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Introducing a new high sensitive surface-enhanced Raman substrate for monitoring PAHs in sea-water

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In-situ monitoring of polycyclic aromatic hydrocarbons (PAHs) in sea-water is of worldwide interest because these chemicals are known to be toxic to biota even at low concentrations, i.e. in the range of ng/l (ppt).
For that purpose, fast response optical sensors based on Raman spectroscopy providing the fingerprint of the probed substance are suitable for rapid identification and quantification of these substances. Surface-enhanced Raman scattering (SERS) was applied to achieve the high sensitivity necessary for trace detection. In the project SENSEnet, funded by the European Commission, a new type of SERS sensor with high sensitivity was developed and adapted for the in-situ detection of PAHs in seawater. Furthermore, newly developed microsystem diode laser modules with two emission wavelengths offer the possibility to introduce shifted excitation Raman difference spectroscopy (SERDS) which dramatically reduces the fluorescence based background from the amplified SERS spectra.
The introduction of a hydrophobic surfactant to sol-gel based SERS substrates will contribute to the improvement of the SERS sensor. This new type of SERS substrate, i.e. the 25,27-dimercaptoacetic acid-26,28-dihydroxy-4-tertbutyl calix[4]arene (DMCX) functionalized silver colloid based sol-gel film, based on the electromagnetic enhancement due to nanoparticle aggregation and a preconcentration of PAHs. The experimental Raman set-up containing a 671 nm microsystem diode laser was applied to achieve high sensitivity of the DMCX functionalized Ag nanoparticle in sol-gel film, i.e. a limit of detection (LOD) of 0.3 nmol/l (60 ppt) for pyrene and 13 nmol/l (1600 ppt) for naphthalene in artificial seawater using SERS technique.
Additionally, SERS applying SERDS (SERS/SERDS) using a microsystem laser diode module with two emission wavelengths (670.8 nm and 671.3 nm) was applied to reduce the LODs of the selected PAHs (100 pmol/l (20 ppt) for pyrene, 310 pmol/l (55 ppt) for anthracene and 670 pmol/l (135 ppt) for fluoranthene, respectively). These LODs are lower than the annual average concentrations of the environmental quality standard for PAHs in seawater proposed by the European Commission.
Details of the in-situ chemical sensor based on SERS/SERDS suitable for the trace detection of PAHs in water will be presented.