Summary
Cavity ring-down spectroscopy (CRDS) is an extremely sensitive mode of absorption spectroscopy, suitable for application in trace detection. It is safe to state that cavity-enhanced techniques are to date the most sensitive modes of absorption spectroscopy, only rivaled by photo-acoustic absorbance spectroscopy (PAS). During the first years of its development, CRDS was exclusively applied to gas-phase studies. However, in the last decade various examples of different modes of CRDS applied to condensed media have also been reported, indicating its potential for these media as well.

Advantages of CRDS include the simplicity and robustness of the set-up as compared to for example the use of Herriot- or White-type absorbance cells, the absolute character of the measurements and the excellent sensitivity.

In chapters 2 – 5 of this thesis, the development of a CRDS-based absorbance detector suitable for conventional-size liquid chromatography (LC) detection and flow-injection analysis (FIA) is described. In the visible wavelength range (at 532 and 457 nm), the detection sensitivity of conventional absorbance detectors is surpassed by a factor of 100. This enhancement factor is even feasible using a tunable laser system that is tuned 13 nm off the design wavelength (470 nm) of the CRDS mirrors used. This shows that using one particular set of CRDS mirrors still provides some freedom in wavelength selection. To further improve user-friendliness, it might be advantageous to use a geometry which incorporates a flow cuvette at 0 degrees in a linear cavity although in such a set-up possible reflection losses play a significant role. This way, mirrors do not need cleaning on a daily basis and the set-up can be used for weeks without need for alignment.

A drawback of the CRDS technique is the limited linear dynamic range: a larger absorbance is associated with a shorter ring-down time and the upper limit of absorbance is determined by the number of data points that still result in a reasonable fit of the decay transient. The linear dynamic range of CRDS set-ups is typically limited to two orders of magnitude. Another disadvantage is the fact that high-reflectivity mirrors are currently not yet available in the UV wavelength range. This explains why, as demonstrated in chapter 5, the sensitivity enhancement for absorption detection in LC studies becomes less pronounced when moving to UV wavelengths. At 355 nm, the performance of the system was a factor of 10 lower than in the visible range. At 273 nm, the mirrors were of too low reflectivity for improving the sensitivity of LC absorption detection compared to conventional LC absorbance detectors.

In recent years several other groups have developed new CRDS methods. Especially promising is the development of cavity-enhanced absorption spectroscopy (CEAS), which can be used in conjunction with incoherent broad-band sources and mirrors with lower reflectivities but applicable over a larger wavelength range. This opens possibilities for obtaining spectral information over a broader wavelength range, which is especially useful in condensed-media studies, where absorbance bands are usually much broader than in the gas-phase. Also useful in this respect is fiber-loop CRDS, although at present this technique is restricted to red or near-infrared (NIR) wavelengths due to substantial optical losses within the fiber material in the visible and UV wavelength region. Another promising mode is polarization-dependent CRDS: the off-resonance optical rotation of molecules of interest can be probed at any convenient wavelength.

A new and interesting development in CRDS is the rapidly evolving evanescent-wave (EW) approach, which combines surface specificity with extremely sensitive absorbance measurements. Many different implementations of this technique are currently being explored. However, also in this application there is a wavelength restriction. It is clear from Fig. ?? that upon shifting the wavelength to the UV range, the prism material becomes
less transparent.

Chapter 6 of this study reports on the development and application to flow-injection analysis (FIA) of an EW-CRDS set-up based on an intra-cavity Dove prism. For analytical chemical purposes the reversibility of the surface binding processes is crucial: a method is needed where repetitive measurements can easily be performed without contamination or degradation of the total internal reflection (TIR) surface of the prism. We observed that when the flow rate as well as the amount of organic modifier used are carefully chosen, repeatable results can be obtained without the need for rigorous cleaning after each measurement. Furthermore, as described in chapter 7, organosilanes can be used to covalently attach a self-assembled monolayer to the TIR surface of the prism, thus influencing surface properties and interactions. Covalently attached self-assembled monolayers may ultimately provide a platform for developing bio-sensors.