

## Abstract

Natural organic dyes suffer from degradation during the time. Therefore, the works of art need to be restored and the identification of dyes by analytical methods is important here. The possibilities of using three separation (thin-layer chromatography - TLC, capillary zone electrophoresis – CZE, and micellar electrokinetic chromatography - MEKC) and two spectroscopic (infrared microspectroscopy - IR and Raman microspectroscopy) methods for the identification of red dyes (acaroid, brazil, dragon blood, kamala, logwood, cochineal, madder, lac, and sandalwood) were studied and critically discussed.

In TLC, under optimised conditions (silicagel with octadecyl, 80/20 (v/v) MeOH/1% TEA in 0.1 mol·dm<sup>-3</sup> acetate buffer, pH 5, and 80/20 (v/v) MeOH/1% TEA in 0.025 mol·dm<sup>-3</sup> tetraborate buffer, pH 7 and 9), the stain broadening of sandalwood, logwood, acaroid, dragon blood, and brazil was observed. Carminic acid, haematein and purpurin were not detected.

A comparison of CZE and MEKC showed that MEKC was superior as it permits separation of all analytes, using 0.015 mol·dm<sup>-3</sup> sodium dodecyl sulfate in 0.01 mol·dm<sup>-3</sup> tetraborate buffer, pH 8.5, at a voltage of 20 kV. The developed method was validated and applied to the identification of dyes in *Rubia tinctorum*, *Rubia cordifolia*, and in the mycelium of fungi *Geosmithia lavendula*.

The IR and Raman microspectroscopic techniques for identification of selected dyes were studied. The specific vibrational bands found for the dyes in IR are 1715, 1378, 1309, 834, 812 and 774 cm<sup>-1</sup> for dye lac, 1551, 1346, 1167 and 1130 cm<sup>-1</sup> for dye kamala, and 1503, 1476, 1293, 1209 and 1056 cm<sup>-1</sup> for dye logwood. The characteristic vibrational bands of the dyes madder and cochineal are hidden under the matrices of these dyes. The Raman microspectroscopy permits only reliable identification of kamala (with specific vibrational bands at 1626, 1600, 1573, 1552 and 1001 cm<sup>-1</sup>) and logwood (1607, 1565, 1413, 1394 and 701 cm<sup>-1</sup>). Other dyes exhibit pronounced fluorescence.

Both the microspectroscopic methods were applied to identification of dyes in model samples of the colour layers of oil paintings and of the dyed wool and viscose fibres before and after an accelerated ageing. Finally, IR was verified for the identification of red dyes in the real dyed textile fibres, too.