

## Organic anion detection with functionalized SERS substrates via coupled electrokinetic preconcentration, analyte capture, and charge transfer

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Detecting ultralow concentrations of anionic analytes in solution by Surface Enhanced Raman Spectroscopy (SERS) remains challenging due to their low affinity for SERS substrates. Two strategies were examined to enable in situ, liquid phase detection using 5(6)-carboxyfluorescein (5(6)-FAM), as a model analyte; functionalization of a gold nanopillar substrate with cationic cysteamine self-assembled monolayer (CA-SAM) and electrokinetic preconcentration (EP-SERS) with potentials ranging from 0 mV to +500 mV. The CA-SAM did not enable detection without an applied field likely due to insufficient accumulation of 5(6)-FAM on the substrate surface limited by passive diffusion. 5(6)-FAM could only be reliably detected with an applied electric field with the charged molecules driven by electroconvection to the substrate surface and the SERS intensity following the Langmuir adsorption model. The obtained limits of detection (LOD) with an applied field were 97.5 nM and 6.4 nM on bare and CA-SAM substrates, respectively. For the CA-SAM substrates, both the ligand and analyte displayed ~15-fold signal enhancement with an applied field, revealing an additional enhancement due to charge transfer resonance taking place between metal and 5(6)-FAM that improved the LOD by an order of magnitude.