

Summary of PhD thesis entitled “Application of Raman spectroscopy in blue car paints analysis - evaluation of evidential value of spectra using visual analysis and by application of statistical and chemometrics approaches”

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Verification of the hypothesis about common origin of recovered and control samples conducted within a comparison problem is one of the most important tasks forensic experts face. Till now such a verification for paint samples described by Raman spectra was usually carried out using highly subjective visual spectra comparison. Such an approach seems to be sufficient only when compared spectra are quite different whereas seems to be pointless in case of very similar spectra. What is more, visual examination does not allow to express evidential value of similarities and discrepancies delivered by such spectra, which is crucial from the forensic perspective. Therefore for making a decision within a comparison problem in the forensic field more objective methods like likelihood ratio (LR) approach are recommended. However, till now LR methodology was not applied in Raman spectra interpretation due to the problem of data dimensionality.

Three methods of data dimensionality reduction which still keep significant information about the analysed samples were discussed. In the first approach areas under the selected pigment bands were used as a new set of variables. In the second approach discrete wavelet transform procedure was used while in the third one Raman spectra were shown in distance representation (Manhattan, Euclidian, square Euclidian, Chebyshev and Pearson correlation coefficient distance) and then linear discriminant analysis was performed. New sets of variables selected upon each procedure were further used for univariate and multivariate LR models construction, which correctness was checked based on the levels of false responses and Empirical Cross Entropy results. Apart from making the evaluation process more objective, it was also stated, that regardless of the applied data dimensionality reduction methodology, multivariate LR models delivered better or at least comparable results to those yielded during visual spectra comparison. In addition these models, in contrary to visual examination, allow to include also the information about inhomogeneity of paint samples influence on the within-object variability.

Analysis of photobleaching process is also noteworthy as it demonstrates its usefulness in obtaining informative Raman spectra for automotive paints, which in ordinary Raman measurements were characterized only by fluorescence.

The evaluation of analytical parameters which could influence the conclusions when solving the comparison problem with the use of likelihood ratio approach is the pioneering element of the thesis. It was stated that for focusing the laser on the surface of both recovered (unknown) and reference samples during Raman measurements, 50× objective magnification should be used. In the case of fluorescent paints the photobleaching pre-treatment may be successfully used prior to normal Raman measurements in such a way that having established one parameter for control and recovered sample e.g. laser power, the second parameter, e.g. time of irradiation does not have to be strictly controlled.

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