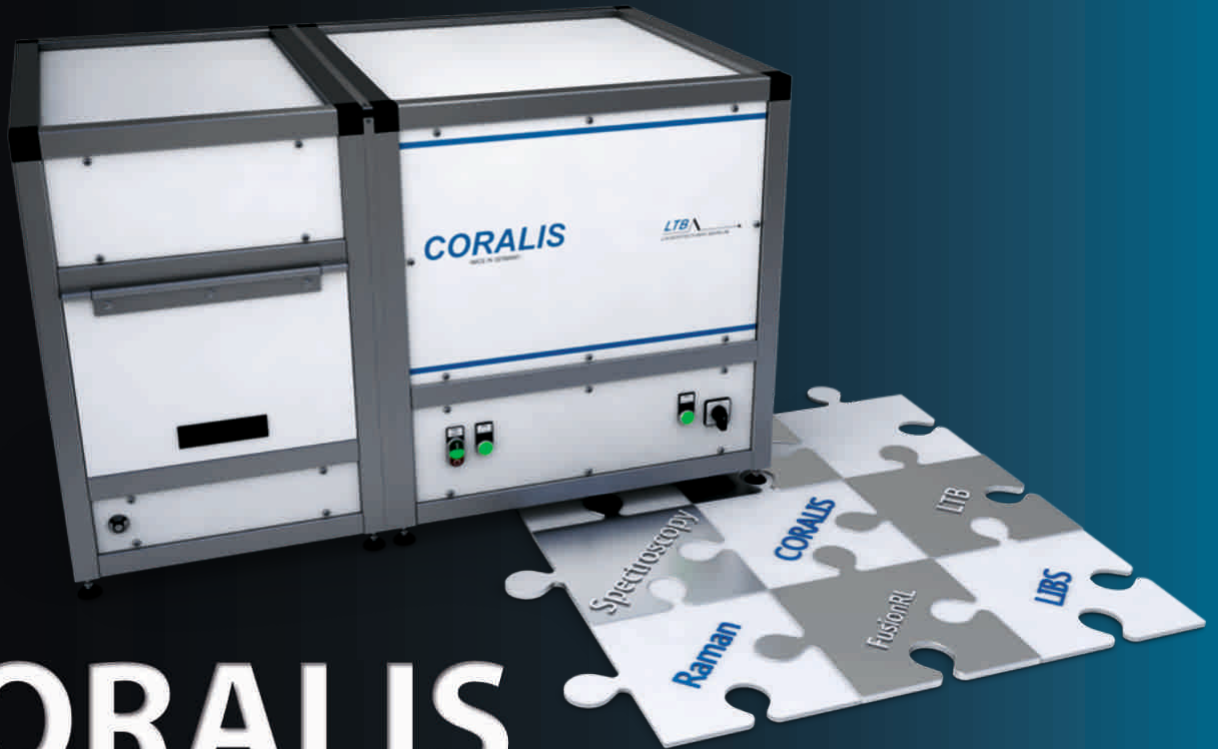


LIGHT. PRECISION. ANALYTICS



# CORALIS

Combined Raman LIBS System



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# CORALIS

## Combined Raman LIBS System

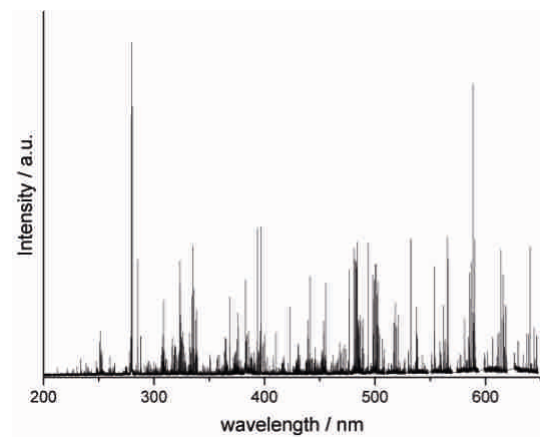
The CORALIS system unites the two high complementary spectroscopic techniques LIBS and RAMAN. The combination allows the determination of elemental and molecular and/or structural composition of a sample on the same sample spot. With CORALIS single and multiple point measurements or large area maps pre-selected from the high quality sample image are possible. Solid and liquid samples can be analyzed either with Raman or LIBS or with both methods sequentially. The ablative nature of LIBS qualifies the instrument for depth profile investigations. The unique two-wing echelle spectrometer as core part is able to provide high spectral resolution, large detection range and high light-throughput on an unrivaled level. The robust housing and the integrated interlocking circuit ensure safe handling of the device and protection of the installed components. Due to the exceptional combination of imaging, molecular and elemental analysis CORALIS provides unique advantages for applications in many fields e.g. technical cleanliness, forensics, geology and battery research.

### What can I analyze?

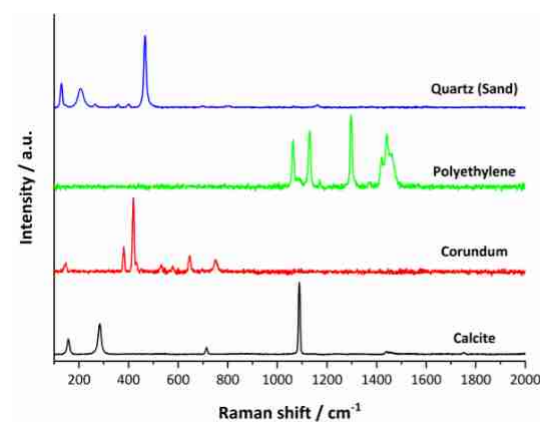
- Solids and liquids
- Particles (automated particle analysis)
- Flat and uneven surfaces
- Ø 50mm accessible sample area
- Ø 10µm (Raman) and 20µm (LIBS) laser spots

### What kind of information can I get?

- Elemental and structural sample composition
- Quantitative analysis of trace elements
- Material classification of unknown samples
- Analysis of layer structures
- Cluster analysis
- Depth profiling of elemental distributions
- Technical cleanliness analysis including particle size



Exemplary LIBS spectrum.



Exemplary Raman spectra of particles from different materials.

## Raman and LIBS - two complementary methods...

Laser-induced breakdown spectroscopy (LIBS) utilizes laser ablation and the subsequent atomic emission from the generated plasma for elemental analysis. Short pulse laser radiation that is focused on the surface of a sample causes a local heating of some 10,000 °C and leads to the generation of a light emitting plasma - consisting of atoms and ions of the ablated material. The spectral analysis of characteristic atomic and ionic emission lines allows the determination of the elemental composition of the sample. Laser ablation is at present the only method for elemental analysis that offers direct sampling from any kind of material (solids, liquids, gases) without sample preparation.

In Raman spectroscopy inelastically scattered light from the sample is detected to acquire information about the molecular structure, and is well established in a vast variety of material-specific applications in science and industry. The combination of Laser-induced breakdown spectroscopy (LIBS) with Raman spectroscopy allows to gain information on the elemental as well as the molecular composition or crystal structure of a sample. Due to the small laser spots (approx. 10 µm for Raman and 20 µm for LIBS) and high-precision stage the information could be obtained with very high spatial resolution.

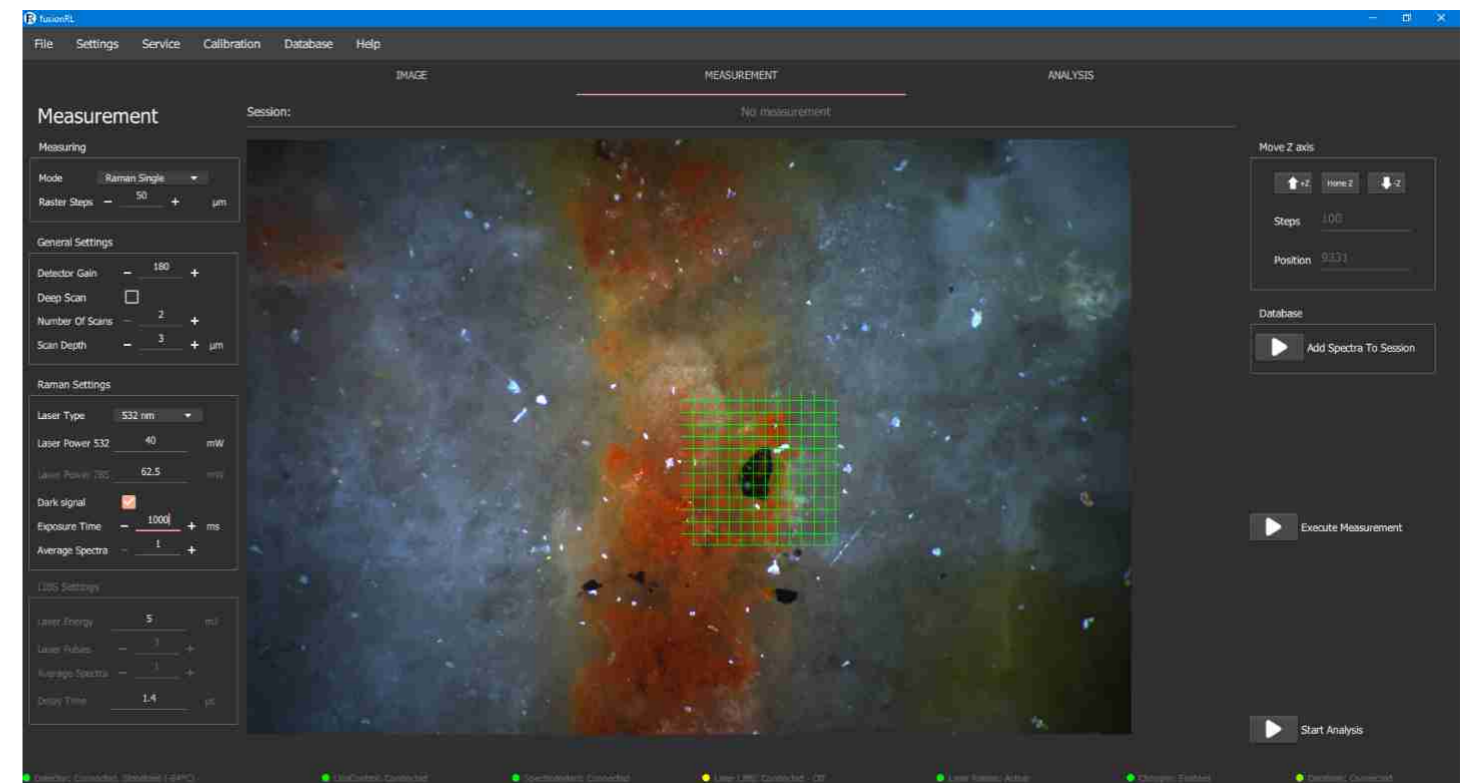
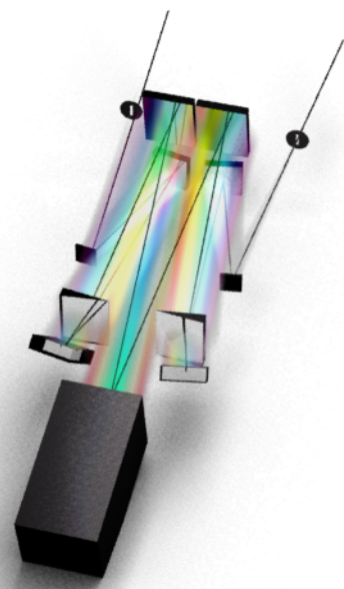
- **Two methods in one instrument**
- **Complementary information on the same spot**
- **Contact-free and almost non-destructive**
- **Spatially- and depth-resolved analysis**

## Enabling technology: Large-range and high-resolution spectroscopy...

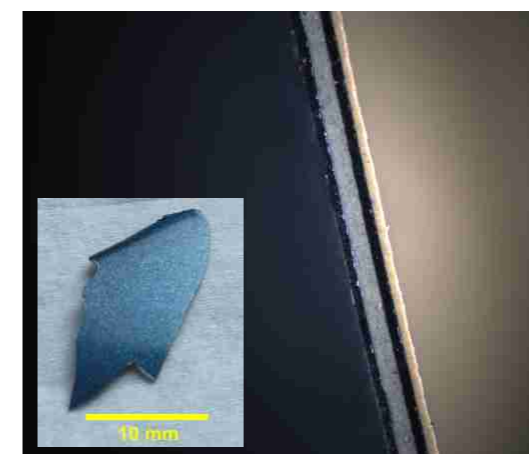
The unique two-wing echelle spectrometer as core part is able to provide high resolution, large range and high light-throughput on an unbeatable level. It combines two separate ARYELLE 400 spectrometers that sequentially illuminate one shared detector in a compact housing – a cost-efficient solution covering a wide spectral range with a very high spectral resolution. Each spectrometer part of the ARYELLE-Butterfly features an aperture of f/10 and a focal length of 400 mm. Both dispersion units consist of echelle grating, prism, imaging optics and entrance slit. The primary use of reflection optics with broadband UV layers prevents chromatic aberrations. The optical and mechanical concept leads to a compact, thermally and mechanically extremely stable instrument. The automatic recalibration of the wavelength scale is carried out by means of a mercury lamp.

- **High-resolution Spectroscopy**
- **Optimized spectral ranges for Raman and LIBS**
- **High sensitivity due to high light-throughput**
- **Large simultaneous wavelength range**

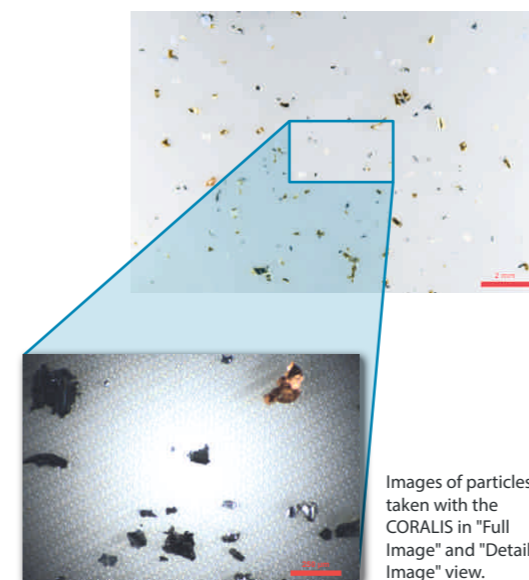
Optical beam path of the two-wing echelle spectrometer.



User interface of the operating and evaluation software FusionRL.



Micrographs of automotive paint samples taken with the CORALIS.

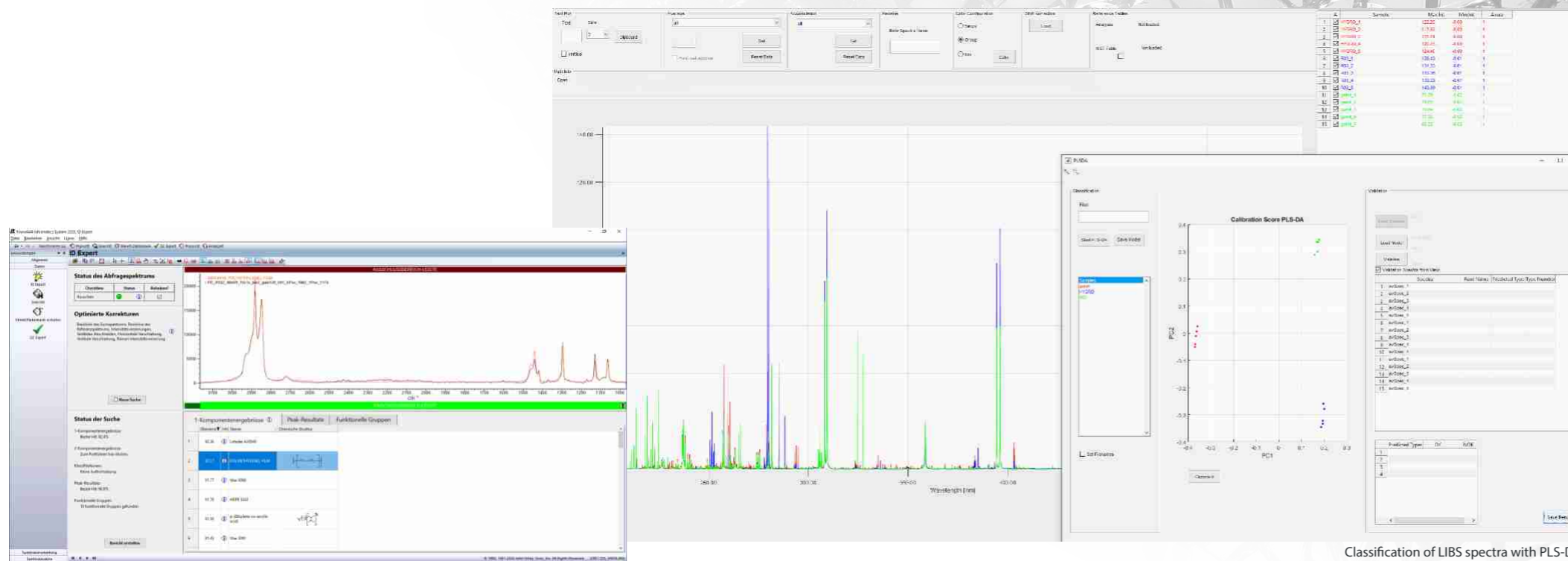


Images of particles taken with the CORALIS in "Full Image" and "Detail Image" view.

## Intuitive instrument operation and easy sample handling...

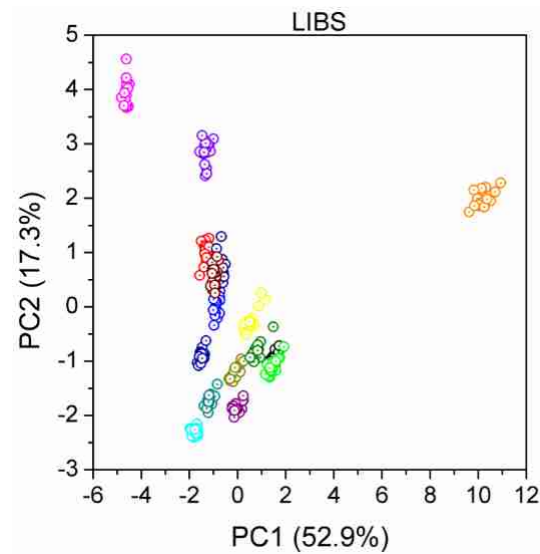
The CORALIS instrument is equipped with the user friendly software FusionRL for interaction of the user with the instrument as well as basic automated data analysis. Whether in manual or automatic mode, all functions are available and flexible to use. The CORALIS delivers both: a highly resolved overview and a detailed close-up image with magnification levels of 10x and 80x using an automated CMOS-based 6 Mpixel camera and two microscopic objectives. The build-in xyz-stage ensures a precise and reliable positioning of the sample. Integrated imaging analysis algorithms provide automatic particle recognition as well as analysis of particle size, size distribution and particle counting. Based on the image, the user can define with a few mouse clicks single or multiple regions of interest by selecting single points or square areas with defined sample point distance. Alternatively, the user can simply define individual sampling pattern based on relative coordinates. Together with the depth scan feature, the system provides nearly unlimited possibilities for real 3-dimensional sample investigations. For the measurement the user can select from six different modi: single or continuous Raman or LIBS measurements and subsequent Raman-LIBS-measurements (first LIBS than Raman and vice versa). After definition of the measurement parameters the measurement is performed automatically. Rapid material analysis with Raman and LIBS has never been so easy. The functional range of FusionRL is enormous.

- **Intuitive user guidance from sample image to analysis result**
- **Sample positioning with µm resolution**
- **High quality sample imaging with two magnification levels (10x and 80x real magnification)**
- **Automated particle recognition**

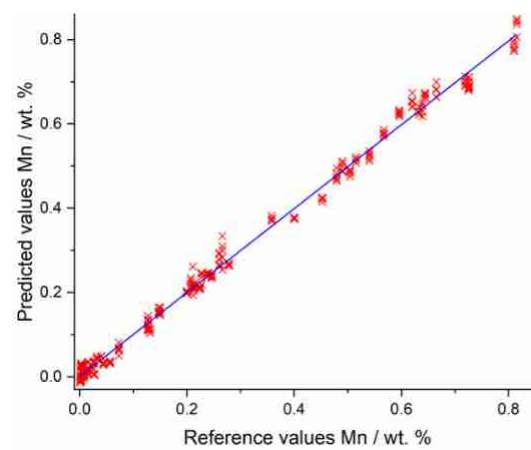


Classification of LIBS spectra with PLS-DA.

Comparison with the KnowItAll database allows identification based on measured Raman spectra.



PCA analysis of LIBS spectra for differentiation of samples.



Calibration curve of Mn for quantitative analysis with LIBS.

## High-end data analysis...

Besides the instrument operation, the FusionRL also incorporates a large variety of data analysis methods. A simple and common one is the identification of elements that are present in the generated LIBS plasma by comparing the observed emission lines with the integrated NIST emission line catalogue. Also for Raman, an extensive set of comparison data is offered. Beside the RUFF database, FusionRL has a user-friendly data exchange with the well-known Wiley software KnowItAll® comprising one of the world's largest Raman reference spectra database. The user has access to a wealth of data manipulation routines, spectra identification and report generation.

In addition, FusionRL offers various univariate and multivariate analysis methods e.g. PCA, PLS-DA, cluster analysis or PLS regression. With that, the user can accomplish ambitious tasks like establishing calibration methods for various material classes (e.g. aluminum, steel), classification models for material analysis or chemical imaging.

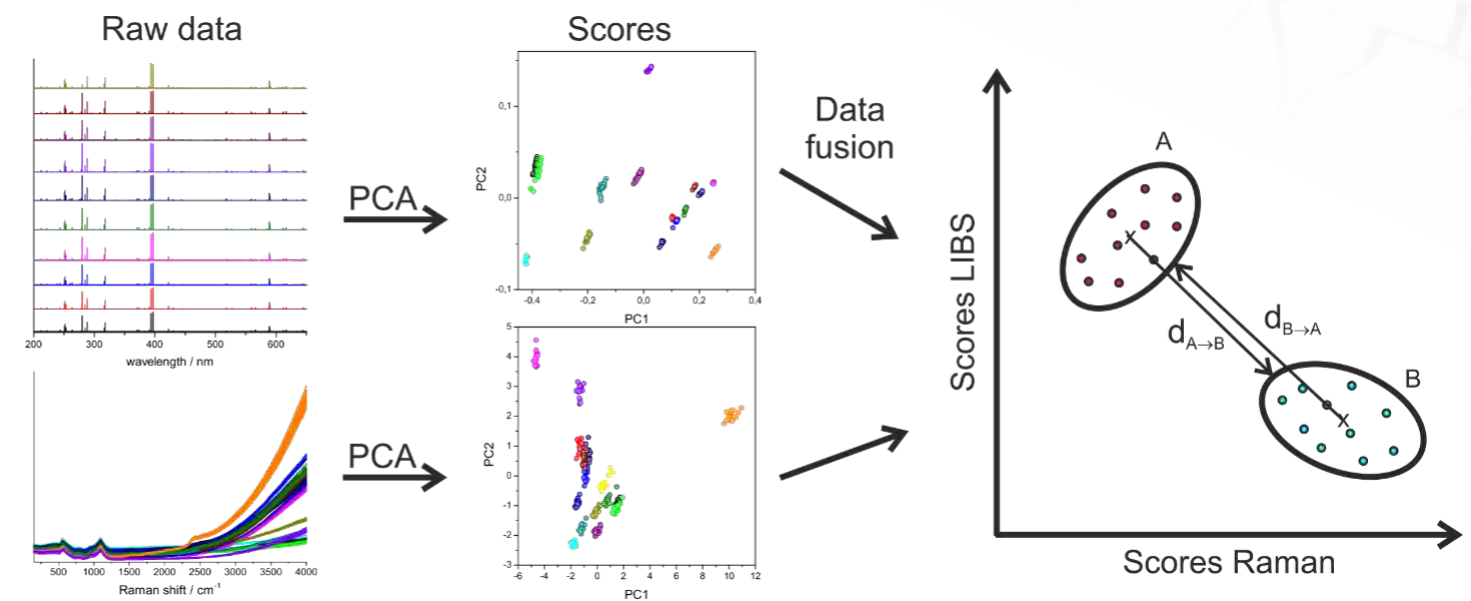
The seamless combination of Raman and LIBS increases the identification rate of unknown samples significantly in comparison to identification by a single technique. Moreover, due to new strategies based on intelligent data fusion routines, the information gain out of the spectra is more than just the sum of LIBS and Raman.

At the end, all instrument settings, measurement parameters and results are fully elaborated in an automatically generated report.

- **Elemental and molecular /structural identification**
- **Material classification**
- **Quantitative element analysis**
- **Very large Raman reference spectra database**
- **LIBS-Raman-data fusion**
- **Choice of pre-defined or user controlled data analysis methods**

## Forensics: Discrimination of automotive glass...

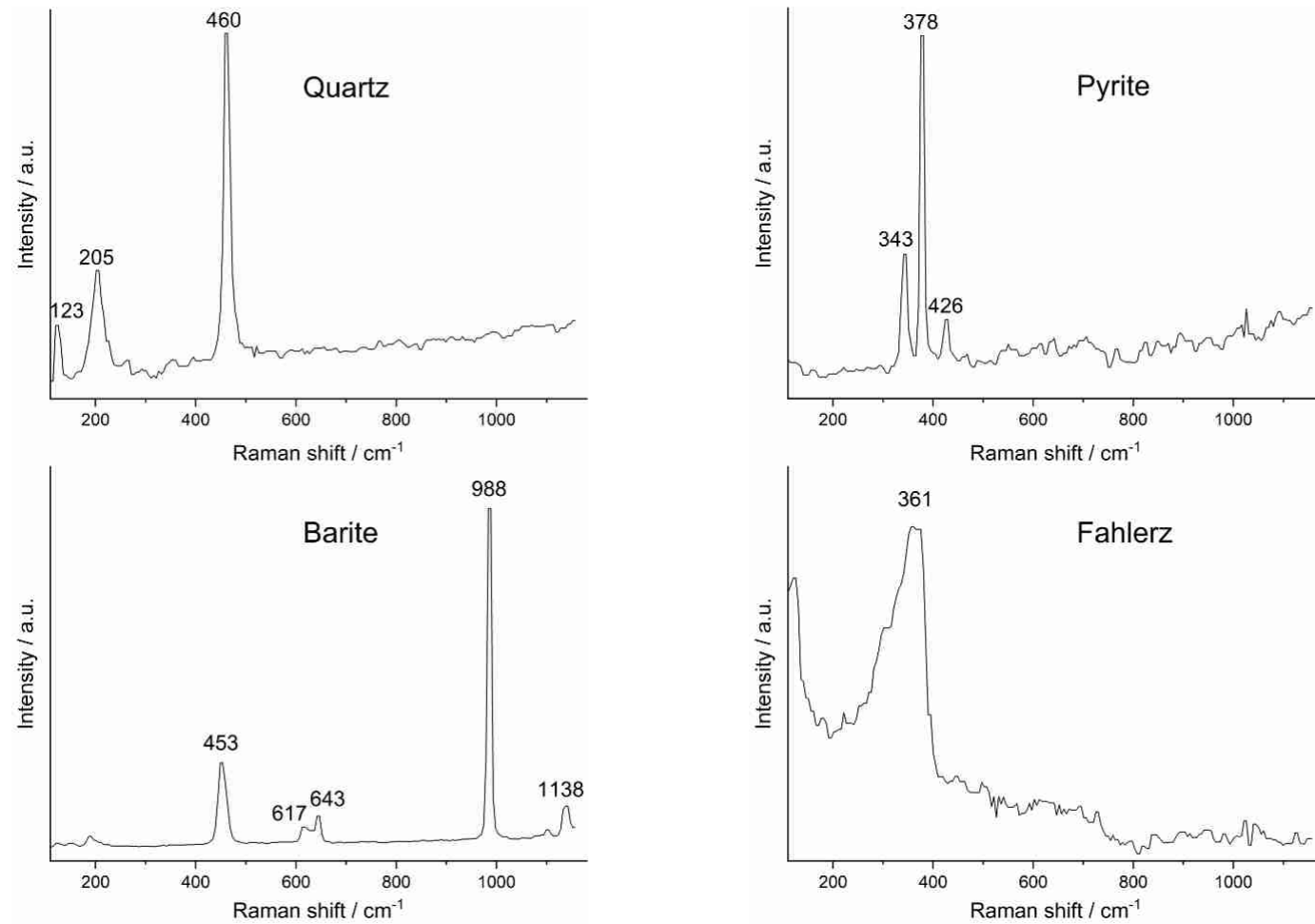
The discrimination of samples found at a crime scene is an important task in forensic investigations. Through the combination of laser-induced breakdown spectroscopy (LIBS) and Raman spectroscopy and high level data fusion we have been able to discriminate sixteen different glass samples by principal component analysis (PCA). Very good discrimination (up to 99 %) was achieved with conjoint LIBS and Raman and high level data fusion. The discrimination is based primarily on different contents of trace elements (e.g., Fe, Ti, Ba, Sr) detected by LIBS and differences in fluorescence and photoluminescence detected by Raman. The results were compared to results obtained with the single methods (LIBS and Raman). This showed that LIBS and conjoint LIBS and Raman have similar discrimination power, but the combination and fusion of LIBS and Raman leads to greater distances between the data in the principal component space due to the additional information added by Raman. This should result in a lower misclassification rate of unknown samples.



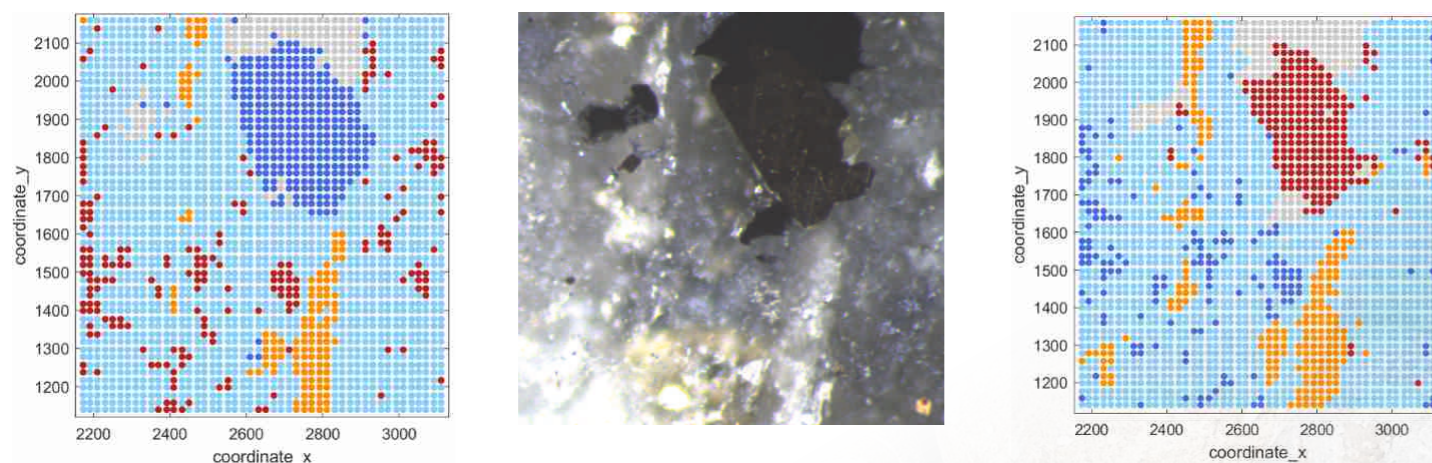
Approach to differentiate automotive glass samples by conjoint LIBS-Raman measurements and high level data fusion. Merk et al., Spectrochim Acta B, 180 (2021)

## Geology: Investigation of rock samples...

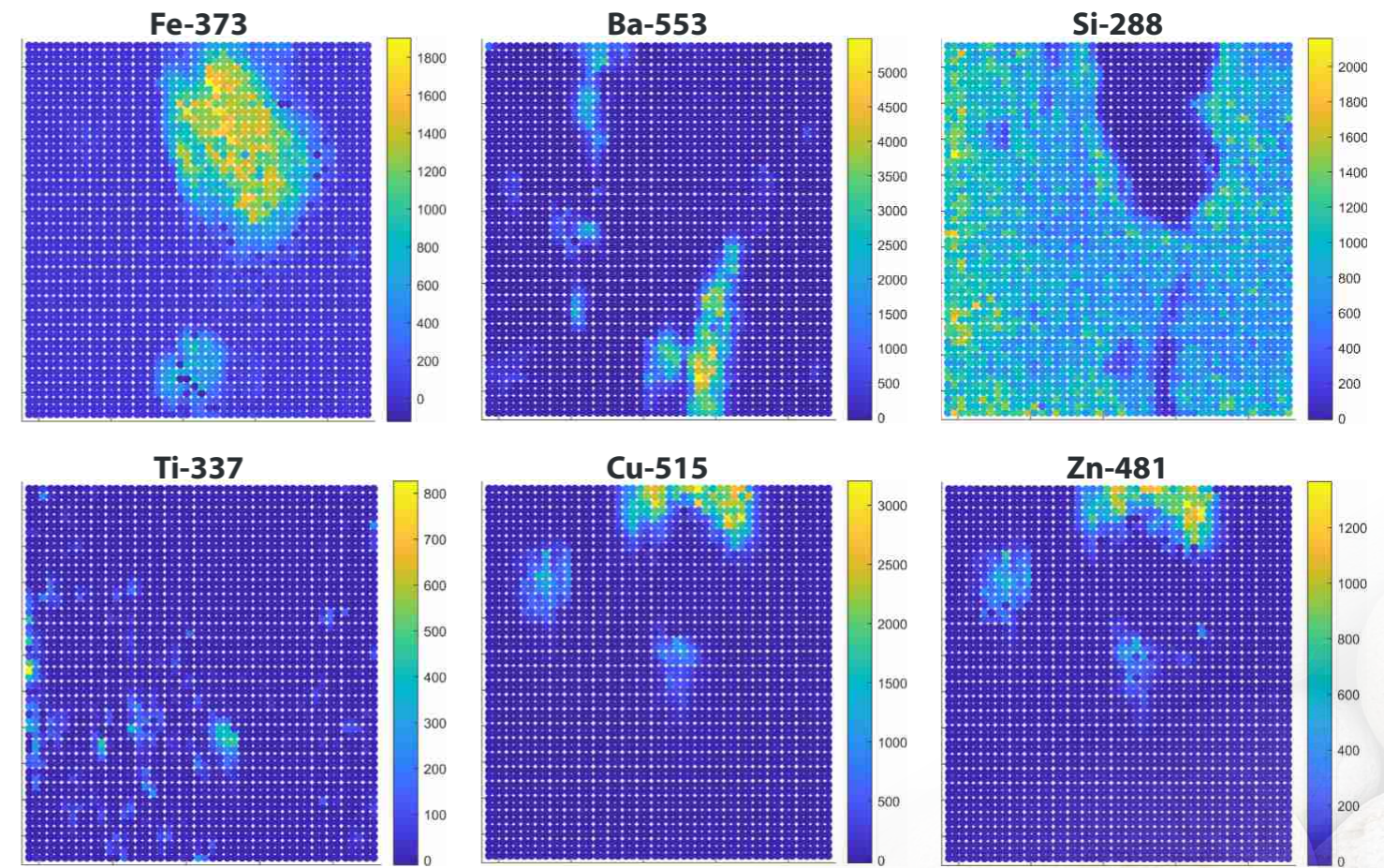
Knowledge of the elemental distribution as well as the mineral phases of large rock areas is an important task in geology. Due to the possibility to obtain LIBS and Raman spectra at the same spot with the CORALIS instrument the combined elemental and structural composition of large areas of rock samples can be determined. As an example Raman spectra of the different minerals detected on a rock sample and the distribution of selected elements determined from the LIBS spectra are shown. By use of k-means clustering, areas with similar elemental or structural composition can be grouped automatically and their distribution on the investigated area can be visualized. The subsequent investigation of the mean group spectra enables classification of the elements or minerals, respectively. In addition, the combination of the LIBS and Raman data enables a correlation of the elemental composition with the mineral phases.



Exemplary Raman spectra of different minerals detected on a rock sample.



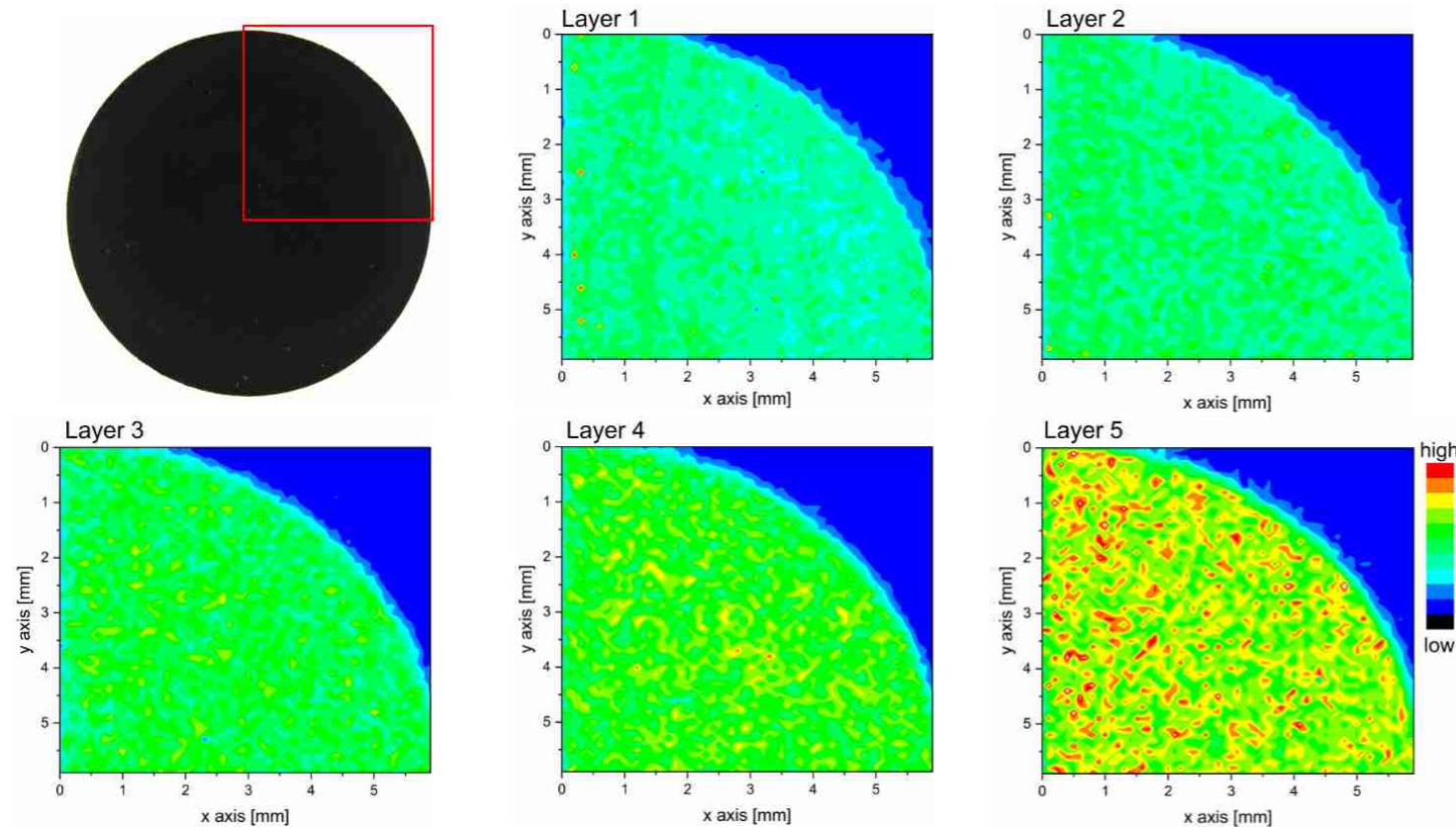
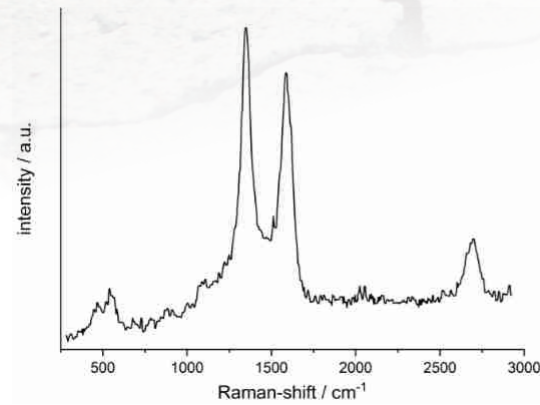
k-means map of Raman spectra (left) and LIBS spectra (right) measured in the area displayed in the middle picture. The colors in the map indicate areas with similar elemental and structural composition, respectively, found by the k-means algorithm.



Intensity maps of different LIBS lines reveal the spatially resolved elemental distribution on large sample areas.

## Battery Research: Depth resolved mapping of electrode material...

Li-Ion batteries consist of metal ions incorporated in a graphene layer structure. Investigation of the distribution of the metal ions as well as the incorporation of the metal ions in the graphene structure delivers essential information for the development of new electrodes, for the quality control as well as for the recycling of such materials. With the CORALIS instrument it is possible to obtain elemental as well as structural information on the same positions allowing the correlation of the two information. Due to the fact that LIBS removes a small amount of the sample subsequent LIBS and Raman measurements allows to obtain the information layer by layer giving a 3D-characterisation of the sample. With Raman information can be obtained on the metal complex as well as the graphene structure. Especially the ratio of the D and G bands around  $1300\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  and the splitting of the G band gives information about the intercalation of the metal ions into the graphene structure. Below a micrograph of an electrode as well as the 3D distribution of lithium determined by measuring five LIBS maps subsequently is displayed.



Intensity of the lithium line at 497.175 nm determined from the LIBS spectra of five subsequent measurements on the same area.

## Specifications

Measuring technique	LIBS	Laser induced breakdown spectroscopy for qualitative and quantitative multi element analysis	
	Raman	For analysis of molecular or crystal structures	
	Imaging	Particle detection Particle size Particle area	
Compatibility	To JOMESA HFD and JOMESA PSE regarding the transfer of spatial coordinates of particles Enables precise approach to particles previously measured with JOMESA		
	Sample formats	Solid	Bulk samples, any shape, (minimum sample size up to $50 \times 50 \times 30\text{ mm}^3$ is guaranteed), Particle on particle carrier (filter)
LIBS	Liquid	In the sample vessel (cuvette, Petri dish, multiwell plate, etc.)	
	Wavelength laser	1064 nm	
Raman	Impulse energy on sample	1.5 - 50 mJ, stepless	
	Wavelength range	193 nm - 520 nm	
	Spectral resolution	13 pm - 35.8 pm	
	Wavelength laser	532 nm and 785 nm	
Raman	Laser power on sample	0.5 - 50 mW, stepless	
	Detection range	532 nm: $100 - 4,000\text{ cm}^{-1}$ 785 nm: $100 - 3,000\text{ cm}^{-1}$	
	Spectral resolution	532 nm: $2.5 - 2.0\text{ cm}^{-1}$ 785 nm: $1.7 - 1.4\text{ cm}^{-1}$	
XYZ - Stage	Travel range	X = 50 mm; Y = 50 mm; Z = 35 mm	
	Resolution	1 $\mu\text{m}$	
	Repeatability	1 $\mu\text{m}$	
Sample imaging	CMOS camera	6 Mpixels	
	Overview image	Field of view (28 x 19) mm	
	Detail image	Field of view (3.5 x 2.5) mm	
General properties	Dimensions	1200 mm x 750 mm x 750 mm	
	Weight	225 kg	
	Laser safety	Class 1	
	Software	Measurement methods	Single measurement
Software		Continuous single measurement	LIBS Raman
		Multipoint measurement	LIBS Raman LIBS/Raman Raman/LIBS
		Mapping	LIBS Raman LIBS/Raman Raman/LIBS
Software		Depth profile combined with single and multi-point measurements, mapping	
	Data security	Integrated NAS with mirrored hard drive (2 x 8 TB) Database for automatic filing and management of data	
Analysis	LIBS	Element analysis (NIST database emission lines) Material classification (PCA or PLS-DA) Material quantification univariate Material quantification multivariate (PLS, Lasso)	
	Raman	Baseline correction Peak identification Database comparison for sample identification Compatibility with Wiley KnowItAll® software	
Accessory parts	Standard samples	Reference materials for LIBS and Raman integrated on the sample table	