

## Surface-Enhanced Raman Detection in Chip-Based Chromatography via a Droplet Interface

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**Abstract :** Raman spectroscopy has attracted much attention as a structurally descriptive and label-free detection method. It is particularly suited for chemical analysis given as it is non-destructive and molecules can be identified via the fingerprint region of the spectra. In this work possibilities are investigated how to integrate Raman spectroscopy as a detection method for chip-based chromatography, making use of a droplet interface. A demanding task in lab-on-a-chip applications is the specific and sensitive detection of low concentrated analytes in small volumes. Fluorescence detection is frequently utilized but restricted to fluorescent molecules. Furthermore, no structural information is provided. Another often applied technique is mass spectrometry which enables the identification of molecules based on their mass to charge ratio. Additionally, the obtained fragmentation pattern gives insight into the chemical structure. However, it is only applicable as an end-of-the-line detection because analytes are destroyed during measurements. In contrast to mass spectrometry, Raman spectroscopy can be applied on-chip and substances can be processed further downstream after detection. A major drawback of Raman spectroscopy is the inherent weakness of the Raman signal, which is due to the small cross-sections associated with the scattering process. Enhancement techniques, such as surface enhanced Raman spectroscopy (SERS), are employed to overcome the poor sensitivity even allowing detection on a single molecule level. In SERS measurements, Raman signal intensity is improved by several orders of magnitude if the analyte is in close proximity to nanostructured metal surfaces or nanoparticles. The main gain of lab-on-a-chip technology is the building block-like ability to seamlessly integrate different functionalities, such as synthesis, separation, derivatization and detection on a single device. We intend to utilize this powerful toolbox to realize Raman detection in chip-based chromatography. By interfacing on-chip separations with a droplet generator, the separated analytes are encapsulated into numerous discrete containers. These droplets can then be injected with a silver nanoparticle solution and investigated via Raman spectroscopy. Droplet microfluidics is a sub-discipline of microfluidics which instead of a continuous flow operates with the segmented flow. Segmented flow is created by merging two immiscible phases (usually an aqueous phase and oil) thus forming small discrete volumes of one phase in the carrier phase. The study surveys different chip designs to realize coupling of chip-based chromatography with droplet microfluidics. With regards to maintaining a sufficient flow rate for chromatographic separation and ensuring stable eluent flow over the column different flow rates of eluent and oil phase are tested. Furthermore, the detection of analytes in droplets with surface enhanced Raman spectroscopy is examined. The compartmentalization of separated compounds preserves the analytical resolution since the continuous phase restricts dispersion between the droplets. The droplets are ideal vessels for the insertion of silver colloids thus making use of the surface enhancement effect and improving the sensitivity of the detection. The long-term goal of this work is the first realization of coupling chip based chromatography with droplets microfluidics to employ surface enhanced Raman spectroscopy as means of detection.

**Keywords :** chip-based separation, chip LC, droplets, Raman spectroscopy, SERS

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