CAVITY RING-DOWN SPECTROSCOPY AS A DETECTOR IN LIQUID CHROMATOGRAPHY

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A novel method for applying cavity ring-down spectroscopy (CRDS) in the liquid phase is presented. Liquid chromatography (LC) is a separation technique that is widely used in many different research areas, e.g. analytical chemistry, pharmaceutical sciences and environmental sciences. Quite often, the scope of these studies is to find traces of the compounds of interest in complex mixtures. Hence, the development of sensitive detection methods is imperative.

Absorption detection is, due to its simplicity and versatility, often the detection method of choice. Since it is non-destructive, this detection method can be used in tandem with other detection methods such as mass spectrometry. The sensitivity of conventional absorbance detection or laser-based techniques is usually dictated by the precision by which $\Delta I/I$ can be determined. Currently, the sensitivity of absorbance detection is limited by the stability of the light source.

CRDS is based on the injection of a short light pulse into a cavity with high-reflectance mirrors, followed by the exponential decay of the energy that is stored in the resonator. Measurements of the rate of decay will be a measure of the absorbance inside the resonator. This technique has two major advantages: the light inside the resonator will only decay significantly after hundreds or thousands of passes, providing for a large path length. Furthermore, the technique is insensitive to laser power fluctuations, since the rate of decay is measured.

In our setup, a flow-cell is formed by clamping a 2-mm thick silicon rubber spacer with a 12-µl hole in it, leak-tight between two high-reflectivity mirrors. The mirrors are in direct contact with the liquid, eliminating scatter losses on surfaces inside the cavity. The eluent from a LC column is introduced inside the cavity via capillary tubing that is inserted into the spacer. Typical ring-down times τ are between 65 and 75 ns. These short ring-down times are due to the short mirror distance and the additional Rayleigh scattering of the solvent. The chromatogram as measured directly in τ can be converted to absorbance units following:

$$\alpha = 2.303\varepsilon C = (n/c)\left[\frac{1}{\tau} - \frac{1}{\tau_0}\right]$$

in which $1/\tau_0$ includes absorption and Rayleigh scatter losses introduced by the liquid and $1/\tau$ is measured when a compound passes through the cavity.

With flow-injection measurements, it is proven that the sensitivity of conventional LC absorbance detectors is surpassed. Measurements of a chromatogram using CRDS in series with a conventional absorbance detector have shown that the peak-to-peak baseline noise, and hence the detection limit, is about a factor of 30 lower for CRDS detection. The peak-to-peak baseline noise is determined to be $2.7 \cdot 10^{-7}$ A.U. as compared to 10^{-4} A.U., which is common for conventional absorbance detectors. The current system can further be improved by designing a Z-shaped flow cell to increase the sample path length or by increasing the laser repetition rate of the laser allowing for more signal averaging.