 1 lists all eleven samples with their respective characteristics.

Sample Name	*Car Model*	*Characteristics*
AudiV	Audi A4	front side of laminated safety glass, bluish tinted
AudiR	Audi A4	back side of laminated safety glass
BVG	Bus stop light	security glass of the light of a bus stop
Chrysler	Chrysler Neon	collected at car accident
LKW	MAN truck	class of headlight
MercedesV	Mercedes-Benz W211	front side of laminated safety glass, bluish tinted
MercedesR	Mercedes-Benz W211	back side of laminated safety glass
Renault	Renault	collected at car accident
SkodaV	Skoda Karoq	front side of laminated safety glass, bluish tinted
SkodaR	Skoda Karoq	back side of laminated safety glass
VW	VW Sharan II	collected at car accident, glass of back window, darkly tinted

Table 1: List of samples with characteristics

The samples had sizes between 0.5 x 0.5 cm^2 and 3 x 3 cm^2. Figure 1 shows a sample of the windshield of a Chrysler Neon in total view (left) and in detail image (right). For every sample, five spectra were measured at five different locations separated from each other by 200 µm.

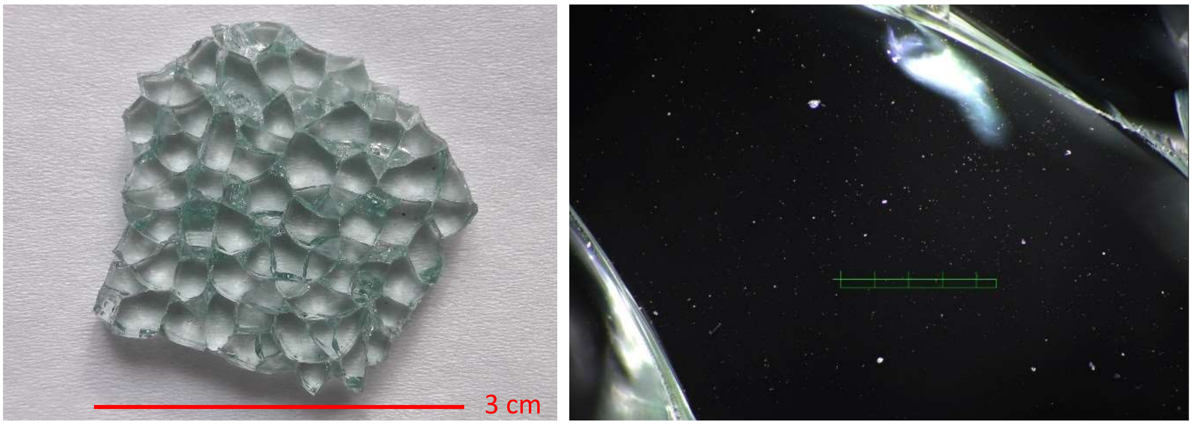

Figure 1: Photograph (left) and micrograph (right) of a glass sample from a windshield of a Crysler Neon

For Raman/fluorescence measurements, the 532 nm continuous laser with an optical power of 46 mW on the sample was applied. To improve the signal-to-noise ratio of the spectra, the gain of the EM-CCD camera was set to 150 and horizontal binning to 2 pixels. Each spectrum is an average of 50 single measurements with an acquisition time of 2 seconds.

LIBS measurements were performed using a q-switched Nd:YAG laser with nanosecond laser pulses at 1064 nm and 5 mJ laser pulse energy on the sample. Again, the gain of the EM-CCD detector camera was set to 150. The signal acquisition started after a delay of 1.1 µs following the laser pulses to eliminate the continuous background radiation of the plasma which occurs immediately after excitation. For each LIBS spectrum, signals of 5 laser shots were accumulated.

To distinguish between the samples based on their spectral characteristics, a Principal Component Analysis (PCA) of the measured spectra was performed. Before running the PCA, the data were preprocessed in the following way. First, the spectral range of the LIBS spectra was confined to two ranges: 250 nm -265 nm and 285 nm - 289 nm. These ranges contain relevant lines of silicon, iron and magnesium and were found to yield maximum discriminability among the samples based on the LIBS spectra. Second, LIBS spectra were normalized using vector normalization. Raman/fluorescence spectra were analyzed between 534 nm and 700 nm, corresponding to relative wavenumbers up to about 4500 cm^{-1} with respect to the excitation at 532 nm. These spectra were also normalized with the method of vector normalization.

The PCA was programmed in the Python 3.7.4 environment using the libraries Matplotlib, NumPy and SciPy. For all 55 spectra three different PCAs were performed: one with only Raman spectra, one with only LIBS spectra and one with combined spectra, which are a concatenation of a Raman and a LIBS spectrum.

Results and Discussion

In Figure 2 an exemplary LIBS spectrum of the sample VW is shown. In the spectrum magnesium (Mg), calcium (Ca), silicon (Si), sodium (Na) and iron (Fe) were identified as the most significant elements. The spectra of all samples show these characteristic lines, however with varying relative intensities and particularly with or without typical lines of iron or titanium (Ti).

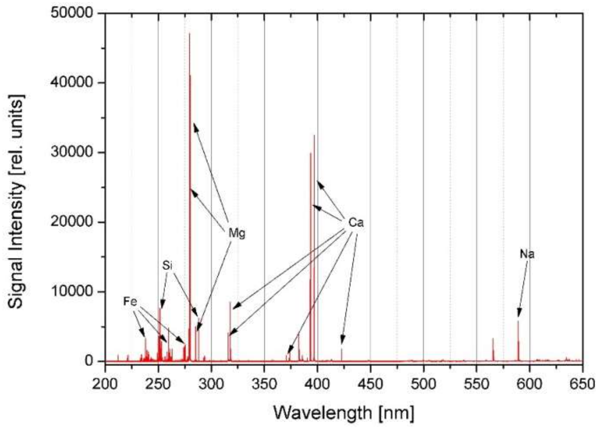

Figure 2: LIBS spectrum of the sample VW with identified elements

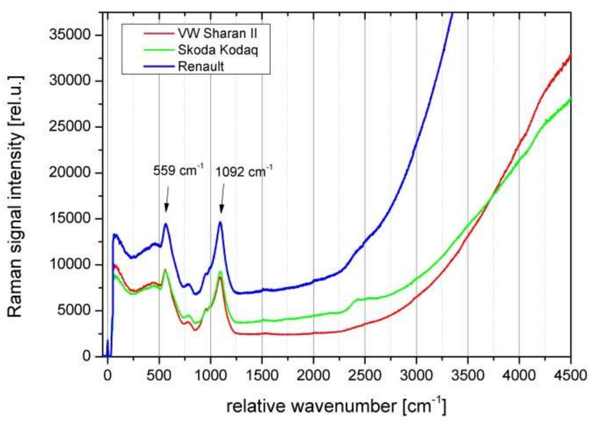

Figure 3: Raman and fluorescence spectra of different glass samples showing two distinct Raman bands and increasing red fluorescence

Figure 4 shows a Raman spectrum of the VW sample after manual baseline correction within a spectral range of 100 cm^{-1} - 1700 cm^{-1}. A comparison with the KnowItAll® database (Bio-Rad, USA) results in a 98 % match with glass. All samples show similar Raman spectra in this wavenumber range. However, as shown in Figure 3, sample-specific differences arise in the fluorescence intensities from 2000 cm^{1} up to 4500 cm^{-1}.

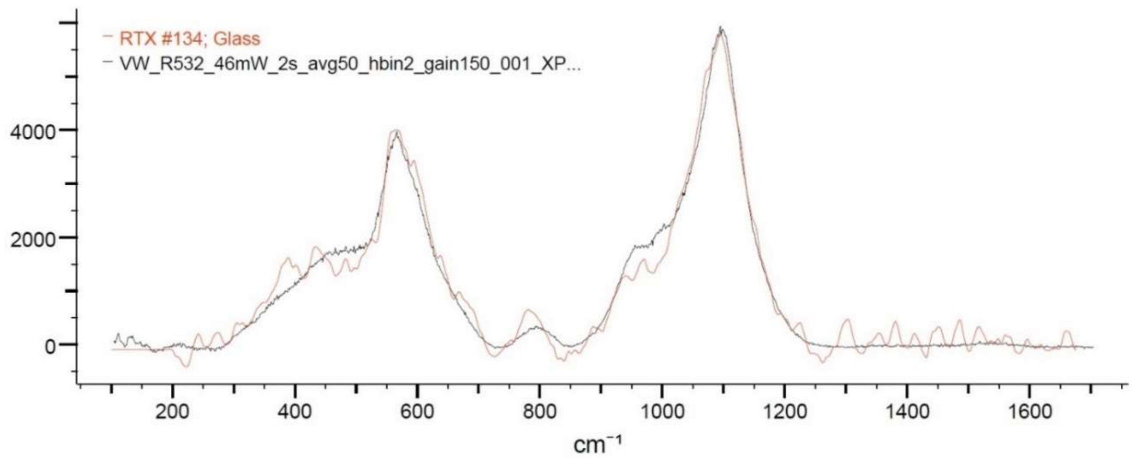

Figure 4: Baseline-corrected Raman spectrum of sample from VW (black) with best match of KnowItAll® database (red)

In the following section, the results of the three PCAs will be shown: first for LIBS spectra alone, second for Raman spectra alone, and third for concatenated LIBS and Raman/fluorescence spectra. The figures show the scores of the first (PC1) against the second principal component (PC2) on the left side and the scores of the second against the third principal component (PC3) on the right side. For better illustration each sample has its own color and the five points with the same color represent the results for the five different measurements on each sample.

Furthermore, the center of each sample group was calculated as a vector point in the three-dimensional space, which is defined by the three principal components. The mean distance between each sample point and the corresponding center point characterizes the variance of signals within a sample. It is illustrated as a bubble around the center point of each sample.

PCA with LIBS spectra:

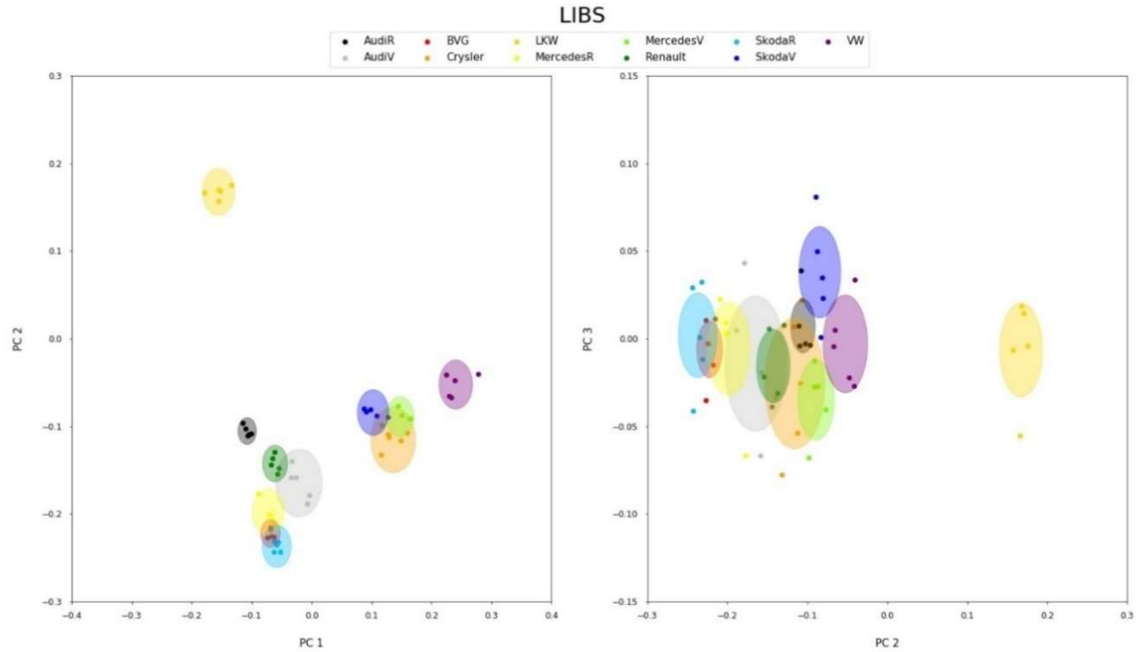

Figure 5: Scoresplots resulting from PCA of LIBS spectra alone

The results of the PCA of the LIBS spectra alone show that only the samples AudiR, MAN truck (LKW) and VW can be distinguished. Most of the bubbles overlap. Moreover, the signals show a rather large variance within one sample (illustrated by the large size of the bubbles), specially to be seen in the right plot of PC3 vs PC2.

PCA with Raman/fluorescence spectra:

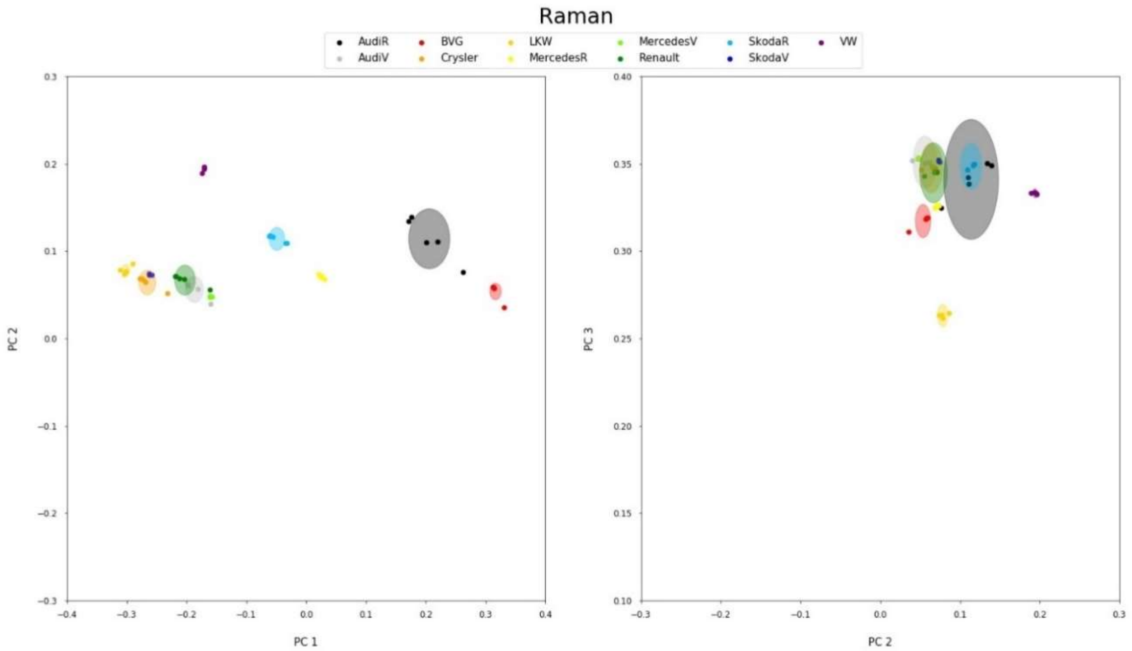

Figure 6: Scoresplots resulting from a PCA of Raman/ fluorescence spectra alone

In contrast to LIBS, with Raman the differentiation of 7 samples (AudiR, BVG, MAN truck (LKW), MercedesV, MercedesR, SkodaR and VW) is possible. Also the bubbles are obviously smaller (compare Figure 5 and 6). This means that the variance of the signals among the 5 measurements is significantly smaller.

PCA with concatenated LIBS and Raman/fluorescence spectra:

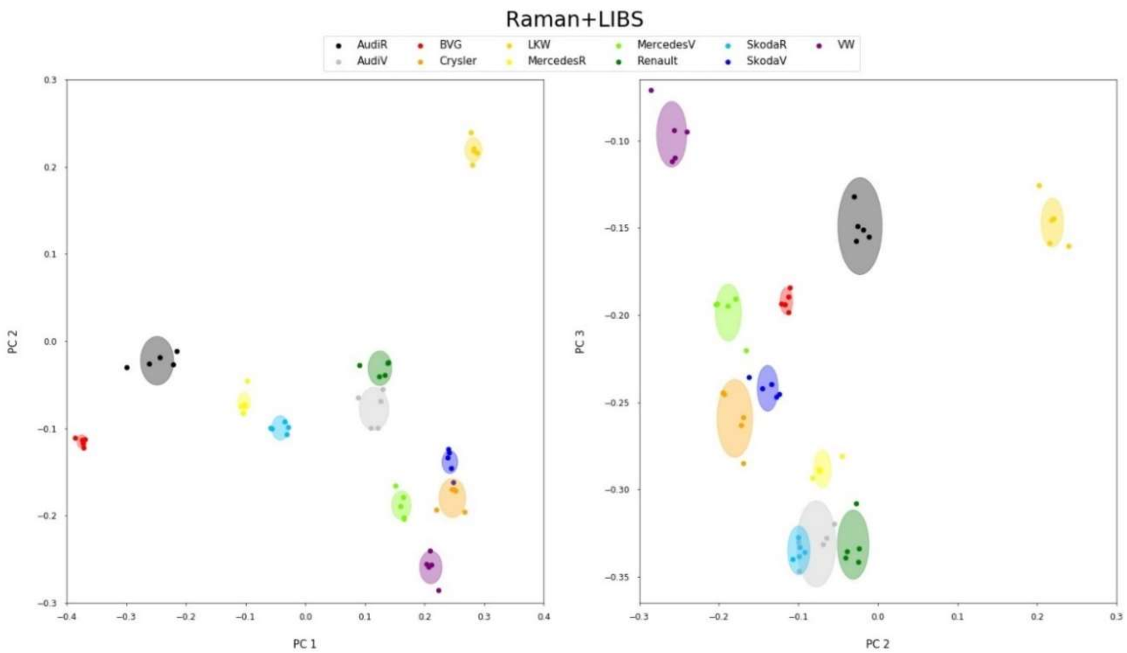

Figure 7: Scoresplots resulting from a PCA of combined Raman and LIBS spectra

When combining the LIBS and Raman spectra it is possible to differentiate all samples using three principal components. The size of the bubbles is between the ones for the LIBS spectra alone and the Raman spectra alone but the distances between the bubbles of the individual sample groups are larger which is specifically visible in the right plot (PC2 vs PC3).

Conclusion

This work shows that the CORALIS system can be used for the differentiation of automotive glass samples of various sources. Through the combination of LIBS and Raman on the same sample spot using the CORALIS system the differentiation of the glass samples was significantly improved. With CORALIS it is possible to use LIBS or Raman spectra, or a combination of both for differentiation purposes.

For the investigated car glass samples, the LIBS spectra showed mainly the presence of the elements Mg, Ca, Na, Si with different relative amounts, and in some samples, also Fe and Ti. All Raman spectra showed the typical Raman signature of glass accompanied by a sample-specific fluorescence.

The spectra were analyzed in a multivariate way using principal component analysis. This shows that the combined analysis of concatenated LIBS and Raman/fluorescence spectra by means of PCA is advantageous against an analysis based on pure LIBS or Raman spectra. The combined analysis resulted in a clear differentiation among all investigated samples. It needs to be emphasized that in the case of Raman spectra, the underlying sample fluorescence is a significant carrier of information.

Our results demonstrate the potential of the CORALIS system to solve forensic problems.

References

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[2] Almirall J, Naes B, Cahoon E, Trejos T. Elemental Analysis of Glass by SEM-EDS, µXRF, LIBS and LA-ICP-MS. Final Technical Report. 2005

[3] Pfeifer L, Damaske S, Werncke W. Investigation of Car Paint Coatings with the Combined Raman LIBS System CORALIS. http://www.ltb-berlin.de/assets/uploads/application-note-forensics_car_paint_coatings.pdf. 06.03.2020

[4] Pfeifer L, Damaske S, Werncke W, Merk V. Depth scans on car paint samples with Raman spectroscopy and LIBS. http://www.ltb-berlin.de/assets/uploads/application_note_Forensics2_depthscan.pdf. 06.03.2020