APPLICATION OF SERS SPECTROSCOPY FOR FORENCIC ANALYSIS OF DOCUMENTS

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Modern tools of falsification of written documents are rapidly improving, it becames easy to forge documents and are difficult to detect.There are chemical methods that allow to detect the loss of authenticity of a document, but usually they are invasive, what is not acceptable in case of old manuscripts. Raman spectroscopy is widely used for studies of chemical constitution of fluids, but it is difficult to apply it for ballpoint pen inks of conventional written documents since the ink layers are extremally thin. Additionally, weak Raman signal is followed by strong fluorescence background arising from the ink and the paper [1]. However, surface enhanced Raman spectroscopy (SERS) usually overcomes such sensitivity and background problems, also can be used to identify document forgery, just some technical problems of the spectroscopic experiment has to be solved [2].

In our study, it was intentionally falsificated one letter in text written by 'M&G Lavender' ball pen using identical-looking ink of 'M&G Poly Doba' pen. Different pen inks cannot be proved neither visually nor measuring conventional Raman spectra obtained without silver colloid solution. There are no Raman spectral bands due to strong fluorescence background. The SERS spectrum was measured, after adding silver colloidal solution onto the areas marked in purple and red in Fig. 1(a). The red arrow indicates the base of the word and the purple - shows the location of the falsification. A 633 nm laser, a 40x objective were used to measure the pen ink spectrum. The laser intensity was reduced to 5 mW in order to avoid sample heating and decomposition.The SERS method allowed to identify different pen inks, even though, the colours appear identical. It can be explained by their slightly different chemical constitution.

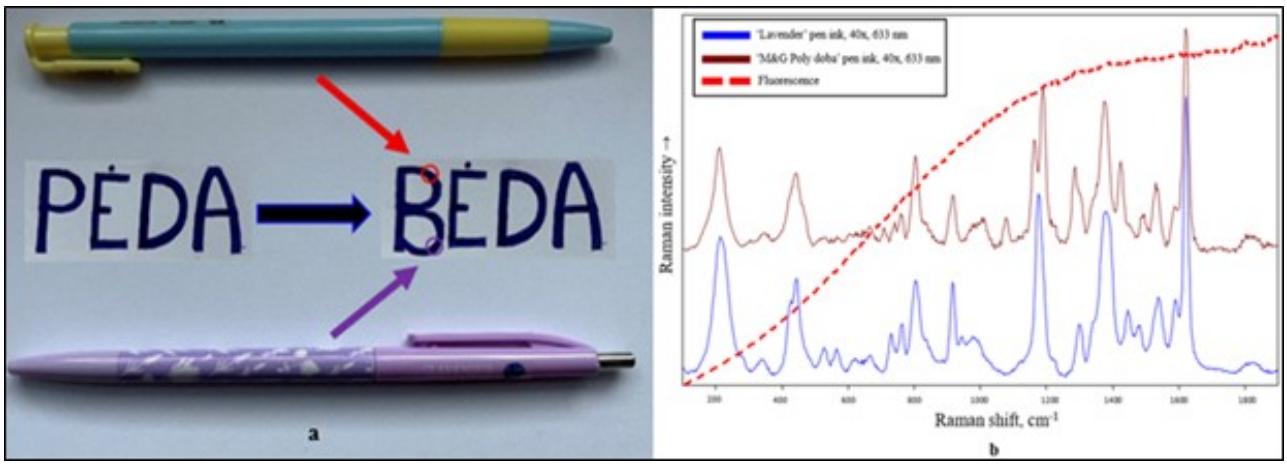

Fig. 1. (a) Word was falsificated to 'BĖDA' using identical-looking pen. Red and purple circles denote places where tiny drops of coloid were added and SERS spectra were measured;(b) SERS spectrum: blue - represents 'Lavender', while maroon – 'M&G Poly Doba' ink. Red broken curve represents fluorescence spectrum of the inks obtained from the same areas of the text before addition of silver colloidal solution.

The analysis of SERS spectra of two identical-looking pen inks reveals spectral differencies related to slightly different chemical constitution of the inks. Inks contain chemical components such as fatty acids and their esters, alcohols and coinsiding spectral bands for both inks can be attributes to these compounds. Clear spectral differences of the inks (Fig. 1(b)) in the spectral regions 500-600 cm^{-1} and 1060-1100 cm^{-1} possibly is related to benzyl alcohol, which is present just in one of the inks.

Analysis of the SERS results indicates that spectral differencies of chemically different ball pens are large enough for detection of forging documents.

Keywords: SERS, forgery, ballpoint pen inks

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