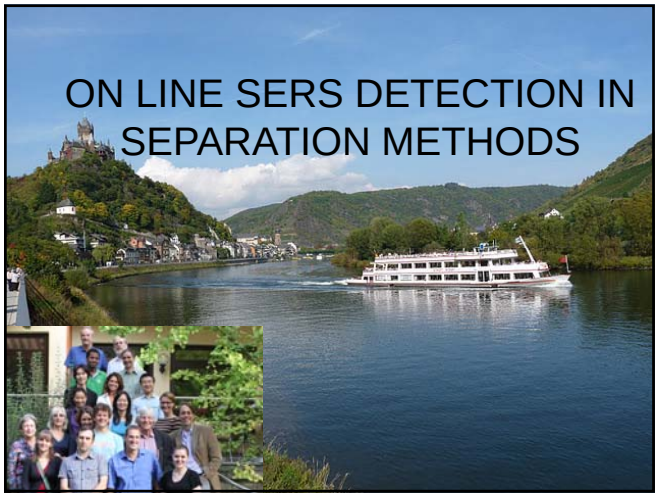
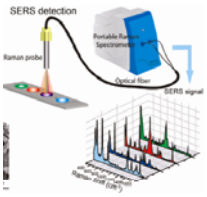
ON LINE SERS DETECTION IN SEPARATION METHODS



Standard Methods / SERS



- Selective detection of target analytes in complex (real) samples is difficult due to spectral overlap
- Using a separation technique prior to detection allows sequential measurement of the separated analytes
- SERS offers molecular specific information and sensitivity

SERS substrate for on line detection

metal colloids??? → memory effects!!!

requirements:

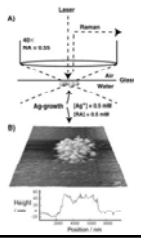
- high Raman enhancement
- easy preparation (e.g. in situ in micro-fluidics)
- high preparation success rate
- **regenerative** (multiple uses)

blank analyte 1 blank analyte 2

Laser-induced growth of Ag-nanoparticles

- Considerations:
  - Prefabrication of SERS substrate prior to use seems to be problematic Memory effects !!
- Idea:

In-situ synthesis of a small substrate in the detection window

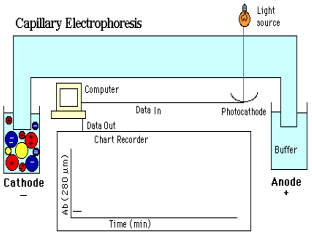


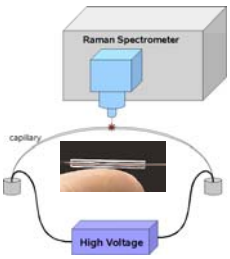
In the presence of citrate (reducing agent) Ag-nanoparticles are formed from aqueous $AgNO_3$ on a glass substrate, by laser irradiation.

Bjerneld E.J., Murty K.V.G.K., Prikulis J., Kall M.
Laser-induced growth of Ag nanoparticles from aqueous solutions
(2002) ChemPhysChem, 3 (1), pp. 116-119.

SERS detection in capillary electrophoresis

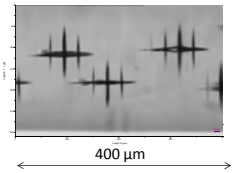
Detection: most used
on-column UV-Vis absorbance
laser-induced fluorescence (LIF)
poor molecular specificity

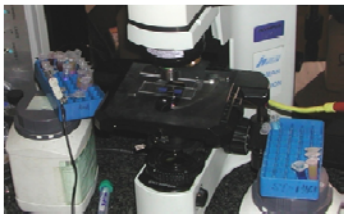


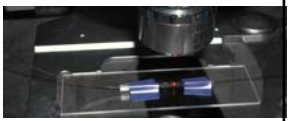


Advantages

-rapid preparation of the silver substrate *in situ*, directly in the capillary connector, during the CE separation process
-high preparation success rate
-high Raman enhancement
~50 µm spot







32 mm glass connector of 250 µm i.d.

On-column CE-SERS

- Separation and detection of R6G and 4-(2-pyridylazo)resorcinol (PAR)

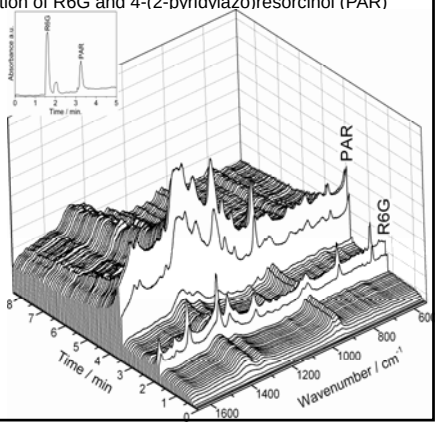
Experimental parameters:

633 nm, 3.6 mW,
acquisition time 5 s

10 mM Citrate buffer,
pH 7, AgNO3 (0.5 mM)

10 s injection, 13 kV
capillary:
active length 29 cm
total length 45 cm

R6G: 20 ppm
PAR: 11 ppm



On-column CE-SERS

- Separation and detection of R6G and PAR Cu(II) complex - $Cu(PAR)_2$

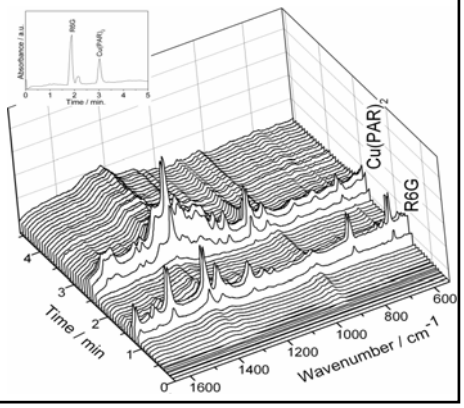
Experimental parameters:

633 nm, 1.4 mW,
acquisition time 5 s

10 mM Citrate buffer,
pH 7, +AgNO3 (0.5 mM)

10 s injection, 15 kV
capillary:
active length 29 cm
total length 45 cm

R6G: 20 ppm
$Cu(PAR)_2$: 25 ppm



On-column CE-SERS

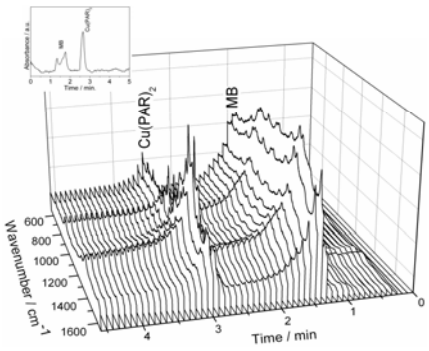
- Separation and detection of Methylene Blue and $Cu(PAR)_2$

Experimental parameters:

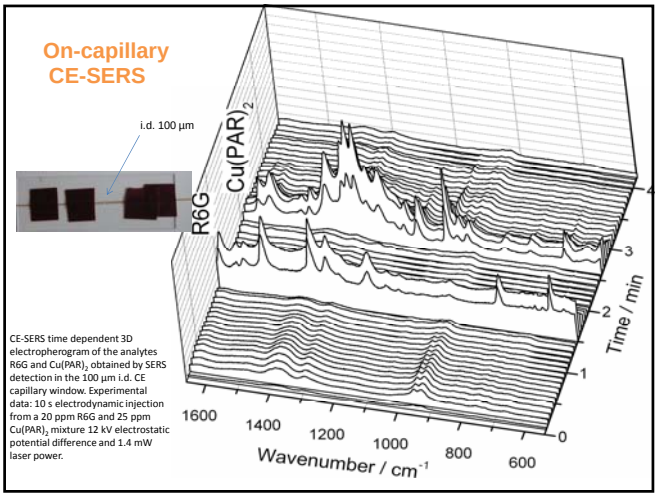
633 nm, 3.6 mW,
acquisition time 5 s

10 mM Citrate buffer,
pH 7, +AgNO3 (0.5 mM)

10 s injection, 14 kV
capillary:
active length 29 cm
total length 45 cm
MB: 0.25 ppm
$Cu(PAR)_2$: 25 ppm



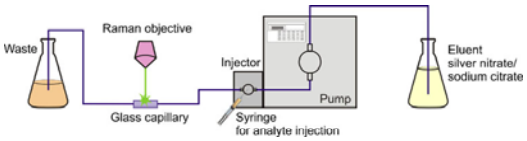
On-capillary CE-SERS

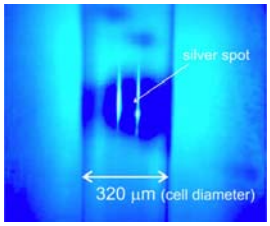


CE-SERS time dependent 3D electropherogram of the analytes R6G and $Cu(PAR)_2$ obtained by SERS detection in the 100 µm i.d. CE capillary window. Experimental data: 10 s electrodynamic injection from a 20 ppm R6G and 25 ppm $Cu(PAR)_2$ mixture 12 kV electrostatic potential difference and 1.4 mW laser power.

Picture from the Raman Spectroscopy Laboratory, UBB.

Sequential SERS detection in a flow system

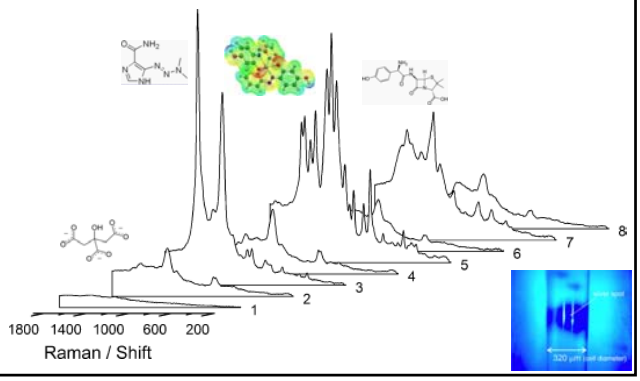




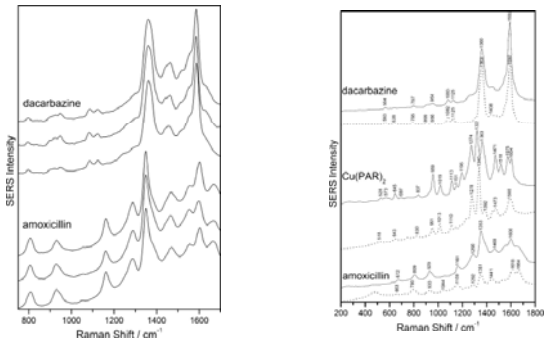
Analyte 1 dacarbazine
Analyte 2 $Cu(PAR)_2$
Analyte 3 amoxicillin

Herman, K., L. Szabó, L.F. Leopold, V. Chiș, and N. Leopold, *In situ laser-induced photochemical silver substrate synthesis and sequential SERS detection in a flow cell*. **Analytical and Bioanalytical Chemistry**, 2011. **400**(3): p. 815-820.

Sequential SERS detection



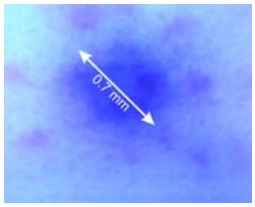
Reproducibility



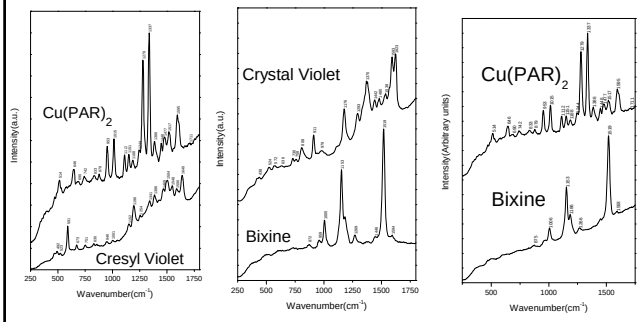
On TLC plate SERS detection

TLC plate is immersed in a $AgNO_3$ solution and dried

eluent: water, ethanol 3:2



On TLC plate SERS detection



K. Herman, N.E. Mircescu, L. Szabó, L.F. Leopold, V. Chiș, N. Leopold, *In situ silver spot preparation and on-plate Surface-enhanced Raman Scattering (SERS) detection in Thin Layer Chromatography (TLC) separation*, **submitted J. Appl. Spectrosc. 2012**