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# Cavity ring-down spectroscopy for detection in liquid chromatography at UV wavelengths using standard cuvettes in a normal incidence geometry $\stackrel{\text{tr}}{\sim}$

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#### Abstract

Liquid chromatography (LC) with cavity ring-down spectroscopy (CRDS) detection, using flow cuvettes (put under normal incidence inside the ring-down cavity), is demonstrated. Fresnel reflections are maintained within the capture range of a stable cavity of 4 cm length. This method circumvents the need for specific Brewster's angles and possible mirror degradation is avoided. The flow cuvettes are commercially available at low cost. At 355 nm (the frequency-tripled output of a Nd:YAG laser), the system surpasses the performance of conventional absorbance detectors; the baseline noise was  $1.3 \times 10^{-5}$  AU and detection limits (injected concentrations) were between 40 and 80 nM for nitro-polyaromatic hydrocarbons with an extinction coefficient  $\varepsilon$  of  $7.3-10.2 \times 10^3$  M<sup>-1</sup> cm<sup>-1</sup>. The system was also tested at 273 nm, but in the deep UV the reflectivity of the currently best available mirrors ( $R \ge 99.91\%$ ) is still too low to show a significant improvement as compared to conventional UV–vis detection. © 2007 Elsevier B.V. All rights reserved.

Keywords: Cavity ring-down spectroscopy; Liquid chromatography; Detection method; Flow cuvettes; Nitro-polyaromatic hydrocarbons

# 1. Introduction

Liquid chromatography (LC) is used in many different research areas, often with UV absorbance detection. Especially for low concentrations or poorly absorbing analytes, the improvement of absorbance detection limits remains a relevant task.

Cavity ring-down spectroscopy (CRDS) is a laser-based absorption technique which owes its high sensitivity (i.e., low minimum detectable absorbance) to the multi-pass effect and the independence towards light source intensity fluctuations [1,2]. A stable optical cavity is built with high-reflectivity mirrors, in which an injected laser pulse will typically make thousands of round-trips. The effective path length through the sample can be as large as meters or even kilometers. Furthermore, instead of light intensity differences, the rate of decay of the light is measured separately after each pulse. Thus, light source fluctuations play an insignificant role. In recent years, CRDS has become an accepted method for trace measurements in the gas phase,

0021-9673/\$ - see front matter © 2007 Elsevier B.V. All rights reserved. doi:10.1016/j.chroma.2007.03.028 but substantial progress has also been made in applying CRDS to the liquid phase [3–9] and developing it as an LC absorption detector [10–14].

Xu et al. measured a weak overtone of liquid benzene between 588 and 613 nm with one or two cuvettes placed inside a resonator; Fresnel reflection losses were minimized by putting the cuvettes under Brewster's angle [3]. Alexander studied reaction kinetics of nitrate radicals with terpenes using the same geometry [7]. Hallock et al. studied reaction kinetics of Methylene Blue using a different approach: in this study, the mirrors were brought in contact with the liquid, forming the outer boundaries of a large-volume flow cell [4,6]. In the group of Loock, fiber-loop ring-down spectroscopy has been applied to the liquid phase [5,8]. Whereas the sensitivity of this approach is still limited, these fiber-loop ring-down devices may nevertheless become promising tools in remote sensing of liquids. Fiedler et al. built a broadband (about 200 nm) cavity enhanced absorption spectrometer, employing cuvettes in which the earlier mentioned weak overtone in liquid benzene was remeasured [9].

In developing CRDS as a detection method for LC, of course the flow cell volume and design is of crucial importance. Furthermore, emphasis should be on features like ease-of-operation and robustness of the system as a whole. Different geometries have been described in the literature [10–14]. Reflection losses can be

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minimized by putting a suitable flow cell under Brewster's angle inside a ring-down cavity, and the group of Zare successfully used this approach to enhance the performance of absorption detection in LC, both for pulsed [10] and continuous-wave [11] CRDS. Their flow cell, with a path length of 300  $\mu$ m through the liquid, was designed to have the correct Brewster's angle at both the air–glass and the glass–liquid interfaces. For LC measurements with continuous-wave CRDS detection at 488 nm and using a cavity length of no less than 1 m, they typically obtained ring-down times of several  $\mu$ s and a baseline peak-to-peak noise of  $2 \times 10^{-7}$  absorbance units (AU =  $\varepsilon Cl$  as in the Lambert–Beer law) [11].

Another approach is to use the full cavity length for measurements by designing a flow cell in which the outer boundaries are formed by the cavity mirrors [4,6,12–14]. No surfaces or Brewster's angles inside the cavity need to be considered, and a large range of eluents with different refractive indices can be used. This is advantageous from an ease-of-operation and system robustness point of view. In such a methodology, the cavity length has to be made small (in order to have a  $\mu$ l-sized flow cell, compatible with LC analysis) and therefore the ring-down times are much shorter. Such short ring-down times do not allow for very accurate determination of the decay rate and hence limit the minimum detectable absorbance. However, although not practiced yet, the repetition rate of the laser and detection system can in principle be increased up to the MHz-range for extra signal averaging.

Previously, a liquid-only cavity flow cell in which the mirrors are clamped leak-tight around a 2-mm thick silicon rubber spacer has been tested extensively [12–14]. The spacer, with an elliptical hole of 3.9 mm length and 1.6 mm width, acts as a 14- $\mu$ l flow cell, and flow is introduced via capillary tubings inserted through the sides of the spacer. Using a tunable pulsed laser source set at 457 nm and 100 Hz, a baseline peak-to-peak noise of 2.7 × 10<sup>-6</sup> AU was obtained. Since the path length in this system was larger than in refs [10,11] (2 mm, i.e., the full cavity length, compared to 300  $\mu$ m) absolute concentration detection limits were better than those reported by Bechtel et al. [11].

When solid surfaces (e.g., cuvettes or flow cuvettes) are placed inside a ring-down cavity, care is usually taken to minimize any possible reflection losses using the Brewster's configuration. However, when the cavity length is sufficiently short in order to preserve any reflections off intra-cavity surfaces, a normal incidence geometry can also be used [9,15-19]. As illustrated by Fiedler et al. [9], multi-mode excitation of a cavity gives rise to a certain angular distribution of the light beam, and a Brewster's angle cannot accurately be defined. Actual losses can therefore be larger than the calculated Fresnel reflection losses (which should be negligible at Brewster's angle). Instead of minimizing reflection losses, it can be advantageous to capture the surface reflections on the normal of both sides of the cuvette inside a small, stable cavity. Reflection losses on the inside of the cuvette (where the liquid touches the cuvette surface) are much smaller due to the smaller difference in refractive indices.

In the present paper, we explore whether – using an isocratic LC separation of a test mixture of nitro-poly-aromatic hydrocarbons (PAHs) as a model system – standard flow cuvettes can be used in LC-CRDS in a straight-forward normal incidence configuration, and whether they allow application in the ultraviolet region; for this purpose laser lines at 355 and 273 nm are involved. A major advantage of the zero degree geometry is that there is no need for a carefully designed, custom-made flow cell. Since there are no Brewster's angles to be considered and the liquid is not in direct contact with the mirrors, a large range of eluents with different refractive indices, including more aggressive liquids such as acids, could be used.

### 2. Experimental

The separation of the nitro-PAHs was carried out isocratically, the eluent was 80% methanol, 20% Milli-Q water. Benzopurpurine and the nitro-PAHs (2-nitrofluorene, 1nitropyrene and 6-nitrochrysene, see Table 1) were obtained from Sigma-Aldrich (Munich, Germany). The flow rate was set to 0.8 ml/min with an Applied Biosystems 400 solvent delivery system; 50 µl of sample (dissolved in methanol) was injected using a six-port injection valve. The column was a Chromsep Microspher (Varian, Middelburg, The Netherlands) C18  $100 \text{ mm} \times 4.6 \text{ mm}$  (length  $\times$  internal diameter) reversed phase column equipped with a guard column. For comparison measurements, we used a Kratos spectroflow 757 UV-visible absorbance detector with an 8-mm path length and 12-µl volume (Applied Biosystems, Foster City, CA, USA), set at the laser wavelength of the CRDS measurements. Steady-state measurements were performed by adding 5-µl aliquots of a 1-ppm aqueous benzopurpurine solution to a standard quartz,  $10 \text{ mm} \times 10 \text{ mm}$  cuvette filled with 2 ml Milli-Q water.

Quartz cuvettes and flow cuvettes, with a surface roughness of less than 0.2  $\mu$ m and a parallelism of the windows better than 0.01 mm were obtained from Hellma, Müllheim, Germany. The cuvettes were mounted on a mirror mount permitting separate alignment in the previously aligned cavity. The flow cuvette used in the LC measurements had a volume of 80  $\mu$ l, a path length of 10 mm and an aperture diameter of 3 mm. Using chromatograms measured with the UV–visible absorbance detector with and without the CRDS flow cuvette on-line, the extra band-broadening introduced by the CRDS flow cuvette was determined to be negligible (around 5% for 1-nitropyrene).

For the CRDS measurements (see Fig. 1), no mode-matching was performed, ensuring multi-mode excitation of our cavities (that are not temperature controlled or locked to a specific laser mode). Transients were recorded using a photomultiplier tube (Hamamatsu, Shimokanzo, Japan) and a fast sampling oscillo-scope of 1 GHz analog bandwidth (Tektronix 5104 5 GS/s).

Table 1

Formula weights (F.W.) of the various test compounds and their extinction coefficients at the applied laser wavelengths

Compound	F.W. (g/mol)	$\varepsilon_{273}  (\mathrm{M}^{-1}  \mathrm{cm}^{-1})$	$\varepsilon_{355} (\mathrm{M}^{-1}\mathrm{cm}^{-1})$
Benzopurpurine	724.73	$32 \times 10^{3}$	$15 \times 10^{3}$
2-Nitrofluorene	211.22	$2.7 \times 10^{3}$	$10 \times 10^{3}$
1-Nitropyrene	247.26	$11 \times 10^{3}$	$8.7 \times 10^{3}$
6-Nitrochrysene	273.29	$28 \times 10^3$	$7.3 \times 10^3$



Fig. 1. Schematic diagram of the set-up. CRDS measurements were performed using a cavity of 4 cm, in which the flow cuvette was placed under normal incidence. A laser beam of 1 mm diameter was coupled into the cavity without any mode-matching.

Measurements at 355 nm were done using a Q-switched, mode-locked and frequency-tripled (355 nm) Nd:YAG laser (Quantel, Clermont-Ferrand, France) delivering 100-ps, 1-mJ pulses at 10 Hz. A ring-down cavity of 4.0 cm length was made using two highly reflective (at 355 nm) concave mirrors (Layertec, Mellingen, Germany, *R* specified as  $\geq$ 99.95%, radius of curvature = 500 mm). Ring-down times for an empty cavity were 500–600 ns, from which it can be calculated (see below) that the actual reflectivity of these mirrors was 99.98%. The ring-down times would decrease to 60–70 ns when a cuvette filled with eluent blank was placed in the cavity. As an example, during elution of a 0.8  $\mu$ M (injected concentration) 2-nitrofluorene plug, the ring-down time decreased down to 35 ns.

Mirrors with a radius of curvature of 500 mm, that were specified to have maximum reflectivity at 266 nm (the fourth harmonic of a Nd:YAG laser) were obtained from Research Electro-Optics (Boulder, CO, USA). In order to determine the reflectivity and wavelength dependence of the mirror set, a reflection curve was taken using a frequency-doubled Quanta-Ray PDL-3 pulsed dye laser with coumarin 152, pumped by the 355-nm output (the third harmonic) of a Quanta-Ray Nd:YAG laser (Spectra-Physics, Mountain View, CA, USA) at a repetition rate of 10 Hz and a pulse duration of 5 ns. The energy of the pulses was 0.5 mJ. Despite the fact that the mirrors were designed for 266 nm, the optimum reflectivity (determined as  $R \ge 99.91\%$  from the maximum ring-down time of an empty cavity) was obtained at a longer wavelength, i.e., at 273 nm, presumably due to unexpected absorbance of the reflecting layers. Thus, all measurements were performed at 273 nm, using the Nd:YAG pumped, frequency-doubled PDL-3 laser system (instead of the quadrupled 266-nm output of the Nd:YAG laser). It should be noted that this reflectivity is far less favorable than the reflectivity at 355 nm.

The cavity at 273 nm was 3.8 cm long and typical ring-down times were 100–140 ns, decreasing to 12–18 ns when a flow cuvette with either eluent or Milli-Q water was placed inside the cavity. For the standard 10 mm  $\times$  10 mm absorbance cuvette, the ring-down times were 19–25 ns. As an example, when 10  $\mu$ M of 6-nitrochrysene was injected, the ring-down time decreased to 4 ns. Mainly due to the long pulses of the laser system giving an instrumental response time of 5.5 ns full width at half maximum,

the precision at which short ring-down times can be measured determines the upper limit for higher absorbances.

## 3. Results and discussion

The intensity *I* as measured behind the cavity decays according to:

$$I(t) = I(0) \exp\left[-\left[(1-R) + (\alpha_{\text{anal}} + \alpha_{\text{solv}})l + \beta_{\text{scatt}}\right]\frac{ct}{n_{\text{avg}}L}\right]$$

where  $\alpha_{anal}$  denotes absorption by the analyte and  $\alpha_{solv}$  denotes absorption and scattering by the solvents, both in cm<sup>-1</sup>;  $\beta_{scatt}$ is the loss due to scattering at the cuvette surfaces per pass; this does not include the reflections off the surfaces that remain in the resonator. *R* is the reflectivity, *c* the speed of light, *t* the time, *L* the length of the cavity, *l* the path length through the sample, and  $n_{avg}$  is the weighted refractive index of the cavity. Fitting of the resulting curves to an exponential decay function yields ring-down times  $\tau$ , defined as the time over which the intensity decreases to 1/e its original value. In order to obtain chromatograms in absorbance units  $\varepsilon Cl$ , we calculated:

$$\varepsilon Cl = \frac{\alpha_{\text{anal}}l}{2.303} = \frac{(L-l)+nl}{2.303c} \left[\frac{1}{\tau} - \frac{1}{\tau_0}\right]$$

where  $\varepsilon$  is the molar extinction coefficient in M<sup>-1</sup> cm<sup>-1</sup> (as used in the Lambert–Beer law) and *C* is the concentration (in the flow cell) in M. *n* is the refractive index of the liquid,  $\tau$  the measured ring-down time when an analyte is passing, and  $\tau_0$  is the ring-down time as measured when only eluent is present and includes background absorption and scatter losses. Data averaging over 1 s (also used in commercial absorbance detectors) is applied afterwards. Figs. 2 and 3 show typical LC-CRDS chromatograms as obtained at 273 and 355 nm for concentrations near the detection limit of the systems.



Fig. 2. LC-CRDS chromatogram at 273 nm of a test mixture of the nitro-PAHs (injected concentration  $1 \mu M$  of each compound), together with calibration curves. Equations for the calibration curves: 2-nitrofluorene (2n-FLU) 0.0018x - 0.0015, 1-nitropyrene (1n-PY) 0.0098x - 0.0061, 6-nitrochrysene (6n-CHR) 0.0223x + 0.0092.  $R^2$  values were better than 0.98, except for 2-nitrofluorene which had an  $R^2$  value of 0.91. Each concentration was measured three times, the error bars show the standard deviations.



Fig. 3. LC-CRDS chromatogram at 355 nm of a test mixture of the nitro-PAHs (injected concentration 80 nM of each compound), together with the calibration curves. Equations for the calibration curves: 2-nitrofluorene (2n-FLU)  $0.0122x - 5 \times 10^{-5}$ , 1-nitropyrene (1n-PY) 0.0063x + 0.0004, 6-nitrochrysene (6n-CHR) 0.0061x + 0.0004.  $R^2$  values were 0.98 or better. Each concentration was measured three times, the error bars show the standard deviation.

In order to fully take chromatographic dilution effects into account, detection limits of the overall set-up were measured rather than calculated. A series of very low concentrations were injected and the corresponding peak heights were compared to the baseline noise close to that peak. A concentration which gives a peak that is three times higher than the baseline noise (r.m.s.) is considered as the concentration detection limit. One can also calculate the minimum detectable concentration (in the flow cell) directly from the standard deviation on  $\tau_0$ , but this will not take into account the chromatographic dilution and thus overestimates the performance of the complete LC-CRDS system. Both types of detection limit are listed in Table 2.

Table 2 sums up some characteristics for the LC-CRDS detection of the separation of nitro-PAH test mixtures. Previously, LC-CRDS detection of the same nitro-PAH separation has been performed at 355 nm using the same laser and detection setup and a liquid-only cavity flow cell [14]. For comparison, the results of that study are also included in the table. Note that three times the baseline noise (second row) corresponds to the concentration inside the flow cell at the detection limit (as listed in the third row). The bottom row lists the experimentally determined injected concentration detection limits. The latter are typically an order of magnitude higher because of the abovementioned chromatographic dilution effect. At 273 nm, the performance of CRDS detection in LC is very close to that of a commercial instrument in both set-ups, detection limits (injected) were in the range of  $0.5-3 \,\mu$ M for the different compounds, depending on the  $\varepsilon$  and the chromatographic dilution. A significant improvement of the baseline noise and detection limits is seen at 355 nm, where the detection limits are in the range of 40–80 nM (injected). In addition, at 355 nm, the present flow cuvette set-up has two-fold lower absolute detection limits compared to the liquid-only cavity geometry.

Calibration curves determined at 273 nm (between 2 and 10  $\mu$ M) and at 355 nm (between 80 and 800 nM) show a good repeatability and linearity for the LC-CRDS measurements (see Figs. 2 and 3). Note that, at 273 nm, the calibration curve of 2-nitrofluorene is still acceptable, despite the fact that the extinction coefficients of 2-nitrofluorene and 6-nitrochrysene differ by an order of magnitude.

When considering the detection limits as obtained at 355 nm for the current flow cuvette system in comparison with those obtained for the liquid-only cavity flow cell, one would expect a factor of five improvement (since the path-length through the sample is now 10 mm as compared to 2 mm). Due to the use of a different column, retention times were somewhat longer and peak widths were broader in comparison with [14], thus counteracting the advantage of the increased path-length. Overall, the improvement in injected concentration detection limits with the current normal incidence set-up is still more than two-fold.

Due to the low reflectivity of the available mirrors at 273 nm, the performance of the system is severely limited by the accuracy with which the ring-down lifetime  $\tau$  can be detected. Furthermore, the instrumental response function (about 5.5 ns full width at half maximum) is more than one quarter of the ring-down lifetime of 20 ns.

In order to further investigate the performance of liquidphase CRDS at 273 nm, steady-state CRDS batch measurements (of 5-µl additions of 1 ppm (=1.38 µM) benzopurpurine to 2 ml of Milli-Q water) were carried out using a conventional 1-cm square quartz cuvette. For 1 min (600 shots) of averaging, the baseline peak-to-peak noise of the blank sample (pure Milli-Q, giving a  $\tau_0$  of 19.1 ns) was 1.1 ns; the detection limit was calculated to be at 15.8 ns (i.e., three times the noise level), this corresponded to the addition of 10 µl of benzopurpurine (making a total concentration of 7 nM benzopurpurine solution in the cuvette). In a scanning absorbance spectrometer, of which the baseline peak-to-peak noise was about  $3 \times 10^{-4}$  AU,

Table 2

Summary of the performance of the flow cuvette set-up at 273 and 355 nm, in comparison with the previously used liquid-only cavity flow cell and a conventional absorbance detector

	272	255	1	
	2/3 nm	355 nm	Liquid-only cavity, 355 nm [14]	UV-VIS detector
Baseline ring-down time (ns)	12–18	60-70	20–25	N.A.
Baseline noise (r.m.s., AU)	$4.2  imes 10^{-4}$	$1.3 \times 10^{-5}$	$1.3 \times 10^{-5}$	$2 \times 10^{-4}$
Conc. in flow cell (nM)	50-470	4-6	20–27	75-100
Detection limits (nM)	500-3000	40-80	80–150	500-1000

The minimum detectable concentration in the flow cell is calculated as three times the (measured) baseline noise. The detection limits are the injected concentrations of nitro-PAHs that result in a peak height three times the peak-to-peak noise level of the baseline.

the detection limit at 273 nm was determined (in a similar way) to be about 20 nM, i.e., three times higher. We therefore concluded that CRDS in a normal incidence geometry can also be employed for batch absorbance measurements when very low concentrations need to be determined. The ring-down times and concentration detection limits were even better (due to longer averaging) than the results for LC separations taking into account the dilution effect in the column: the detection limit for 1-nitropyrene at 273 nm was 1  $\mu$ M or 5 × 10<sup>-11</sup> mol injected. From the peak width, it can be calculated that this corresponds to a concentration of about 60 nM in the chromatographic peak. Corrected for the extinction coefficient differences, this would correspond to a concentration of 20 nM of benzopurpurine.

# 4. Conclusion

In this study, an LC-CRDS detection system employing commercial flow cuvettes in a normal incidence geometry is described for the first time. This geometry is simple to implement: instead of designing and producing a flow cuvette, the cuvettes used in this study are standard laboratory equipment. The absence of any Brewster's angle ensures that a wide variety of eluents with different refractive indices can be used. With this design, degradation of the mirrors is not an issue since they are not in contact with the solvents, thus permitting the use of more aggressive liquids such as acids and bases which would not be possible with a liquid-filled cavity.

The system was tested at 273 and at 355 nm. Whereas the reflectivity of the mirrors at 273 nm was inadequate and did not (yet) lead to an improvement of the performance in absorbance detection, at 355 nm the concentration detection limits improved significantly (15-fold). The baseline peak-to-peak noise was only  $1.3 \times 10^{-5}$  AU, compared to  $2 \times 10^{-4}$  AU of a conventional UV–vis absorbance detector.

The normal incidence geometry system has certain advantages over the liquid-only cavity flow cell as used in previous studies [12–14]. Despite the 80- $\mu$ l detection volume, only a 5% peak broadening was observed (for 1-nitropyrene), compared to about 15% for the liquid-only cavity flow cell [14]. The absolute detection limits improved by a factor of 2–3. We are currently testing new options to improve the performance of CRDS at 273 nm.

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