

COUPLING UV-RESONANCE RAMAN AND SURFACE-ENHANCED RESONANCE RAMAN SPECTROSCOPY TO CAPILLARY ELECTROPHORESIS

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Abstract: This contribution describes the development and application of deep-UV resonance Raman and of SERRS as detection techniques, adding extra selectivity and identification potential to analytical separation systems.

Capillary electrophoresis (CE) is an attractive analytical technique because of the high separation efficiencies and small sample volumes required. However, sensitive detection remains a problem, especially if the analytes are non-fluorescent. More importantly, detection methods are needed that provide detailed spectroscopic information: for extra selectivity in the case of overlapping peaks, for the identification of unknowns and for peak confirmation in case of drifting migration times. The vibrational fingerprinting features of Raman spectroscopy would be very suitable for this purpose, but the typical concentrations and sample volumes are too low for conventional Raman. In order to increase the sensitivity two different strategies are currently being followed: resonance excitation at very short wavelengths (UV-RRS) and surface enhanced resonance Raman spectroscopy (SERRS). In both cases the Raman detection system will primarily be used for qualitative purposes; a UV absorption detector in series is preferred for quantitative purposes.

UV-RRS was successfully coupled to capillary electrophoresis (and also to liquid chromatography and flow injection systems)[1]. For resonance excitation the CW output of a frequency-doubled Argon laser is used; best results in terms of signal-to-background are usually obtained at 244 nm. In agreement with the findings of Asher and coworkers [2], there is in that wavelength region negligible interference from fluorescence and even for strong fluorophores such as pyrene derivatives high-quality spectra could be obtained. The Raman signal is detected in back-scatter mode in order to circumvent inner-filter effects; the flow system prevents photodegradation. Computational chemistry is used to assign the Raman bands to specific vibrations.

The SERRS approach makes use of a deposition interface and a moving substrate, on which the separated analytes are recorded as spots, to be interrogated under a Raman microscope [3]. Current research focuses on the development of novel substrates, as alternatives to silver colloid added in an off-line mode to a silica TLC plate. The latter method offers relatively high intensities, but for several reasons an on-line approach in which the active silver surface is already part of the substrate would be preferred. The following substrates are being tested: etched silver, vacuum deposited silver islands on quartz [4], colloidal gels, and silver-coated microspheres. Surface characteristics are studied with atomic force microscopy. Ink dyes and food colorants are used as test compounds. Analytical aspects to be considered include sensitivity, spot dimensions and homogeneity (hotspots or homogeneous response?), stability (possibilities for storage/ archiving), and suitability for positive, negative and neutral analytes.

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