

# Application Note - Forensics 1

## Investigation of Car Paint Coatings with the Combined Raman LIBS System CORALIS

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### Introduction

The aim of this technical paper is to demonstrate the suitability of the CORALIS instrument for forensic investigations. Of particular interest in this work is the combination of Raman and LIBS spectroscopy for analyzing samples.

As a test sample, car paint was chosen. Typical analysis of car paint usually involves determining the kind of dye used as pigment, the chemical composition of the layered structures, or the nature of inorganic pigments and fillers. Well established methods for forensic applications are infrared, Raman and XRF spectroscopy. [1] All of these spectroscopic methods have their specific advantages and strengths. The CORALIS, however, provides a combination of both Raman and LIBS analysis within one instrument. Raman spectroscopy enables the investigation of the chemical constitution and LIBS of the elemental constitution of the samples on a micrometer scale. This powerful combination enables fast and reliable sample investigation at exactly the same sampling points without the need for sample preparation or realignment.

In the following section, spatially resolved measurements with Raman and LIBS are described with the aim of characterizing a previously unknown sample.

### Instrument

CORALIS is an instrument combining the advantages of two complementary spectroscopic methods: Raman spectroscopy and Laser-induced breakdown spectroscopy (LIBS).

The key hardware features of CORALIS are:

- A pulsed Nd:YAG laser (1064 nm) for LIBS with continuously variable laser energy
- Two lasers for Raman spectroscopy (532 and 785 nm) with continuously variable laser power
- Laser spot size on sample: 10 µm (Raman) and 20 µm (LIBS)
- Sample stage for X,Y,Z movement of samples with accuracy of 1 µm



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- Spectrometer: Aryelle Butterfly spectrometer (LTB Lasertechnik Berlin) equipped with a DU940P BU2 detector (Andor Technologies, Northern Ireland)
- Instrument control software “FusionRL” enabling microscopic sample imaging, data acquisition, spectra visualization, and comprehensive and advanced data analysis.

Raman spectra analysis is done with peak finding, baseline correction methods and spectra comparison using a large spectra database (KnowItAll®, Bio-Rad, USA). For LIBS spectra analysis, an element finding algorithm, spectral classification with PCA and PLS-DA and multivariate quantification methods are available.

### Material and Methods

Samples under investigation were collected on the street from residues of car accidents. The samples were used as found without any further treatment (e.g. cleaning, grinding or polishing). An example of a sample is seen in Figure 1.

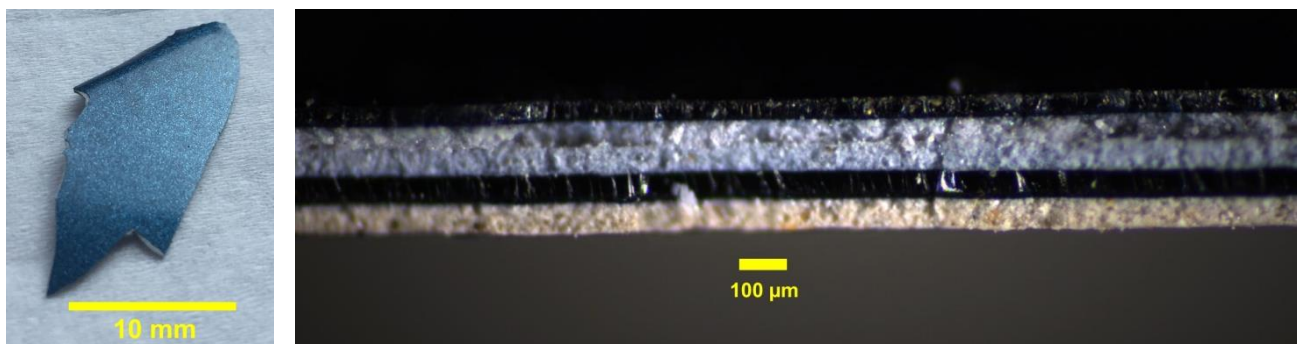


Figure 1: Car accident sample (car model: Renault Megane, collected 28.5.2019) seen from top (left) and in profile (right), sample size is appr. 27 x 11 mm, sample thickness is appr. 250 μm

Measurements in raster scan mode are done from top of the sample and in line scan mode across the profile.

Raman measurements were done with 532 nm excitation. Typically, the laser power on the sample was 2 or 3 mW. The acquisition time per spectrum was set to 100 s. Horizontal binning of the detector camera was set to 4 pixels in order to improve signal-to-noise ratio. The spectral resolution of the detector for Raman measurements was about 2.5 cm<sup>-1</sup>.

For LIBS, typically a laser energy of 3 mJ per pulse was used. Accumulation of laser pulses per LIBS spectrum was set to 5. The temporal delay of starting the signal acquisition after the laser pulse was adjusted to 1 μs in order to effectively exclude the unspecific continuous background signal from the specific elemental radiation in the plasma plume. The spectral resolution of the LIBS arm of the spectrometer was in the range of 13 to 35 pm, depending on the wavelength between 190 and 520 nm.

## Results and Discussion

A raster scan measurement of the sample in Raman mode from top as seen in Figure 2, left, resulted in 25 very similar spectra with a pronounced fluorescence maximum at a relative wavenumber of  $2240\text{ cm}^{-1}$  to the excitation wavelength of  $532\text{ nm}$  (appr.  $604\text{ nm}$ ) and Raman signatures on the rising and falling edge of the signal.

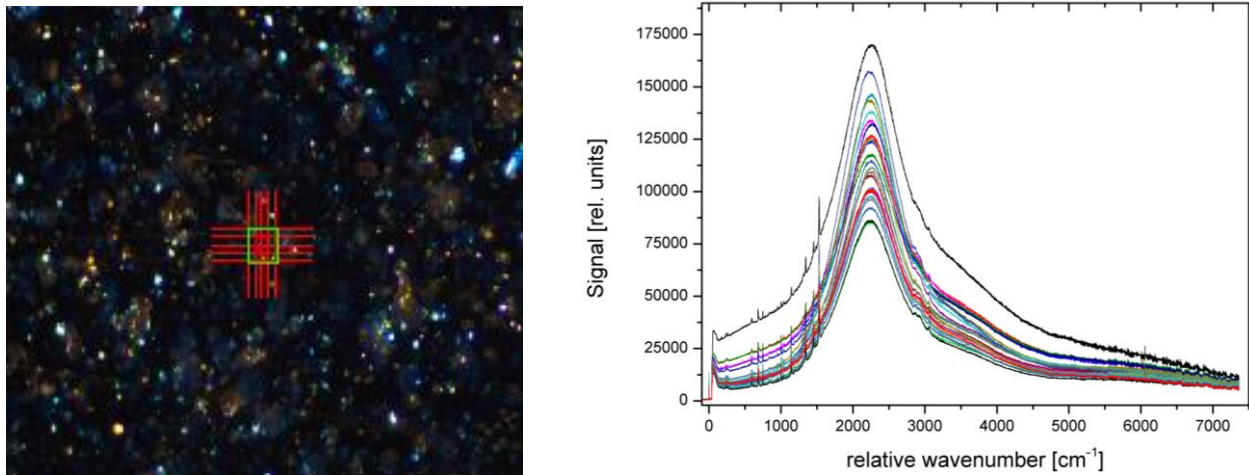


Figure 2: Detailed image of sample surface with  $10\text{ }\mu\text{m}$  spaced raster of  $5 \times 5$  sample points (left) and all 25 untreated spectra (right)

All 25 spectra were used to calculate the average spectrum. The baseline was estimated manually using the Origin software package (Version 8.5.1, OriginLab Corporation, USA) and subtracted.

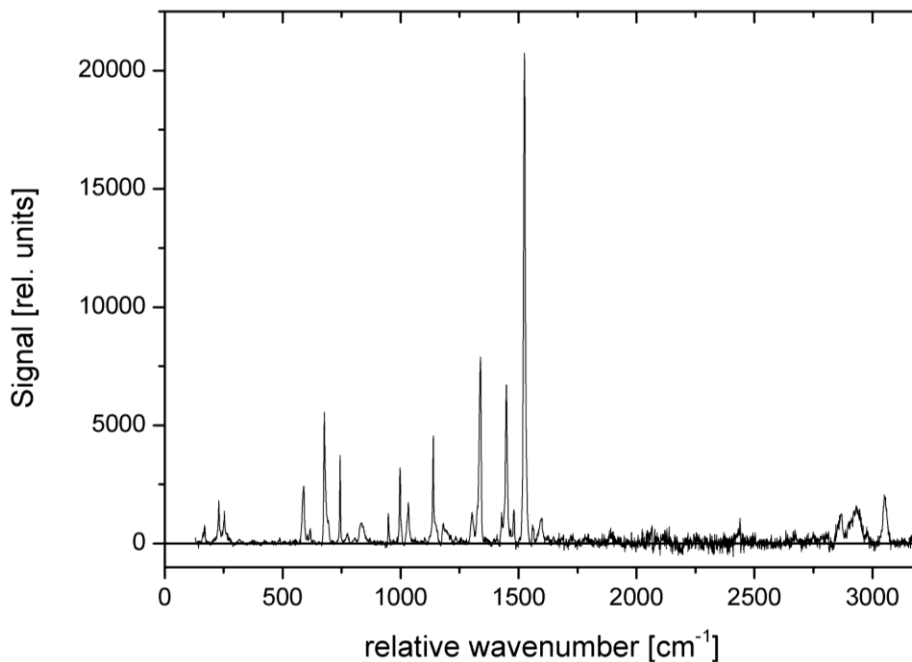


Figure 3: Baseline-corrected average Raman spectrum of car paint sample seen from top

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The KnowItAll® database search with all appr. 25000 reference spectra resulted in an 80 percent match with Cu-Phthalocyanine as best outcome.

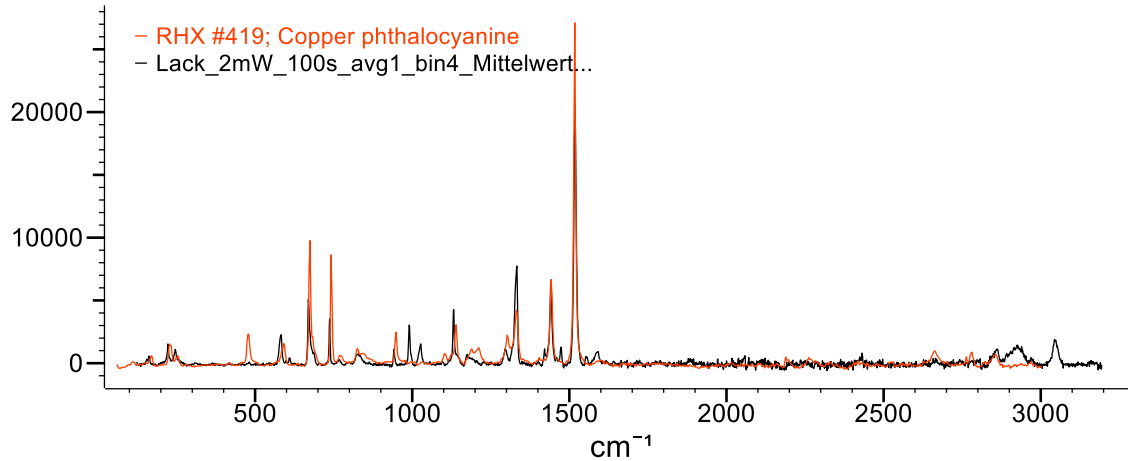


Figure 4: Best KnowItAll® database match of the on-top average spectrum

As seen in Figure 4, most peaks are in accordance between the measured and the reference spectrum. However, some structural features of the measured spectrum are not explained by Cu-Phthalocyanine. These are the bands at 997 and 1034  $\text{cm}^{-1}$ . Also, the signal structures at around 3000  $\text{cm}^{-1}$  are not well represented by the reference spectrum. In addition, the band at 480  $\text{cm}^{-1}$  of the Cu-Phthalocyanine spectrum is not found in the sample spectrum.

A database search using 2 or more components did not result in better spectral matching. The agreement of the main Raman band at 1529  $\text{cm}^{-1}$  with the reported value of 1530  $\text{cm}^{-1}$  in [2] is nevertheless a strong indication of the presence of Cu-Phthalocyanine pigment in the sample.

Next, a line scan across the side-on profile of the sample was performed, first in Raman mode and then in LIBS mode. Here the step size was set to 20  $\mu\text{m}$ .

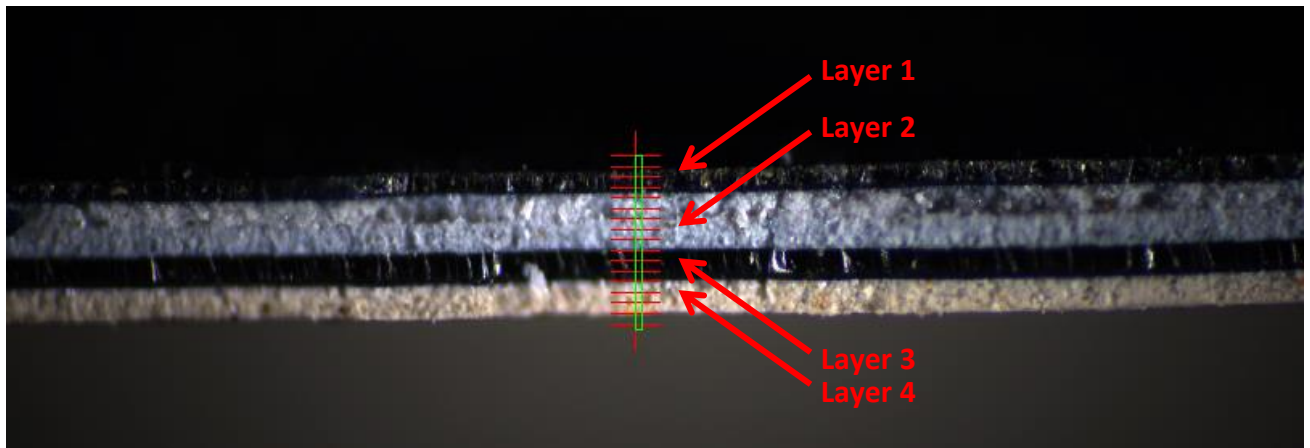


Figure 5: Detailed image of sample surface with 20  $\mu\text{m}$  spaced raster line across the sample layers



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Visually, four different layers can easily be differentiated (see Figure 5):

1. a dark layer about 50  $\mu\text{m}$  thick
2. a light whitish layer about 110  $\mu\text{m}$  thick
3. a second dark layer approximately 60  $\mu\text{m}$  thick
4. a light yellowish layer about 65  $\mu\text{m}$  thick

However, by means of the untreated Raman spectra, five different spectra types can be distinguished:

- a) Type 1 is located in layer 1 (top layer) characterized by a narrow fluorescence band at around 2200  $\text{cm}^{-1}$  and Raman bands on the rising edge of the spectrum,
- b) Type 2 is located in layer 2 and characterized by two prominent Raman bands at 448 and 611  $\text{cm}^{-1}$  and a broad fluorescence distribution between 1000 and 3000  $\text{cm}^{-1}$ ,
- c) Type 3a is located in layer 3 and only shows a sparse Raman signature on a broad fluorescence background with maximum at 15560  $\text{cm}^{-1}$ , the sparse Raman signal has a band at 1002  $\text{cm}^{-1}$ ,
- d) Type 3b is seen in only one spectrum and located at the bottom of layer 3. This spectrum type has a weak and broad fluorescence background and several Raman bands between 500 and 1600  $\text{cm}^{-1}$ ,
- e) Type 4 is located in layer 4 (bottom layer), has the largest fluorescence background and, like layer 2, has two prominent Raman bands at 448 and 611  $\text{cm}^{-1}$ .

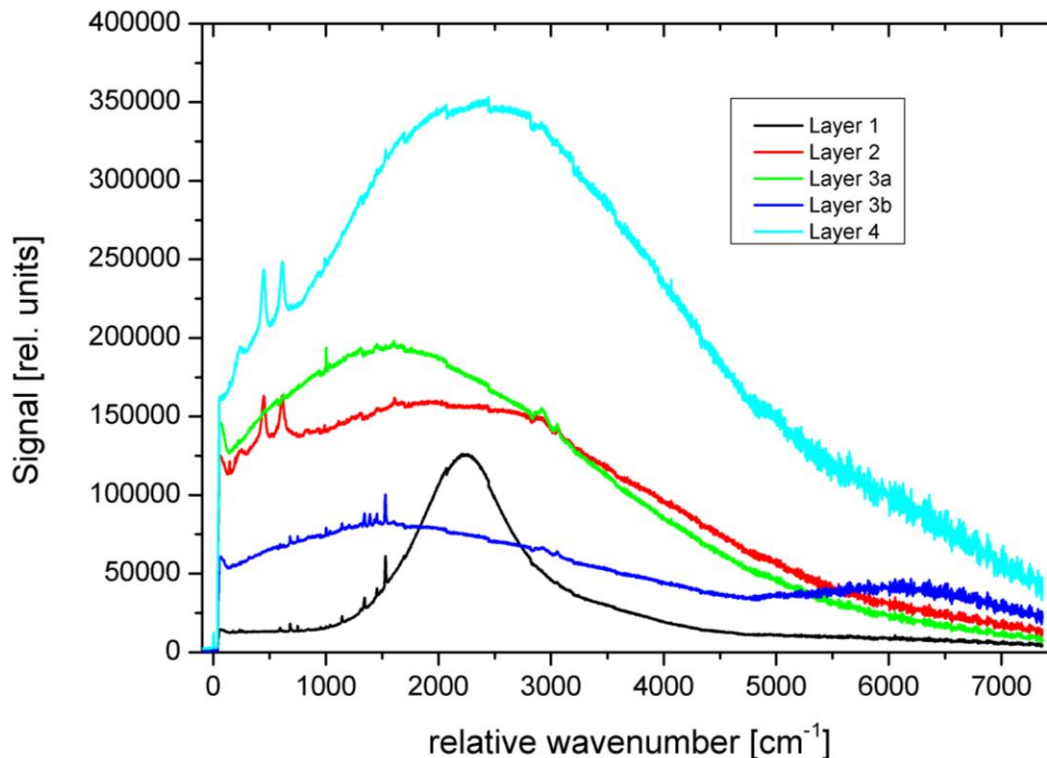


Figure 6: Five different characteristic Raman spectra across the cross-section of a car paint sample

For the analysis of the Raman spectra, all spectra were pretreated with automated baseline correction (method airPLS, see [3] for details). Table 1 below lists the results of the one component database search with

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KnowItAll® together with the maximum correlation coefficient. The comparison range was restricted to 150 - 3200 cm<sup>-1</sup>.

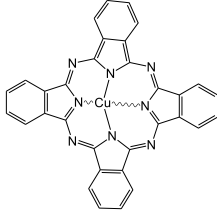
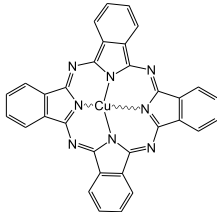
| Type of spectrum | Best database match                                | Correlation coefficient [%] | Chemical structure   |
|------------------|--|-----------------------------|--|
| Type 1           | Cu-Phthalocyanine                                  | 82,67                       |   |
| Type 2           | Rutile   | 92,98                       | TiO <sub>2</sub>   |
| Type 3a          | Clearstrength W500 (Atofina Chemicals Inc.)        | 87,99                       | -  |
| Type 3b          | Irgalith Blue<br>Chemical Class: Cu-Phthalocyanine | 77,26                       |  |
| Type 4           | Rutile   | 96,91                       | TiO <sub>2</sub>   |

Table 1: Results of Raman spectra analysis of the 5 different types of spectra

From Table 1 it seems probable that both type 1 and type 4 spectra mainly consist of Cu-Phthalocyanine. However, due to the high background fluorescence and the need for baseline correction, the signal-to-noise ratio is not sufficient for a more precise determination of the chemical nature of the layers.

In order to verify if Cu-Phthalocyanine is indeed the dominating dyeing agent within the car paint, a LIBS-line scan was performed on exactly the same line where the Raman scan was performed. Figure 7 shows the sample after performing the LIBS line scan measurement.

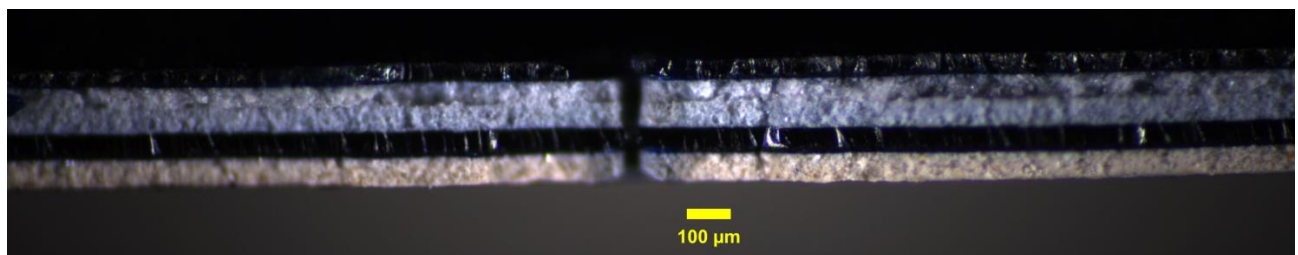


Figure 7: Car paint sample after LIBS line scan with 20 µm step width

The line where sample material is ablated by the laser pulses is clearly visible. The cross-section is V-shaped with a width at the bottom of about 50 µm.

Figure 8 (left) shows an example LIBS spectrum obtained from layer 2 (spectrum at position 6).

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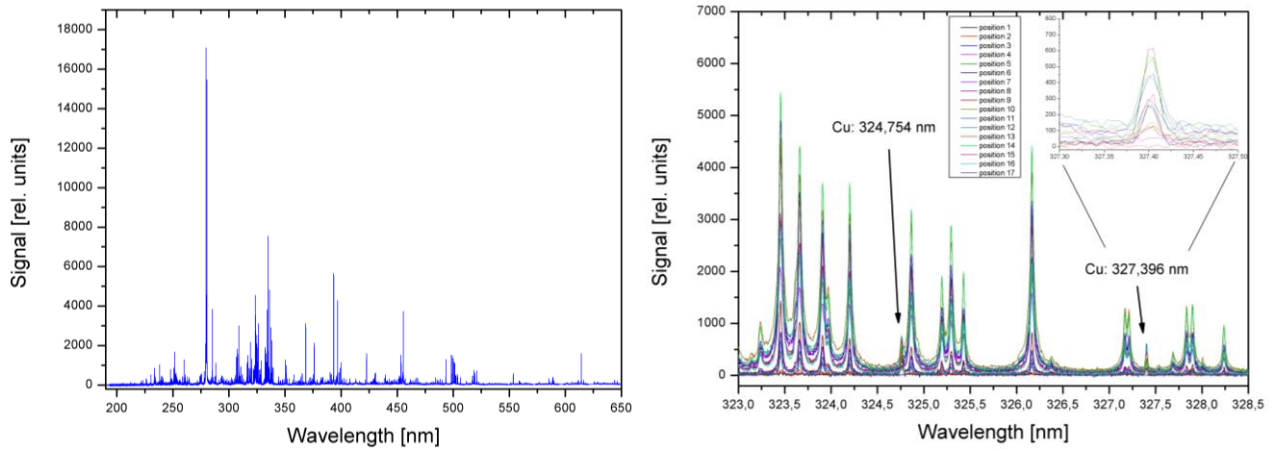


Figure 8: Left: LIBS spectrum of the 6th sample point across the side of the car paint sample; Right: Detail of LIBS spectra at all 17 sample positions with marked Cu-lines

The analysis of the elemental lines within the LIBS spectra revealed that among others these elements contributed to the spectra: C, Ti, Si, Ba, Fe, Mg, Ca, Zn and Cu.

Cu has the strongest lines at 324,754 nm and 327,396 nm according to the NIST database. A zoom into the overlaid 17 LIBS spectra (Figure 8, right) shows that in order to analyze the relative Cu distribution across the sample the line at 327,396 nm is better suited than the line at 324,754 nm, which is found as a shoulder on a much more intensive Ti line at 324,860 nm.

In order to analyze the elemental distribution across the sample line integrals were estimated. For example, Figure 9 shows the elemental distribution of Cu, Ti and C across the sample cross section. All three elements show a different distribution: C is quite evenly distributed; Ti has pronounced maxima around positions 7 and 14; and Cu has maxima at positions 3 and 12.

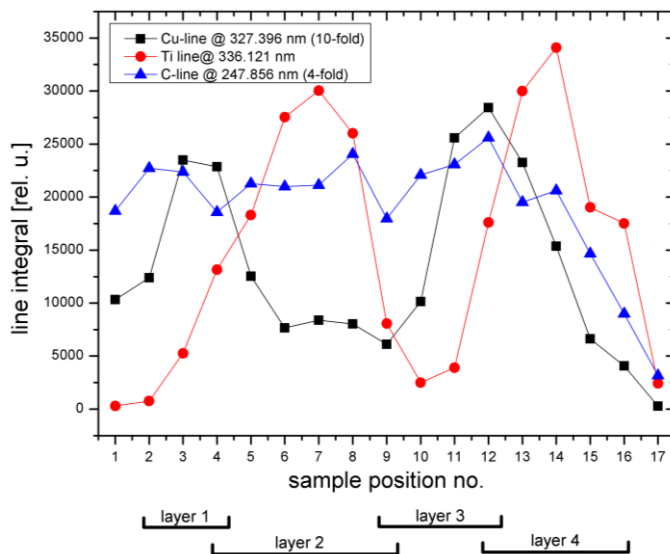


Figure 9: LIBS line integrals according to measurement position on the sample. Note: Cu-line intensity is magnified by 10 and C-line intensity by 4

This distribution pattern is in excellent agreement with both the sample geometry and the Raman line scan. Cu is found mainly in layers 1 and 3 (refer to Figure 5), where the second Cu maximum is at the base of layer 3, corresponding to type 3b of Raman spectra. Ti is found mainly in layers 2 and 4 as already suggested by the Raman spectral analysis where Rutile (TiO<sub>2</sub>) was identified. The broader first maximum of the Ti distribution indicates the larger width of layer 2 in comparison to the three other layers. The smooth distribution of C indicates the organic composition of all four layers of the sample.

The signal distribution of the metals is broadened in comparison to the actual widths of the individual sample layers. This is due to the fact that the focus diameter of the Nd:YAG laser on the sample surface is nearly 20 µm. The resulting crater after a single measurement has an even larger diameter. Nevertheless, the sample structure with the individual layer thicknesses is impressively mirrored in the Raman and LIBS signal distribution.

## Conclusion

It has been shown that the combination of LIBS and Raman spectroscopy is able to provide more information than either method by itself. One particular advantage is the possibility to perform consecutive measurements at the same sample points with either measurement technique, which offers a multiplicity of analysis opportunities to the experimenter.

Within this work, simple line scans were performed with both methods. They resulted in the confirmation of Cu-Phthalocyanine as the major pigment in this car paint sample. Also, the distribution of several elements, including Cu and Ti, in the cross section of the sample was revealed. All measurements were executed with a spatial resolution of 10 to 20 µm for Raman spectroscopy and 20 to 30 µm for LIBS.

In the next step of this experimental series, the depth profiling of samples will be investigated. LIBS measurements and the necessary material ablation they cause will be used to penetrate samples. Using alternating Raman and LIBS measurements at one or several points, the sample can be progressively scanned from the surface to points well below it and analyzed with both spectroscopic techniques.

## References

- [1] Zieba-Paulus J, Borusiewicz R. Examination of multilayer paint coats by the use of infrared, Raman and XRF spectroscopy for forensic purposes. *Journal of Molecular Structure*. 792–793. 2006. p 286-292
- [2] Bovill AJ, McConnell AA, Nimmo JA and Smith WE. Resonance Raman Spectra of  $\alpha$ -Copper Phthalocyanine. *J. Phys. Chem.* 1986. 90. p. 569-575
- [3] Zhang Z-M, Chen S, Liang Y-Z. Baseline correction using adaptive iteratively reweighted penalized least squares. *Analyst*. 2010. 135. p 1138–1146