



## Condense-Phase BBCEAS Measurements at UV Wavelength

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### ABSTRACT

Broadband cavity enhanced absorption spectroscopy (BBCEAS) has been used to make measurements on liquid phase species using a UV LED and an optical cavity formed by  $R \geq 0.99$  ultra violet mirror set. The detector is an Andor CCD spectrograph. Measurements is made on a number of dyes dissolved in water and placed in a 1 cm quartz cuvette at zero degrees angle of incidence between the cavity mirrors. The most sensitive measurements are made with the  $R \geq 0.99$  mirror set on congo red at 397 nm which produced an  $\alpha_{min}(t)$  value of  $2.1 \times 10^{-6} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  and a  $LOD$  of 0.19 nM.

**Keywords:** Broadband cavity enhanced absorption spectroscopy; BBCEAS; Liquids; Absorption spectroscopy; Ultraviolet light emitted diode; UV-LED

### 1. INTRODUCTION

In the last two decades, the use of optical cavity in absorption spectroscopy has proved to be an efficient method to achieve a high performance in absorption sensitivity, rate resolution, and precision. Generally, the sensitivity of absorption measurements in the gas phase has been greatly increased by using CRDS, CEAS and variants of these techniques on numerous electromagnetic wavelength regions. This gain in sensitivity has been achieved on the visible region [1-3], ultraviolet region [4-6], and near infrared region [7]. More recently, most studies have considered cavity absorption measurements of liquid phase on the visible

region [8,9]. The applicability of these techniques would, however, be greatly increased if measurements could be extended to shorter wavelengths into the UV as most common analytes have strong absorptions in the UV region from 200 to 400 nm, as only a few studies have been published on this region [10,11].

Previous studies have placed optical components in the cavity at Brewster's angle in order to minimize losses due to reflection. Xu et al. [12] were the first to demonstrate this idea by inserting a UV-Visible cuvette oriented at Brewster's angle into a ring-down cavity to study the C-H stretching fifth vibration overtone of benzene. Their technique was limited because the refractive index of the liquid sample and the material of cuvette, which was used, needed to be approximately similar. Synder and Zare [13] resolved these limitations by designing a flow cell with wedged angles that could be used for liquid samples of any given refractive index. Of the few previous liquid phase cavity-based studies, there have been only two liquid-phase cavity studies on the ultraviolet wavelength region. Van der Sneppen et al. [14] used CRDS as a detection system for LC separation in the ultra violet region (using the same setup of previous two studies at visible light) for azo dyes ( $\lambda = 457$  nm) and nitro-polyaromatic hydrocarbons (nitro-PAHs) ( $\lambda = 355$  nm). The sensitivity of measurements at  $\lambda = 457$  nm was improved by a factor of 100 compared to the conventional absorbance detector, while for 355 nm the improvement of the sensitivity was less, due to the limitation of providing a mirror with high reflectivity in the deep ultra violet wavelength.

Another geometry of LC-CRDS technique has been described in van de Sneppen's paper [15], using a 1 cm flow cuvette placed inside the ring down cavity for detection in liquid chromatography of test mixture of the nitro-PAHs at UV wavelength. Two sets of mirrors were used in the setup; the first set had a reflectivity of 0.9995 at  $\lambda = 355$  nm and the second had a reflectivity of 0.9991 at  $\lambda = 273$  nm. The flow cuvette was inserted inside the cavity at 0 degree; therefore, the reflection loss was very small due to the smaller difference between the refractive index of the liquid and the quartz surface of cuvette.

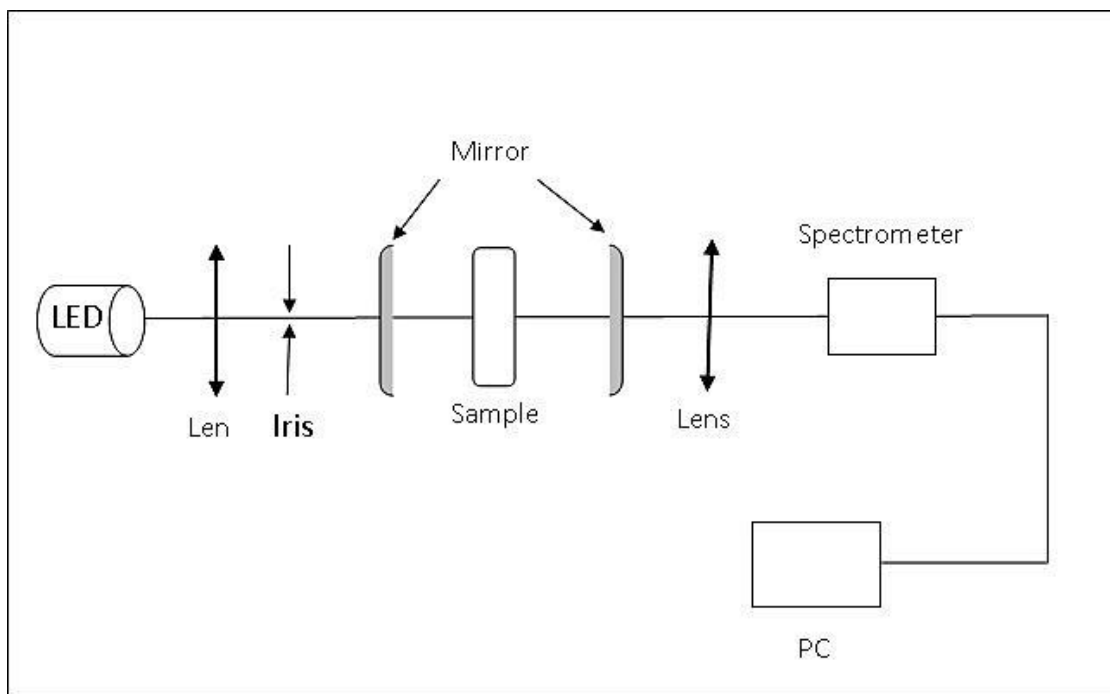
The most directly relevant studies to this research are those which have made measurements in cavities placed at 0 degrees. In the first CEAS study using an incoherent broadband (IBB) source (a xenon arc lamp) rather than a laser, Fielder et al. [16] showed that a similar local minimum in the optical losses also existed at 0 degrees angle of incidence when they measured the fifth overtone of the C-H stretch in benzene in comparison to the single-pass visible absorption measurements. Islam [17] developed BBCEAS using a cheaper LED excitation for the liquid phase in a 2 mm cuvette to investigate the absorption properties of several dye solutions.

This study had to demonstrate a novel implementation of broadband cavity enhanced absorption spectroscopy (BBCEAS) in order to perform sensitive ultraviolet wavelength measurements on liquid-phase solutions in a 1 cm cuvette.

## **2. EXPERIMENTAL SETUP**

A schematic of the experimental setup is shown in Figure 1. The light from the ultra violet light emitted diode (UV-LED) was introduced into the optical cavity by using a series of achromatic lenses and irises to decrease light divergence. The LEDs used for this study were from the Hexagonal high power UV-LED H2A1 uv-series (Roithner Laser Technik). The thin GaN chip LEDs with (1×1) mm and lambertian silicone lens are mounted on

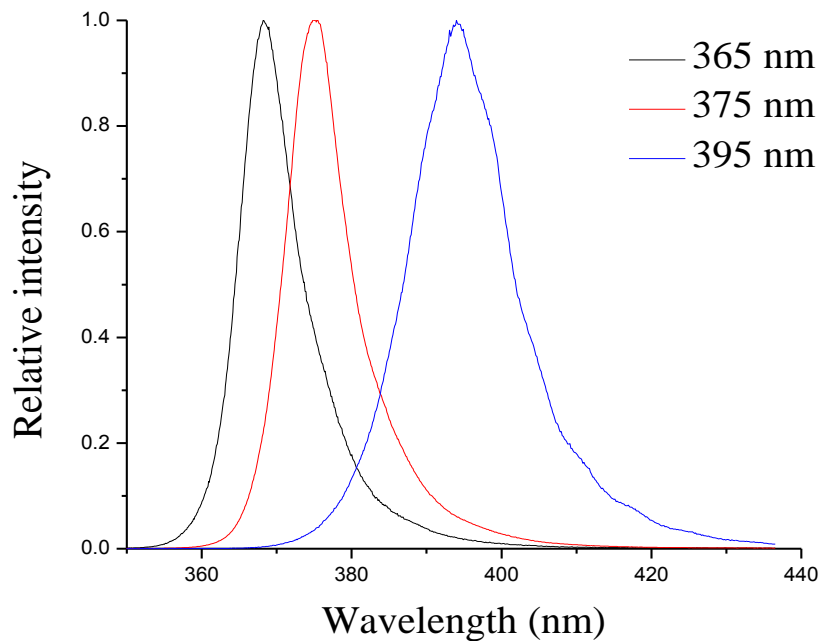
hexagonal shaped aluminium, which has a diameter of 2 cm enabling them to be tightly packed together for a wide range of applications. This provides basic cooling, makes it easy to mount the emitter, and to adjust the centre point of the light. The LEDs were powered with a DC forward current of 350 mA. The central emission wavelengths were 367, 375, and 397 nm, respectively, whilst the bandwidths were approximately ~9, ~10, and ~15 nm respectively, and the outputs are shown in Figure 2.



**Fig. 1.** A schematic of the experimental setup for the liquid-phase UV-BBCEAS measurements at.

The cavity consisted of two high reflectivity mirrors separated by 10 cm. Both concave UV-mirrors have a reflectivity of  $R \geq 0.99$  (Thorlabs, UK), a radius of curvature = 20 cm, and a diameter of 25 mm. The effective wavelength range of these mirrors is from 310 to 430 nm. The mirrors were mounted into a custom mirror holder unit. Three micrometer screws were attached to each mirror to allow fine adjustment during cavity alignment. The detection system was an Andor's cooled CCD spectrometer. The light was collimated in a fine beam by lenses in order to pass through the first mirror where it underwent several reflections inside the cavity. At each reflection a small fraction of light was transmitted by the second mirror and focused by a short focal length lens ( $f = 50$  mm) directly onto the entrance slit of the spectrometer. The spectrometer was connected to the computer for data collection via a USB connection. Spectra were analysed and plotted using the Excel spreadsheet application.

The achievement of the alignment process of the cuvette in the cavity was the same as described in Islam study [17]. The integration time was ~10 ms with typically 100 averages for these measurements.



**Fig. 2.** Relative intensity versus wavelength spectra for uv- LEDs

### 3. EXPERIMENTAL METHODOLOGY

The absorbance cavity measurements of an analyte is not widely used as the Beer-Lambert law which states that the absorbance is linearly proportional to concentration is only valid for small absorbance values. At higher absorbances the relationship is non linear. As mentioned in previous study, the absorption in a gas phase cavity experiment can be expressed by [17]:

$$\left(\frac{I_0(\lambda)}{I(\lambda)}\right)_{cavity} = 1 + \frac{2.303 \varepsilon_{\lambda} C l}{(1-R)} \quad (1)$$

$I_0(\lambda)$  and  $I(\lambda)$  are the measured transmitted intensities with and without the absorber in the cavity,  $l$  is the optical path length through the sample in the cavity in cm,  $R$  is the average mirror reflectivity,  $\varepsilon_{\lambda}$  is the wavelength dependent molar extinction coefficient in  $M^{-1} cm^{-1}$ , and  $C$  is the concentration of the sample in M. This expression which is valid for all reasonable absorptions shows that in a cavity experiment  $I_0(\lambda)/I(\lambda)$  is linearly proportional to the concentration of the analyte. It can be seen from equation 1 that the enhancement offered by a cavity experiment over a single pass experiment is due to the term  $1/(1-R)$ . If this is set to be the *CEF*, then the expression can be rearranged in terms of *CEF*:

$$CEF(\lambda) = \frac{\left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)_{cavity}}{2.303 \varepsilon_{\lambda} C l} \quad (2)$$

Therefore, the *CEF* can be calculated at a given cavity absorption and concentration if the molar extinction coefficient of the analyte at a given wavelength  $\epsilon_\lambda$  and the base pathlength of measurement are known.

The *CEF* values could be averaged over several concentrations to obtain a more representative value. Alternatively if  $\left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)_{cavity}$  is plotted versus concentration and the gradient of the plot divided by  $2.303\epsilon_\lambda l$  then a value of the *CEF* at a given wavelength and averaged over a range of concentrations is obtained. This was the approach taken in this study with a linear regression fitted through a plot of cavity absorption versus concentration to obtain the gradient by a least squares method. Much greater confidence can be attached to the *CEF* values obtained in this manner

The *CEF* value can be used to calculate the effective pathlength of measurement ( $l_{eff} = l \times CEF$ ) where  $l$  is the base pathlength. The effective pathlength is used in the calculation of the sensitivity of the measurement which is defined in terms of the minimum detectable change in the absorption coefficient  $\alpha_{min}$ . This is given by the expression:

$$\alpha_{min} = \frac{2.303 \Delta ABS_{min}}{l_{eff}} \quad (3)$$

where  $\Delta ABS_{min}$  is the minimum detectable absorbance change. Before the start of a series of measurements two successive  $I_0$  spectra were recorded and an absorbance spectrum calculated by treating one of the spectra as the  $I$  spectrum. This 'blank' spectrum consisted of a flat line centred around an absorbance of zero.  $\Delta ABS_{min}$  could be calculated from this spectrum by measuring the standard deviation in absorbance around the wavelength of measurement which was usually the wavelength of peak cavity absorption.

The value of  $\alpha_{min}$  could also be used to calculate the limit of detection (*LOD*) of an analyte which is defined as the smallest amount that can be reliably measured. It was calculated from the expression:

$$LOD = \frac{3\alpha_{min}}{2.303\epsilon_\lambda} \quad (4)$$

#### 4. RESULTS

BBCEAS measurements have been obtained with liquid-phase on the ultraviolet wavelength region. All measurements were taken for a series of analytes at the peak emission wavelength for each LED at 367 nm, 375 nm, and 397 nm with a cavity formed by two high reflectivity  $R \geq 0.99$  UV-mirrors.

Liquid-phase BBCEAS measurements were carried out in a 1 cm cuvette for a series of dyes, rhodamine B (Sigma Aladrich, U.K), congo red (Sigma Aladrich, U.K), and holmium (Sigma Aladrich, U.K) which were dissolved in deionised water using an appropriate UV-LED and a cavity formed by two high reflectivity  $R \geq 0.99$  UV-mirrors.

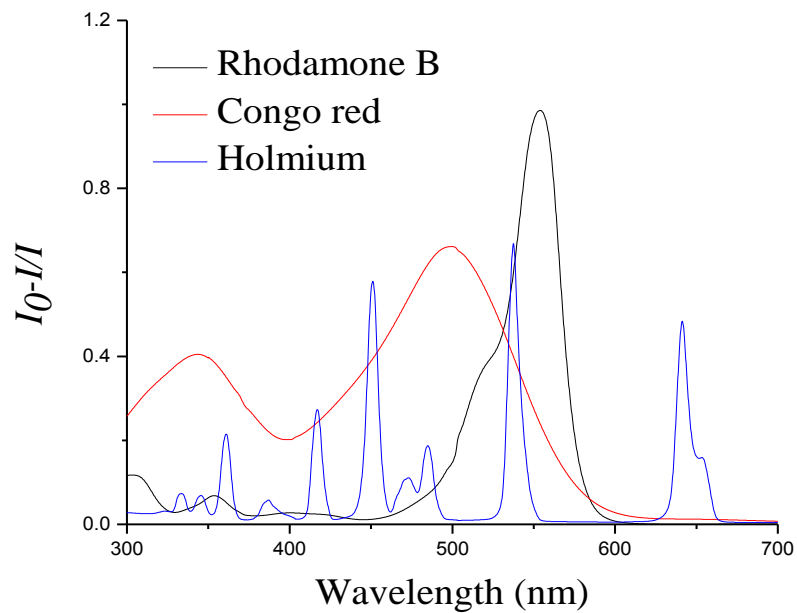
The series of measurements were made on each dye individually and these measurements are summarised in Table 1 which lists important figures of merit obtained from these data such as the *CEF*, the wavelength of measurement, the total acquisition time, the

sensitivity  $\alpha_{min}$  and also the time independent  $\alpha_{min}(t)$  ( $\alpha_{min} \times \sqrt{(\text{total acquisition time/s})}$  for each measurement, the *LOD* for each analyte and the molar extinction coefficient ( $\epsilon$ ) of the analyte at the wavelength of measurement.

**Table 1.** A summary of the results obtained in terms of analyte with  $R \geq 0.99$  mirror set, the wavelength of measurement, the CEF value, the total acquisition time, the sensitivity  $\alpha_{min}$  and also the time independent  $\alpha_{min}(t)$  ( $\alpha_{min} \times \sqrt{(\text{total acquisition time/s})}$  for each measurement, and the *LOD* of the analyte calculated from  $\alpha_{min}$  and  $\alpha_{min}(t)$ .

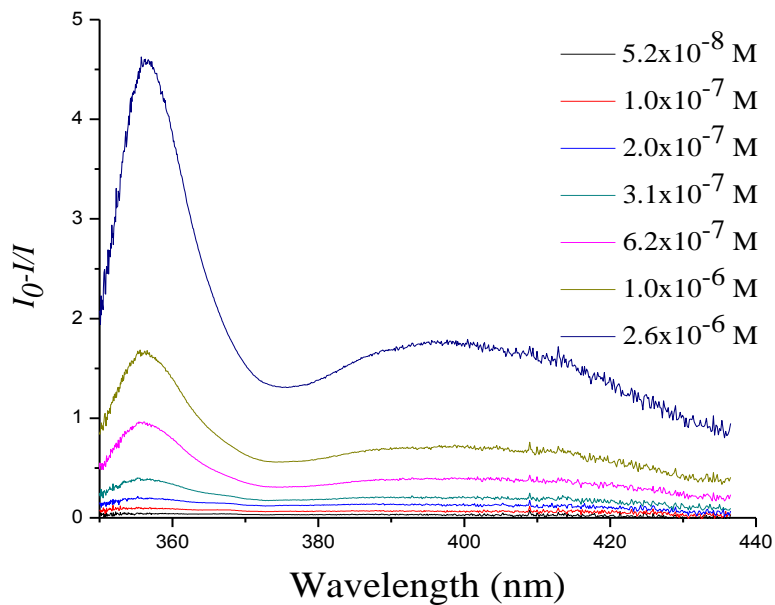
Analytes	$\lambda$ (nm)	CEF	Total acquisition time (s)	$\alpha_{min}$ ( $\text{cm}^{-1}$ $\times 10^{-6}$ )	$\alpha_{min}(t)$ ( $\text{cm}^{-1}\text{Hz}^{-1/2}$ $\times 10^{-6}$ )	<i>LOD</i> (M)	<i>LOD(t)</i> (M)	$\epsilon$ ( $l/M \cdot \text{cm}$ )
Rhodamine B	367	86	1	4.0	4.0	$1.4 \times 10^{-9}$	$1.4 \times 10^{-9}$	$3.5 \times 10^3$
Rhodamine B	375	82	1	2.7	2.7	$1.2 \times 10^{-9}$	$1.2 \times 10^{-9}$	$2.7 \times 10^3$
Rhodamine B	397	86	1	2.2	2.2	$8.6 \times 10^{-9}$	$8.6 \times 10^{-9}$	$3.3 \times 10^3$
Congo red	367	85	1	4.0	4.0	$2.4 \times 10^{-10}$	$2.4 \times 10^{-10}$	$2.1 \times 10^4$
Congo red	375	84	1	2.6	2.6	$1.8 \times 10^{-10}$	$1.8 \times 10^{-10}$	$1.8 \times 10^4$
Congo red	397	89	1	2.1	2.1	$1.9 \times 10^{-10}$	$1.9 \times 10^{-10}$	$1.4 \times 10^4$
Holmium	359	85	1	1.9	19	$2.1 \times 10^{-5}$	$2.1 \times 10^{-5}$	1.177
Holmium	381	84	1	5.2	5.2	$3.4 \times 10^{-5}$	$3.4 \times 10^{-5}$	0.1976
Holmium	418	85	1	14	14	$1.2 \times 10^{-5}$	$1.2 \times 10^{-5}$	1.4445

BBCEAS technique allows measured the spectral absorption of analyte over a wide wavelength ranges which is limited by the bandwidth of light source and cavity mirrors. In the UV-region of the electromagnetic radiation, LEDs are available at selected wavelengths in the UV region which is emitted a narrow bandwidth of light, likewise the available mirrors in this region have a narrow bandwidth; therefore; our measurements have been limited by a narrow of both LED and cavity mirrors. Consequently the spectral range of measurements was recorded over  $\sim 100$  nm wavelength range. The spectra of analytes under study were clarified over a broad bandwidth range from 300-700 nm using a double beam Jasco spectrometer as shown in Figure 4.



**Fig. 4.** Single pass absorption ( $I_0-I/I$ ) spectra of rhodamine B, congo red, and holmium dissolved in water, recorded in a 1 cm path length cell with a double beam spectrometer.

#### 4. 1. Rhodamine B

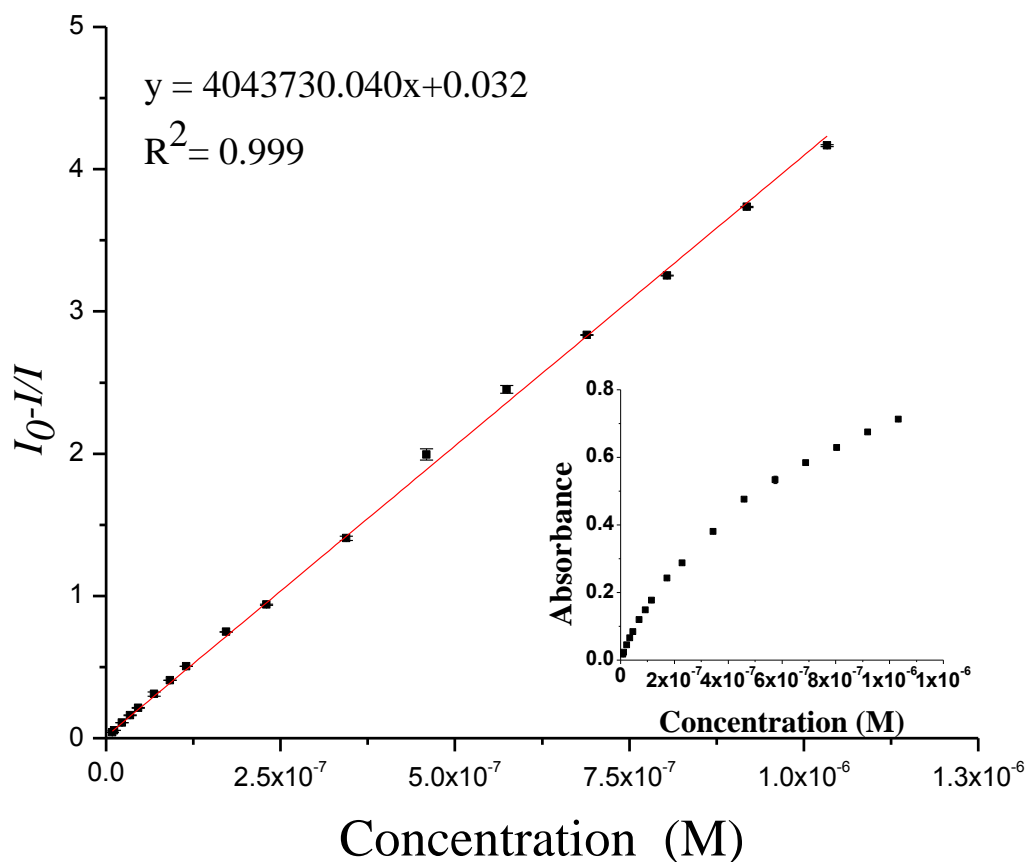


**Fig. 5.** Absorption ( $I_0-I/I$ ) spectrum of rhodamine B in distilled water in the range 350-435 nm, obtained with the UV-LED at 367 nm peak emission wavelength and the  $R \geq 0.99$  uv-mirror set.

Figure 5 shows representative absorption ( $I_0-I/I$ ) spectra recorded over a  $\sim 100$  nm wavelength range in a single measurement for rhodamine B using the UV-LED at 367 nm peak emission wavelength and the  $R \geq 0.99$  UV-mirror set.

#### 4. 2. Congo red

Figure 6 shows plots of the linearity between absorption ( $I_0-I/I$ ) and concentration for the congo red at  $\lambda_{\max} = 367$  nm and a range of concentrations from  $\sim 8.6$  nM to  $\sim 1$   $\mu$ M. The inset figure shows an absorbance versus concentration plot of congo red. Three replicate measurements were made at each concentration and the error bars for each concentration represent the standard deviation of the measurements. A linear least squares regression through the linear part of the plot yields a straight line (equation of the line is given in Fig. 6) with the correlation coefficient  $R^2 = 0.999$ .

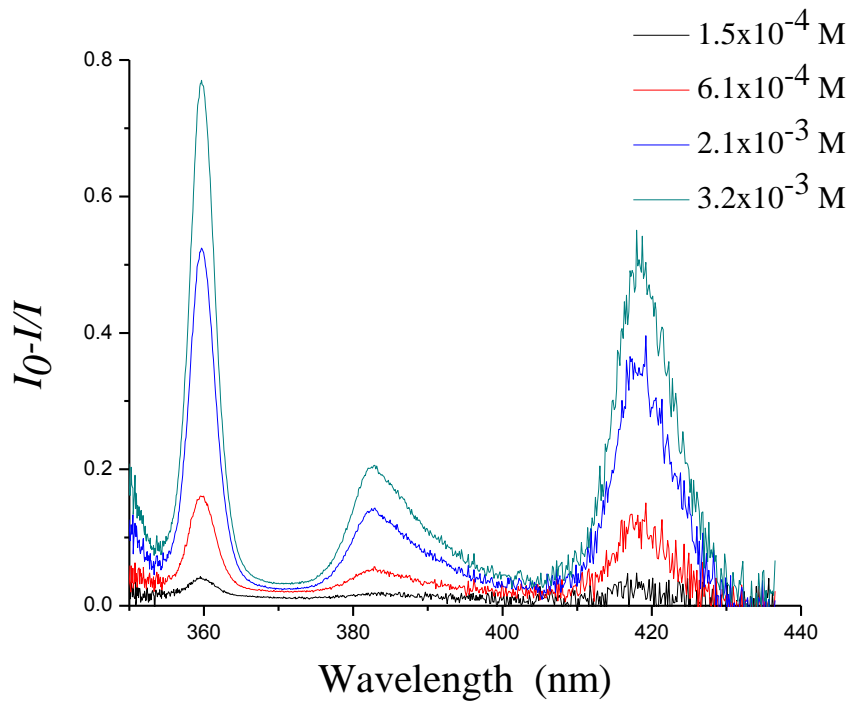


**Fig. 6.** Absorption ( $I_0-I/I$ ) versus concentrations plot of congo red, in the range  $\sim 8.6$  nM to  $\sim 1$   $\mu$ M, obtained using the UV-LED at 367 nm peak emission wavelength, the  $R \geq 0.99$  uv-mirror set and a cooled Andor spectrometer. The inset figure shows an absorbance versus concentration plot for congo red. The error bars represent the  $1\sigma$  error limit of three replicate measurements at each concentration.

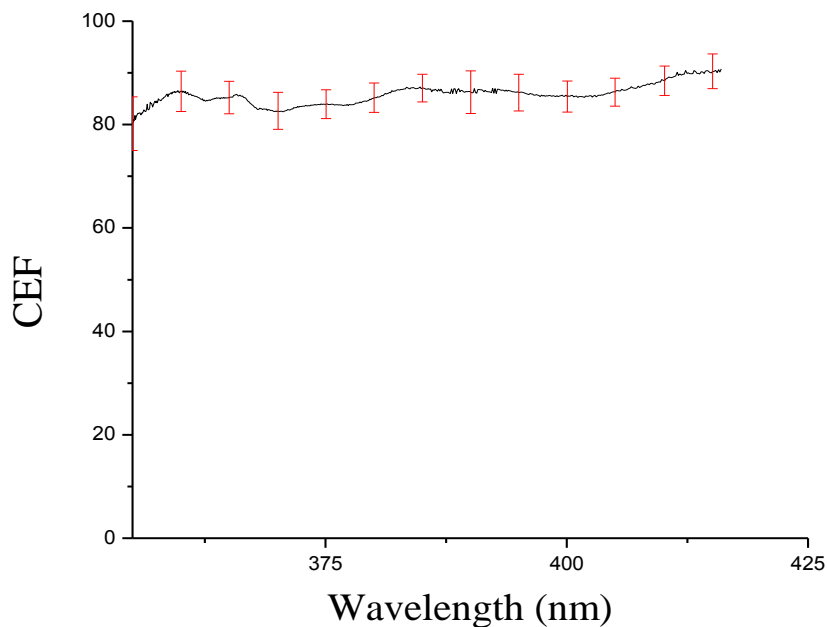
The equation on the diagram refers to a linear least squares fit to the measurements shown in the absorption plot.



### 4. 3. Holmium



**Fig. 7.** Absorption ( $I_0 - I / I$ ) spectrum holmium in distilled water in the range 350-435 nm, obtained with the UV-LED at 359 nm peak emission wavelength and the  $R \geq 0.99$  UV-mirror set.



**Fig. 8.** The CEF values as a function of wavelength in a 1 cm cuvette (rhodamine B and congo red dissolved in distilled water), recorded with UV-LED and the  $R \geq 0.99$  UV-mirror set. Representative error bars obtained from the standard deviation of the CEF values for five concentrations.

Figure 7 shows representative absorption ( $I_0-I/I$ ) spectra recorded over a  $\sim 100$  nm wavelength range in a single measurement for holmium using the UV-LED at 359 nm peak emission wavelength and the  $R \geq 0.99$  UV-mirror set. The  $CEF$  value across  $\sim 60$  nm wavelength was recorded for two analytes separately, rhodamine B and congo red, by stitching three selected ranges of ultraviolet wavelength region to produce a single plot.

Figure 8 shows a plot of the average of  $CEF$  value as a function of wavelength recorded with rhodamine B and congo red dissolved in distilled water in a 1 cm cuvette. Representative error bars were obtained from the standard deviation of the  $CEF$  values for five concentrations. The average standard deviation in the  $CEF$  value across the wavelength range was  $\sim 3.3$ .

## 5. DISCUSSION

The first reported application of BBCEAS detection to liquid phase in a 1 cm cuvette at ultraviolet wavelength region has been demonstrated by this study. Initially, the main figures of merit obtained for liquid-phase in a 1 cm cuvette have been discussed. The main figures of merit obtained were values of the  $CEF$ , the  $\alpha_{min}$ , and also the  $LODs$  for each analytes. After that, a comparison will be made with previous cavity studies with the liquid-phase analytes. Finally, some suggestions will be given on the experimental setup to improve the sensitivity of measurements.

The main figures of merit obtained with the  $R \geq 0.99$  UV-mirror set at three selected UV-wavelength ranges for the rhodamine B, congo red, and holmium are listed in Table 1. The  $CEF$ 's values for all analytes at all selected wavelength regions are approximately the same. These values are restricted by interface losses from the cuvette windows of  $7.2 \times 10^{-4}$  per pass. The small difference is generally due to the variation in the reflectivity profile of the mirror set as a function of wavelength. It should be noted that the  $CEF$ 's values are calculated for the analyte at the central emission wavelength of the UV-LED. The small difference between two analytes at the same wavelength is probably due to the alignment of the cuvette inside the cavity. By comparison measurements on rhodamine B at 555 nm in the 1 cm cuvette (our previous study) [18] yielded a  $CEF$  of 81. These results indicate that background scattering and absorption losses by the cuvette windows leads to small increase in the  $CEF$  value for this because the new cuvette was used in this study.

The  $\alpha_{min}$  values, which are indicated to the sensitivity of the BBCEAS measurements, are determined for all measurements in this study and only a small difference was found. As mentioned before, the lower  $\alpha_{min}(t)$  values which depend on the baseline noise and the  $CEF$  values as well as the total acquisition time were  $2.2 \times 10^{-6} \text{ cm}^{-1} \text{ Hz}^{-1/2}$ ,  $2.1 \times 10^{-6} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  and  $5.2 \times 10^{-6} \text{ cm}^{-1} \text{ Hz}^{-1/2}$  for rhodamine B, congo red and holmium respectively with the  $R \geq 0.99$  uv-mirrors. From Table 1 it can be seen that the value obtained in this study increased with the increase the deep of the uv-wavelength region.

The  $LOD$  values have been calculated for all analytes based on the sensitivity of the measurement value and  $\varepsilon$  of the analyte. Comparing the values calculated using both  $\alpha_{min}$  and  $\alpha_{min}(t)$  the  $LOD$  values are similar for the measurements due to use a short integration time with the  $R \geq 0.99$  uv-mirror set. It is obvious from Table I that the lower value of  $\alpha_{min}$  and higher value of  $\varepsilon$  produced a lower  $LOD$  value of  $1.8 \times 10^{-10} \text{ M}$  for congo red.

Table 2 compares some of the figures of merit for this study with previous liquid-phase cavity measurements, in terms of the technique, the mirror reflectivity, base path length, the wavelength of measurement, the lowest value of  $\alpha_{min}$ , the base pathlength normalised  $\alpha_{min}$  values, the lowest LOD, and the molar absorption coefficient for the analyte. The base pathlength normalised  $\alpha_{min}$  values normalised to a base pathlength of a 1 cm were obtained by multiplying the value of  $\alpha_{min}$  by the base pathlength in cm unit and allows fairer comparison between studies with different base pathlengths.

From Table 2, it can be seen that the mirror reflectivity used in this study was much lower compared to the previous studies. Mirror reflectivity of  $R \geq 0.99$  produced the lowest  $\alpha_{min}$  value which was  $2.1 \times 10^{-6} \text{ cm}^{-1}$  at 397 nm. This is the lowest reported value to date for a liquid-phase measurement. Obviously from Table 2, only two previous HPLC-CRDS studies at ultraviolet wavelength region are available. Both studies have been performed by van der Sneppen et al [14,15]. In the first study the interface losses were ignored by using a silicon rubber spacer of 0.2 cm pathlength which was clamped tightly between two high reflectivity mirrors to form a volume of a flow cell of 12  $\mu\text{L}$ . This setup was tested at visible wavelength region and then checked with ultraviolet wavelength region at 355 nm.

**Table 5.** A comparison between this study and previous liquid-phase cavity studies as a function of technique, the mirror reflectivity, base pathlength, the wavelength of measurement, the lowest value of  $\alpha_{min}$ , the minimum LOD for an analyte, and the molar extinction coefficient  $\epsilon$  for that analyte.

Study	Technique	$R \geq$	$l$ (cm)	$\lambda$ (nm)	$\alpha_{min}$ ( $\text{cm}^{-1}$ )	Normalised $\alpha_{min}$ ( $\text{cm}^{-1}$ )	LOD (M)	$E$ ( $1/\text{M}\cdot\text{cm}$ ) $\times 10^4$
This study	BBCEAS	0.99	1	397	$2.1 \times 10^{-6}$	$2.1 \times 10^{-6}$	$1.9 \times 10^{-10}$	1.4
van der Sneppen et al. [14]	CRDS	0.99993	0.2	457	$1.0 \times 10^{-5}$	$2.0 \times 10^{-6}$	$1.2 \times 10^{-8}$	3.6
van der Sneppen et al. [14]	CRDS	0.9995	0.2	355	$5.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	$7.5 \times 10^{-8}$	1.02
van der Sneppen et al. [15]	CRDS	0.9995	1	355	$3.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	$4.0 \times 10^{-8}$	1.02
van der Sneppen et al. [15]	CRDS	0.9991	1	273	$1.0 \times 10^{-3}$	$1.0 \times 10^{-3}$	$5.0 \times 10^{-7}$	-

The sensitivity of measurement with the van der Sneppen setup was better at visible wavelength region than at ultraviolet wavelength region due to the fabrication of high mirror reflectivity at UV-wavelength being more complicated. The use of high reflectivity mirrors and the reduction of losses due to the direct contact between the solution and mirrors resulted in low values of  $\alpha_{min}$  for the measurement at 457 nm ( $1.0 \times 10^{-5} \text{ cm}^{-1}$ ), whilst the  $\alpha_{min}$  value was worse at 355 nm due to the quality of the mirrors in UV range. Compared to the sensitivity of our study, it had a significantly worse  $\alpha_{min}$  value of  $5.0 \times 10^{-5} \text{ cm}^{-1}$ .

This is about five times higher than the current study and was obtained using a more expensive experimental setup, with higher reflectivity mirrors and a more complex experimental methodology.

The second study of van der Sneppen [15] used a 1 cm super polished cuvette in HPLC-CRDS technique to reduce the scattering losses from the cuvette windows. The sensitivity of our setup is better by a factor of 14 compared to the best sensitivity of van der Sneppen's last study which used a more complicated experimental setup, higher mirror reflectivity but with the same base pathlength. The lowest *LOD* of 190 pM was obtained for congo red in this study. This value represented the lowest value compared to the previous study as shown in Table 3.

## 6. CONCLUSIONS

The first reported application of a BBCEAS to liquid phase at UV-wavelength region has been demonstrated in this study. A simple BBCEAS experimental setup has been shown for the measurement of three representative liquid-phase analytes in a 1 cm cuvette placed at 0 degrees inside the cavity. Measurements were made with UV-LED at three selected regions (397, 375, and 367) and an  $R \geq 0.99$  UV-mirror set on a liquid phase of rhodamine B, congo red and holmium. The *CEF* values were calculated with liquid for many UV-wavelength ranges in this study. The best value of  $\alpha_{min}$  of  $2.1 \times 10^{-6} \text{ cm}^{-1}$  was obtained with liquid-phase. However, in comparison to previous liquid-phase studies, this value represents the most sensitive liquid-phase absorption reported to date at uv-wavelength region. On the other hand, the best *LOD* values of 190 pM and 4.5  $\mu\text{M}$  are obtained for congo red. Three UV-LED with three selected wavelength regions were used to calculate *CEFs* values as a function of wavelength for  $\sim 60 \text{ nm}$ . Many modifications could be used for the experimental setup in order to improve the sensitivity of measurements through the use of a more powerful LED with a broad bandwidth, the use of higher reflectivity cavity mirrors with a broad bandwidth, and the increase of the base pathlength of the sample. To date, there are many challenges to manufacture high reflectivity mirrors with a broad bandwidth and UV-LED with high intensity and a broad bandwidth.

## References

- [1] R. Engeln, *Review of scientific instruments*, 69 (1998) 3763.
- [2] J. M. Langridge, S. M. Ball, A. J. L. Shillings, and R. L. Jones, *Review of scientific instruments*, 79 (2008) 123110.
- [3] Ventrillard-Courtillot, E. Sciamma O'Brien, S. Kassi, G. Méjean, D. Romanini, *Applied Physics B Laser and Optics*, 101 (2010) 661.
- [4] M. D. Buzaianu, V. I. Makarov, G. Morell, and B. R. Weiner, *Chemical Physics Letters*, 455 (2008) 26.
- [5] J. P. M. Hoefnagels, Y. Barrel, W. M. M. Kessels, and M. C. M. Van de Sanden, *Journal of Applied Physics*, 96 (2004) 4094.

- [6] T. Gherman, D. S. Venables, S. Vaughan, J. Orphal, and A. A. Ruth, *Environmental Science and Technology*, 42 (2008) 890.
- [7] W. Denzer, M. L. Hamilton, G. Hancock, M. Islam, C. E. Langley, R. Peverall, and G. A. D. Ritchie, *Analyst*, 134 (2009) 2220.
- [8] S. E. Fiedler, A. Hese, and A. A. Ruth, *Review of scientific instruments*, 76 (2005) 023107.
- [9] Islam, L. N. Seetohul, and Z. Ali, *Appl. Spectrosc.*, 61(2007) 649.
- [10] L. Van der Sneppen, A. Wiskerke, F. Ariese, C. Gooijer, and W. Ubachs, *Appl. Spectrosc.*, 60 (2006) 931.
- [11] L. Van der Sneppen, F. Ariese, C. Gooijer, and W. Ubachs, *Journal of Chromatography A*, 1148 (2007) 184.
- [12] S. Xu, G. Sha, and J. Xie, *Rev. Sci Instrum.*, 73 (2002) 255.
- [13] K. L. Snyder and R. N. Zare, *Anal. Chem.*, 75 (2003) 3086.
- [14] L. van der Sneppen, A. Wiskerke, F. Ariese, C. Gooijer, and W. Ubachs, *Appl. Spectrosc.*, 60 (2006) 931.
- [15] L. van der Sneppen, F. Ariese, C. Gooijer, and W. Ubachs, *Journal of Chromatography A*, 1148 (2007) 184.
- [16] S. E. Fiedler, A. Hese, and A. A. Ruth, *Review of scientific instruments*, 76(2005) 023107.
- [17] M. Islam, L. N. Seetohul, and Z. Ali, *Appl. Spectrosc.*, 61 (2007) 649.
- [18] N. Sh. Qas Nouna, "Application of Broadband Cavity Enhanced Absorption Spectroscopy to condensed Phase Analytes", PhD. Thesis submitted to the Teesside University, 2011.

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