

Solid-Phase BBCEAS Measurements at UV wavelength

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ABSTRACT

Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS) is employed in this study as a sensitive technique for measuring the absorption of thin films deposited onto a glass substrate. A thin film of the analytic Rhodamine B was deposited on glass microscope coverslips. Drop coating method was used to deposit a thin film over the microscope coverslips. The most sensitive measurements as determined by the minimum detectable loss per pass ($\Delta F_{min}(t)$) at 397 nm and the $R \geq 0.99$ ultra violet mirror set. A value of $\Delta F_{min}(t) = 5.2 \times 10^{-6}$ was obtained.

Keywords: Broadband cavity enhanced absorption spectroscopy; BBCEAS, Thin films; Drop coating method; Absorption spectroscopy; Ultraviolet emitted diode; UV-LED.

نوره شمعون اوراها قس نونا

منظومة محلل الامتصاص الطيفي المحسن ذات المدى العريض (BBCEAS) استخدمت في الدراسة الحالية كتقنية ذات حساسية عالية لدراسة طيف الامتصاص لغشاء رقيق مترسب على شريحة زجاجية. غشاء رقيق من صبغة Rhodamine B رسبت على شريحة المجهر الزجاجية باستخدام تقنية الطلاء بواسطة التقطير. النتائج الاكثر حساسية تم حسابها عند قياس اقل خسارة بالطاقة لكل انعكاس بالضوء ($\Delta F_{min}(t)$) عند الطول الموجي 397 nm و باستخدام مرآة ذات انعكاسية $R \geq 0.99$ عند المنطقة فوق البنفسجية. قيمة ($\Delta F_{min}(t)$) التي تم الحصول عليها من خلال هذه التقنية كانت مساوية الى 5.2×10^{-6} .

Introduction

The measurement of lowest optical absorbance values is a continuous preoccupation of the trace analyst. The improvement of the limits of the absorbance detection for analytes by a conventional absorption spectroscopy is a main challenge in the analytical chemistry method development. In recent decades, several absorption techniques have been explored for making ultrasensitive absorption measurements at high resolution. Cavity ring down spectroscopy (CRDS) [1] and more recently, cavity enhanced absorption spectroscopy [2] (also referred to as integrated cavity output spectroscopy (ICOS) [3]). While CRDS and CEAS have been used most frequently in the study of gasses [4-7] and liquid [8-11], there have been a few attempts to extend CRDS technique to the study of thin films. Most previous studies were performed in the infrared range because of lower scattering and absorption losses from the substrate [12-14]. Two studies have made CRDS measurements on thin films in the visible range [15, 16].

An another experimental arrangement for the cavity enhanced absorption measurement of thin films involves using a prism placed in an optical cavity and aligned such that an evanescent wave (EW) is produced at the prism interface where total internal reflections (TIR) occurs. The absorption of the thin film is studied by depositing the thin film on this interface. CRDS and CEAS were coupled with total internal reflection spectroscopy as an evanescent wave CRDS or an evanescent wave CEAS to study the absorption for solid/gas or solid/liquid interfaces unlike single pass internal reflection spectroscopy, EW-CRDS and EW-CEAS are very sensitive techniques due to the multipass reflection[17-24].

This study aims to investigate the application of UV-LED BBCEAS to thin films of rhodamine B, deposited on a thin glass microscope slide and placed at 0 degrees in an optical cavity formed by two high reflectivity ($R \geq 0.99$) ultra violet mirrors. Drop coating method for creating thin films was used.

Experimental setup

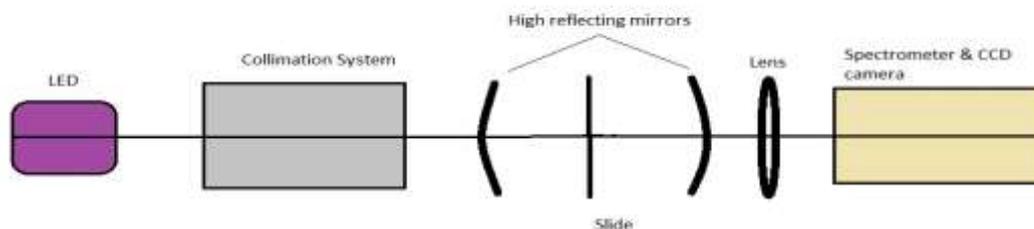


Fig. 1: A schematic of the experimental setup for the solid-phase BBCEAS measurements.

A schematic of the experimental setup is shown in figure 1. Most of the apparatus i.e. the LED light source, the collimation components (the lens and irises), the optical cavity mirrors and the detection system (the cooled Andor spectrometer) were the same as used in our previous study [25]. The main difference was the use of thin films deposited on glass slides. These were clamped to a custom made polymer holder which was itself attached to a kinematic lens mount. A glass slide was inserted into the cavity at 0 degrees to minimize the absorption and scattering losses. The experimental procedure consisted of first recording a background spectrum with a blank uncoated glass slide followed by recording a sample spectrum with the thin film coated glass slide.

Drop coating Method for depositing thin films

The thin film is a layer of material which has a monolayer thickness of a nanometer or less up to a thickness of several microns. There are many applications of thin films, such as the protection of substrate materials against corrosion, oxidation and wear. The act of applying a thin film to a surface is called thin-film deposition. There are two broad classes of deposition techniques, depending on whether the process is primarily chemical or physical. Many industrial applications use thin film in areas of optical coatings and electronic semiconductor devices. These films can be created by a variety of methods. These methods include dip coating, spin coating, and drop coating.

Drop coating is probably the simplest method for depositing a uniform thin film of desired molecule on a glass slide. In this method, the solution used to create the thin film is prepared from a volatile solvent. The solution is simply dropped onto the substrate and the thin film is created following the evaporation of the solution. The drop coating method has two main advantages: it is simple to use, and it can be used to create the sample

directly in-situ inside the cavity without disturbing the alignment of the coverslip within the cavity.

Experimental Methodology

As noted in previous studies, CEAS is not a self-calibrating absorption technique in which the absorption coefficient (α) can be directly calculated. CEAS requires a reliable calibration procedure in order to determine the reflectivity of the mirror either by using CRDS or by measuring the absorption of a reference compound of known concentration known extinction coefficient in the cavity. The cavity enhancement factor (CEF) or the number of passes through the cavity can be obtained through calibration. The single pass measurement of the thin films was carried out using a standard double beam UV-Visible absorption spectrometer (Jasco V630). The same slides were used to perform the cavity measurements, thus avoiding errors due to differences in thin film thickness. The cavity enhancement factor CEF for the thin film measurements can be calculated by the following equation [23]

$$CEF = \frac{\left(\frac{I_0}{I} - 1\right)_{cavity}}{2.303\varepsilon Cl} \quad (1)$$

Obviously, in solid phase measurements it was not straightforward to determine either the base pathlength of measurement (l) or indeed the molar extinction coefficient of the rhodamine B thin film (ε). The quantity in the denominator εCl however, is just the single pass absorbance of the thin film for a given concentration and thus if the cavity absorption is measured the CEF determination is straightforward. In practice the gradient of a plot of cavity absorption versus dye solution concentration was divided by 2.303 times the gradient of a plot of the single pass absorbance versus dye solution concentration. This gave a CEF value averaged over several concentrations.

The calculation of the sensitivity of the technique requires the measurement of the baseline absorbance noise or the minimum detectable change in absorbance, ΔABS_{min} . This was obtained from the standard deviation of the absorbance value at the peak wavelength of the analyte. A blank absorbance spectrum was calculated by recording two successive I_0 spectra with a blank glass slide in the cavity and treating one spectrum as the

sample spectrum. To allow fairer comparison between different experiments the time independent minimum detectable absorbance change $\Delta ABS_{min}(t)$ ($\Delta ABS_{min} \times \sqrt{(\text{total acquisition time/s})}$) was calculated. Unlike the liquid phase measurements α_{min} was not used to measure the sensitivity, as the measurement of the base pathlength was not straightforward. Two alternative measures of sensitivity are the minimum detectable absorbance change per pass which can be calculated by dividing ΔABS_{min} by the *CEF* value and the minimum detectable per pass fractional loss (ΔF_{min}). The minimum detectable fractional loss could be calculated as:

$$\left(1 - \frac{\Delta I_{min}}{I_0}\right) = 1 - 10^{-\Delta ABS_{min}} \quad (2)$$

The per pass fractional losses could be calculated by dividing this by the *CEF* value. This latter value is quoted in the results section as it seems to be more widely used in the literature. The limit of detection (*LOD*) was calculated from $\Delta ABS_{min}(t)$.

$$LOD = \frac{3\Delta ABS_{min}(t)}{\epsilon l_{eff}} \quad (3)$$

Where l_{eff} is the effective pathlength ($l \times CEF$). As a result of the uncertainty in the measurement of thickness and the molar extinction coefficient of the thin film, the *LOD* could be obtained by dividing the numerator by the gradient of a plot of cavity absorption versus solution concentration and multiplying by 2.303.

Results and Discussion

This represents the first time that BBCEAS has been applied to solid-phase in which results have been obtained for solid-phase BBCEAS measurements in a thin film of rhodamine B deposited on a glass microscope coverslips at ultraviolet wavelength region.

Experiments have been performed on thin films of rhodamine B dye deposited on (22 mm × 64 mm) 0.14 mm thickness glass microscope coverslips (Fisher Scientific, UK). All measurements were taken for Rhodamine B 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. All measurements are summarised in Table I. The Table lists important figures of merit obtained from these data such as the *CEF*, the

wavelength of measurement, the thickness of thin film l , the minimum detectable per pass fractional loss ΔF_{min} , the time independent minimum detectable per pass fractional loss $\Delta F_{min}(t)$ and an estimation of the LOD for each analyte.

Table I: summarises the measurements made in terms of the thin film of analyte studied.

Analyte	CEF	λ/nm	l/nm	ΔF_{min}	$\Delta F_{min}(t)$	LOD/M	LOD(t)/M
Rhodamine B	66	367	2.4	7.2×10^{-6}	7.2×10^{-6}	4.5×10^{-6}	4.5×10^{-6}
Rhodamine B	69	386	2.4	1.1×10^{-5}	1.1×10^{-5}	9.8×10^{-6}	9.8×10^{-6}
Rhodamine B	72	397	2.4	5.2×10^{-6}	5.2×10^{-6}	5.1×10^{-6}	5.1×10^{-6}

The CEF values obtained at selected wavelength regions are similar and the small difference was due to the vibration in the reflectivity profile as wavelength. The sensitivity of measurements was calculated using the minimum detectable per pass fractional loss (ΔF_{min}) and the time independent minimum detectable per pass loss ($\Delta F_{min}(t)$). Comparing between different wavelength regions the value of (ΔF_{min}) was lower at 397 nm due to the minimum increase number of passes in that region.

As stated before, the LOD values which were calculated from ΔABS_{min} largely mirrored the trends shown by ΔF_{min} with the lowest LOD shown the measurement on the thin slides with the $R \geq 0.99$ UV-mirrors. The LOD for rhodamine B thin film has been calculated.

Figure 2 shows representative absorption (I_0-I/I) spectra of rhodamine B deposited on a borosilicate coverslip recorded with the UV-LED at 367 nm peak emission wavelength, $R \geq 0.99$ UV-mirror sets and a cooled Andor spectrometer.

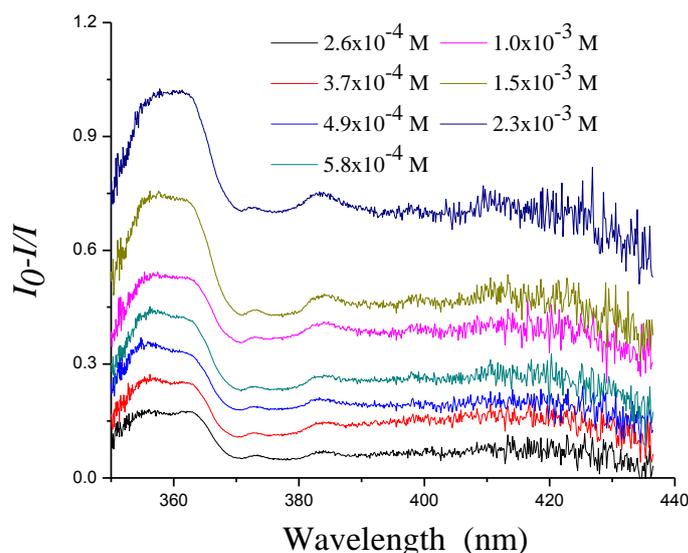


Fig. 2: Absorption (I_0-I/I) spectra of rhodamine B thin film deposited on the borosilicate coverslip obtained using the UV-LED at 367 nm peak emission wavelengths, a cooled Andor spectrometer, and the $R \geq 0.99$ UV-mirror set.

Figure 3 shows the plot of absorption (I_0-I/I) versus concentration for a thin film of rhodamine B. The rhodamine B measurements were made at 386 nm and a range of (2.6×10^{-4} - 2.6×10^{-3}) M for the solution concentration of the dye. The inset plot shows the relation between concentration and absorbance. Three replicate measurements were made at each concentration and the error bars for each concentration represents 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. 3) with the correlation coefficient $R^2 = 0.993$.

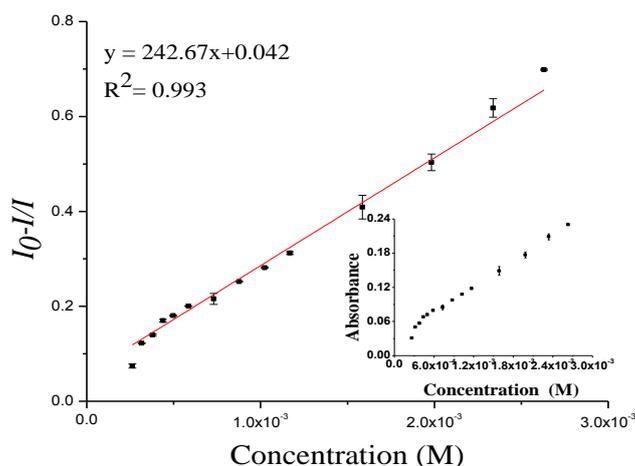


Fig. 3: Absorption ($I_0 - I/I$) versus concentrations plot of rhodamine B deposited on the borosilicate coverslip. The inset plot an absorbance versus concentrations plot of rhodamine B, in the range (2.6×10^{-4} - 2.6×10^{-3}) M.

Figure 4 shows the plot of absorption ($I_0 - I/I$) versus concentration for a thin film of rhodamine B. The inset plot shows the linear relation between concentration and absorbance by using a conventional absorption technique. Three replicate measurements were made at each concentration and the error bars for each concentration represents 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. 4) with the correlation coefficient $R^2 = 0.997$.

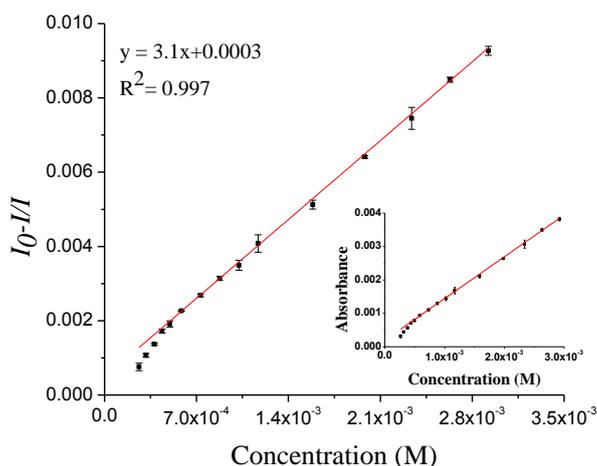


Fig.4: Absorption ($I_0 - I/I$) versus concentrations plot of rhodamine B, obtained using a standard double beam UV/VIS absorption spectrometer (Jasco V630). The inset plot an absorbance versus concentrations plot of rhodamine B, in the range (2.6×10^{-4} - 2.9×10^{-3}) M.

Although the operation of our solid-phase BBCEAS technique at UV-wavelength region produces good results, the improvements in the experiments with the $R \geq 0.99$ UV-mirrors are unlikely unless spectrometers which allow sub millisecond integration times are used with more powerful light sources. The high powerful UV-LED is available for most ultraviolet wavelength region but it has a narrow bandwidth (10-20 nm); therefore, to cover the UV wavelength region required several LEDs were emitted at different UV-wavelength range. The sensitivity could also be improved by using higher reflectivity mirrors. Such mirrors are available in many regions, though not in the ultraviolet where optical absorption and scattering in the mirror layers tends to limit reflectivities. The bandwidth of the UV-mirror also narrows compares to the mirror at visible wavelength region. UV-mirrors with broad bandwidth which cover the range 250-400 nm with $R \geq 0.99$ reflectivity are now available but the production of UV-mirrors with higher reflectivity and broad bandwidth are more problematical.

Conclusion

The first reported application of a BBCEAS to solid phase at UV-wavelength region has been demonstrated in this study. A simple BBCEAS experimental setup has been shown for the measurement of rhodamine B thin film which is deposited on a thin glass microscope coverslip by using a drop coating method 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 solid-phase of a thin film of rhodamine B. The *CEF* values were calculated with solid phase for many UV-wavelength ranges in this study. The best value of ΔF_{min} of 5.2×10^{-6} was obtained with solid-phase. 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 and the use of higher reflectivity cavity mirrors with a broad bandwidth. To date, there are many challenges to manufacture high reflectivity UV- mirrors with a broad bandwidth and UV-LED with high intensity and a broad bandwidth.

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