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Parts-per-billion Limits of Detection via Absorbance Spectroscopy: An Ultraviolet (254 nm) Absorbance Detector for Liquid Chromatography using a Light Emitting Diode (LED)

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ABSTRACT
An absorbance detector for high-performance liquid chromatography (HPLC) was developed using a commercially available light emitting diode (LED) at 254 nm. Use of the LED was investigated due to its low output power fluctuation, which should minimize noise and maximize performance. This detector has been characterized and used to perform several separations of relevance to the atmospheric chemistry of airborne particulate matter, specifically, brown carbon (BrC) or humic-like substances (HULIS). The study of atmospheric BrC can be aided by sensitive and general detection schemes, such as absorbance detection. Owing to the exceptional output stability of the LED, the absorbance detector exhibited 3σ detection limits of 130 nmol/L (18 ppb) for the chromatography of 4-hydroxybenzoic acid and the detector itself demonstrated noise-equivalent absorption of approx. 180 μAU. The detector was applied to the separation of products resulting from the photo-Fenton reaction of guaiacol. No fewer than 15 individual peaks are noted in the resulting chromatogram. The sensitivity provided is a valuable tool for the chemical analysis of complex samples requiring chromatography.

Keywords: chromatography, aerosol, UV detection, LED

INTRODUCTION

Sensitive, and broadly applicable detection schemes for high-performance liquid chromatography (HPLC) is a vital measurement tool for analytical chemists. Frequently, refractive index, evaporative light scattering, or absorbance detection are utilized in this capacity due to these detectors ability to respond to most analytes. Sensitive detection is crucial not only to quantify analyte, but in many cases the detection event triggers data-dependent scans of mass spectrometers or begins fraction collection. Lowering limits of detection (L.O.D.) for chromatographic absorbance detectors is therefore crucial for exploratory science on complex samples.

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Within this topical area, an exciting recent development is the emergence of light emitting diodes (LEDs) as spectroscopic sources [1, 2]. LEDs offer several advantages within detection systems including the lack of a required warm-up period, optical switching with nanosecond rise-times, and extremely stable output intensity. While visible light LEDs have long been used for chemical sensing applications, a historical caveat of LED use for spectroscopy was lack of availability of high-output intensity devices in the deep ultraviolet. The availability of deep UV LEDs is crucial for the advancement of the technology due to the large number of organic molecules that can be detected by light absorption at wavelengths below 300 nm. In recent years, ultraviolet LEDs of sufficient intensity and lifetime have become commercially available. Indeed, many research groups have begun exploring the promise of deep-UV LEDs for chemical sensing / separation applications. Li *et al*. have used a deep-UV (235 nm) LED for on-column detection in capillary ion-exchange chromatography for iodide, nitrite, and nitrate analysis [3]. Li *et a*l. also developed an innovative miniaturized medium-pressure LC system with four-color detection (including 255 nm) based upon LEDs with minimal detectable absorbances in the mAU range based upon the figures presented in the manuscript [4]. The group led by M. Macka have used an UV-LED to construct an absorption detector for capillary electrophoresis (CE) that allowed detection of *p*-nitrophenol and oligonucleotides at millimolar concentrations [5]. In a later work, Ryvolova *et al.* [6] used an UV-LED as a spectroscopic source for fluorescence measurements that were combined with simultaneous VIS absorption and conductivity probes made at a single spatial point in capillary separations.

A specific application area that requires the development of enhanced absorbance detection for HPLC is aerosol brown carbon (BrC) analysis [7-8]. Simply stated, BrC comprises a complicated mixture of vast array of aromatic compounds present in atmospheric particulate matter that exhibit absorption in the near-ultraviolet and blue region of the spectrum (hence appear brown in color). Aerosol brown carbon is of scientific interest due to its unknown origins, and its ability to affect climate by absorbing solar radiation in Earth's atmosphere [9-20]. While the exact chemical nature of aerosol phase BrC remains nebulous due to analytical limitations, several classes of chemical compounds have been implicated as potential candidates including nitroaromatics, oligomeric condensation products of lignin sub-units, oligomers of isoprene, imidizoles, charge-transfer compounds, and reaction products of carbonyls with amines [21-29]. To complicate matters further, airborne particles are consistently exposed to a mixture of reactive gases such as ozone, oxides of nitrogen, peroxides, and sunlight that can functionalize or fragment molecules further [30-35]. Consequently, it is not uncommon to observe hundreds of organic compounds within atmospheric particulate matter [36-38].

Given the molecular complexity of aerosol BrC, an HPLC separation step prior to collection of electrospray mass spectra (ESI-MS) or fraction collection for nuclear magnetic resonance (NMR) or infrared (IR) analysis is often required for structure determination. In

turn, the detection of a chromatographic bands elution is critical to begin collecting additional data or fractions for off-line analysis. Therefore, sensitive detection is critical to success.

In this manuscript, a simple modification to a commercially available ultraviolet (UV) absorbance detector for liquid chromatography is described. The modification involves using a light emitting diode (LED) as the light source rather than a mercury lamp or deuterium lamp. Light emitting diodes have already garnered some attention as deep-UV spectroscopic sources for chromatography and capillary electrophoresis due to the very high stability of their output. Multiple authors have constructed LED-based devices that demonstrated short-term noise on the order of 4-60 micro-absorbance units (μAU)[39-41]. However, the preceding authors have reengineered both light source and light detection in their apparatus. In the current work, a laboratory absorbance detector is modified for use with the alternate UV-LED light source. This modification is simpler to achieve for investigators who lack the time and/or skills required to construct an integrated detection system, but whom desire to enjoy the benefits of using the UV-LED source. In addition, the current work focuses specifically on the analysis of aerosol BrC using the UV-LED source. Improving sensitivity for post-column analysis is crucial for triggering data-dependent scans of mass spectrometers used to acquire structural information regarding the chemical constituents of aerosol BrC.

EXPERIMENTAL

Chemicals and Reagents. Guaiacol (>99%) and 4-hydroxybenzoic acid (>99%) were obtained from Acros Organics. Chromatographic grade, anhydrous methanol was obtained from Malinckrodt. All reagents were used as acquired and not subjected to additional purification steps. Water was purified by reverse osmosis prior to use. Chromatographic mobile phases were prepared as either 50:50 v/v methanol and water or 40:60 v/v methanol in water.

Chromatography. A Hitachi L-6200A reciprocating piston pump was used to deliver mobile phase at a flow rate of 0.8 mL / min. Typical column pressures were 1600-1700 psi. Sample injection occurred thru a Rheodyne six port valve (model 7125) using a 20 μL loop. A 15 cm length, 4.6 mm i.d., Apollo C18 column (Grace) packed with 5 micrometer particles was used for reversed phase chromatography.

Absorbance Detector. A variable wavelength detector (Spectra 100, SpectraPhysics) was modified to utilize the LED according to **Figure 1**.

Briefly, the LED (λ=254 nm, Optan255 H-BL, Crystal IS) was affixed to a circuit board and heat sink provided by the manufacturer. Heat transfer compound was applied per manufacturer instructions. The LED apparatus was then mounted to a 2 cm height spacer tube. The spacer tube was then affixed to the chromatograph flow cell of 1 cm path-length and 1 mm aperture (SpectraPhysics). On the opposite face of the flow cell, a 1.25 cm diameter band-pass filter centered at 254 nm was placed (Andover Corp). The band-pass filter served to filter stray light that might be present, and constrain the detection wavelength. The

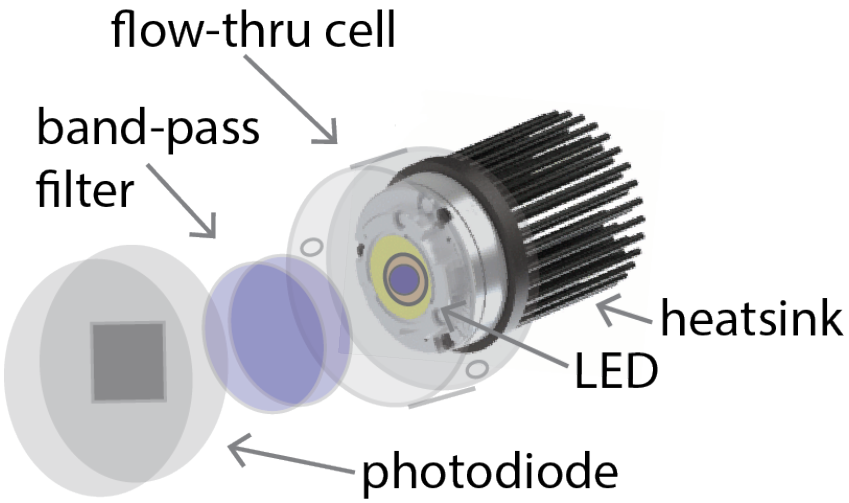

Figure 1. Illustration of LED based absorbance detector at 254 nm

photodiode of the Spectraphysics detector served as the transducer and the analog voltage out signal of the detector was routed to an external low-pass filter circuit (f_{cut} = 9.3 Hz) and an 8-bit National Instruments MyDAQ board for digitization. Data was acquired within Labview software, with a VI written in-house. The LED was powered by a constant current supply at 100 mA. The manufacturers data sheet specifies an optical output power of 0.5–1.0 mW at 100 mA drive current, but this was not experimentally verified. (http://www.cisuvc.com/content/documents/files/CIS.OptanBallLens.DS-1004-1509.pdf).

UV-VIS Analysis. Absorption spectroscopy was carried out on an Agilent UV-VIS spectrophotometer using a standard 1 cm quartz cuvette. Samples of guaiacol and 4-hydroxybenzoic acid were measured dissolved within chromatographic mobile phase. Molar absorptivity at 254 nm was found to be 587 and 18,292 L/mol cm for guaiacol and 4-hydroxybenzoic acid, respectively. The measured molar absorptivity values were subsequently used to estimate limits of detection (LOD) values and noise equivalent absorption.

RESULTS AND DISCUSSION

Comparison of LED with Mercury Lamp. An experiment was performed to evaluate the output stability of the UV LED compared to a mercury lamp. In this experiment, both lamps were sequentially switched 'on' and light shone on the same photodiode after using the band-pass filter to spectrally select light to 254 nm. The experiment was conducted sequentially on a laboratory bench-top. The mercury lamp experiment utilized the manufacturers power supply (Pen-Ray PS-1) while the UV-LED experiment used a laboratory DC regulated supply (BK Precision 1670A). Results are illustrated in **Figure 2**.

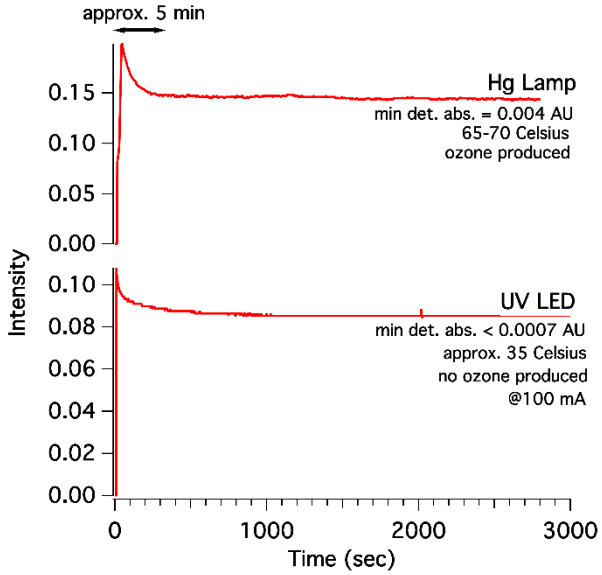

Figure 2. Comparison of the stability of a mercury lamp and the UV LED after power up

As observed, both lamps required 5-10 minutes for output power to stabilize. It is often advertised that UV LEDs require no 'warm-up' period, however, the data does not reflect this. This phenomenon is likely caused by drift in the power supply that drove the LED rather than being a characteristic of the diode itself. Several minutes were required for both lamps to reach stable output intensity. However, after the warm-up period the output of the LED was exceptionally stable. Drift in LED output over the final 2000 seconds of the experiment was less than the least significant bit of the data acquisition device (here equiv. to 1.1 mV). The mercury lamp (Hg lamp) exhibited a baseline noise > 4 times larger compared to the LED, generated more heat, and produced ozone due to light of λ<240 nm being present in the lamp's output spectrum. The experiment demonstrates the UV LED output intensity was considerably more stable, allowing lower limits of detection for absorption spectroscopy. In this experiment, temperatures were measured with an IR thermometer.

Detector Performance. After initial testing of the stability of UV LED output intensity, the LED was installed within the chromatography detector and experiments were performed to evaluate the sensitivity of the apparatus. To accomplish this, standard solutions of guaiacol dissolved in the chromatographic mobile phase were perfused directly thru the flow cell of the detector, and the output voltage was monitored using the data acquisition system. This procedure assured a known concentration of analyte is present within the detection cell for calibration and characterization of the detector. **Figure 3** illustrates the results of this experiment when a blank (0 μM) and three guaiacol standards (12, 151, 303 μM) were present within the flow cell.

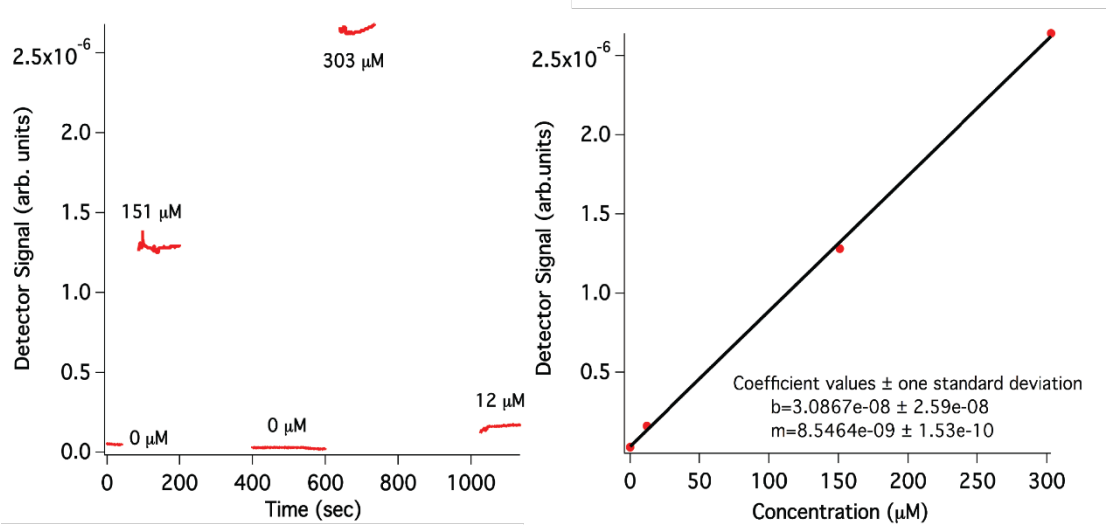

Figure 3. Calibration of the absorbance detector

As observed, the detector response varied in a manner that is linearly proportional to analyte concentration. The corresponding mathematical relationship links the detector response (or noise therein) to a corresponding guaiacol concentration. Since guaiacol's molar absorptivity was measured as 587 L/mol cm in a separate experiment, the detector output can be converted directly to absorption units (A.U.). The standard deviation of the baseline noise was then used to determine a noise-equivalent absorption (in A.U.). The resultant noise-equivalent absorption was found to be 180 µAU.

Chromatography of Standard Solutions. Upon completion of detector characterization experiments, reversed phase liquid chromatography was performed on standard solutions of 4-hydroxybenzoic acid and guaiacol. These analytes were chosen because they are often produced during pyrolysis or degradation of lignin, and previous work suggests this process may be a route to BrC formation [23]. Results of these experiments are illustrated in **Figure 4**.

As observed the more polar 4-hydroxybenzoic acid (t=85 s) elutes much earlier than guaiacol (t=500s). The observed peak heights produced by the absorbance detector were linear with the concentration of the injected sample for both analytes. Notice that because of the vast difference in molar absorptivity between the analytes (ε = 587 vs. 18292 L/mol cm), very different concentration limits of detection (L.O.D.) were observed. For the strongly absorbing 4-hydroxybenzoic acid, a very impressive L.O.D. of 130 nM or 18 ppb was observed. While for the weakly absorbing guaiacol, an L.O.D. in the µM range was encountered. Nonetheless, the absorbance detector was proven to function in chromatographic mode, and allow quantitation of analyte concentration.

Chromatography of BrC Proxies. The final focus of this project was to evaluate the use of the LED-based absorbance detector for studies of the chemical evolution of BrC. To

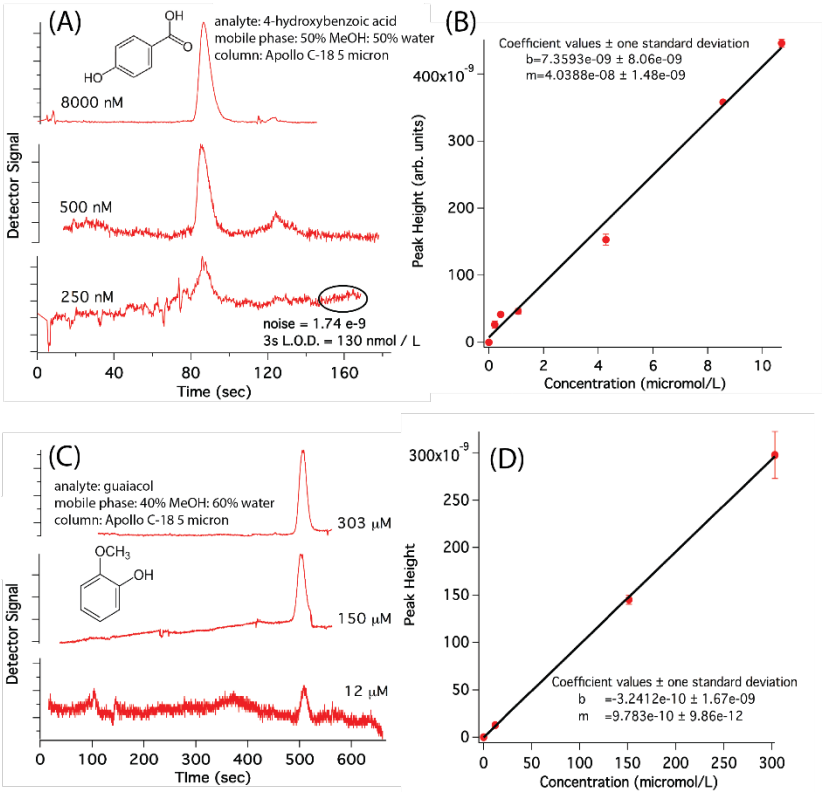

Figure 4. (A) Chromatograms of various concentration of 4-hydroxybenzoic acid. (B) Calibration line of chromatographic peak height vs. concentration. (C) Chromatograms of various concentration of guaiacol. (D) Calibration line of chromatographic peak height vs. concentration of guaiacol

accomplish this, a solution of guaiacol (9 mM) was prepared in deionized water, and 1 mM H_2O_2 was added. The mixture was then illuminated within a UV reactor [42]. A previous publication [23] has demonstrated that these reaction conditions rapidly promote the formation of BrC materials through a complex chemical mechanism mediated by free-radical chemistry. While the reaction begins with only guaiacol as the sole organic compound present, functionalization, fragmentation, and oligomerization of the guaiacol is believed to occur in solution simultaneously during reaction. This quickly leads to a complicated mixture of products, and chromatographic separation of the products prior to structural determination is required. **Figure 5** illustrates chromatograms for this reaction system at several different reaction times.

The peak at approx. 500 seconds is guaiacol, and the remaining peaks are reaction products of unknown identity. Plot (F) is the chromatogram for t=80 min zoomed in to show all peaks present. At least 15 peaks are observed as indicated by lower case letters. Several peaks (such as i, m, n, o) appear as broad bands and may be unresolved. The UV LED based absorption detector has provided sufficient sensitivity to observe the presence of many analyte peaks in this complex sample. Mobile phase was 40% MeOH and 60% water v/v.

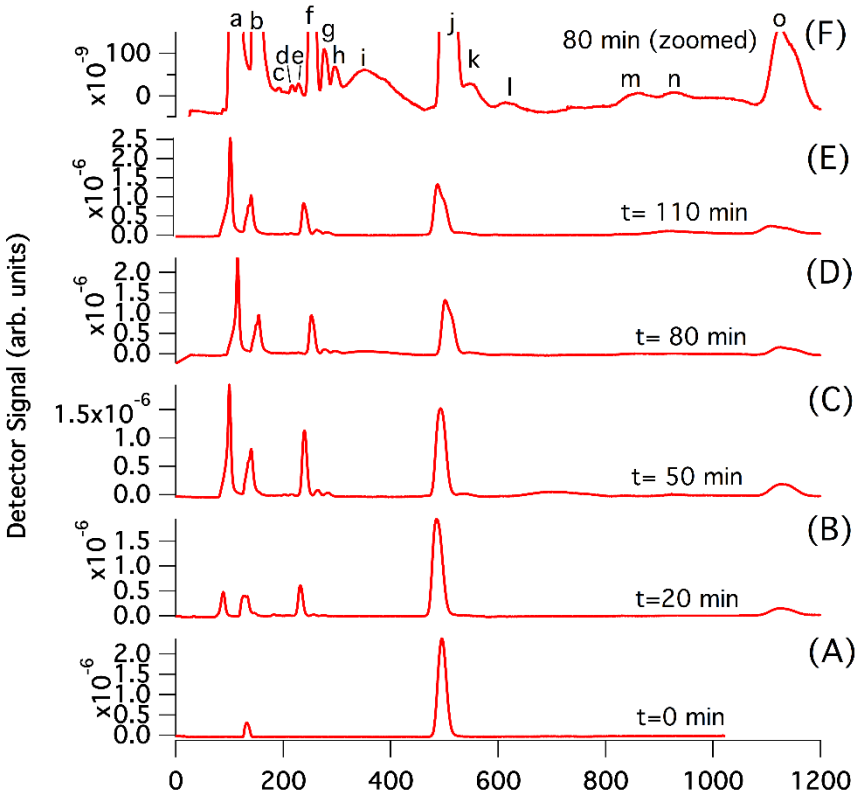

Figure 5. Chromatograms of the guaiacol reaction mixture at various reaction times. The peak at approx. 500 seconds is guaiacol, and the remaining peaks are reaction products of unknown identity. Plot (F) is the chromatogram for t=80 min zoomed in to show all peaks present. At least 15 peaks are observed as indicated by lower case letters. Several peaks (such as i, m, n, o) appear as broad bands and may be unresolved. The UV LED based absorption detector has provided sufficient sensitivity to observe the presence of many analyte peaks in this complex sample. Mobile phase was 40% MeOH and 60% water v/v

As observed, over the course of the reaction the guaiacol peaks at t=500 s becomes smaller as this reactant is partially consumed. Simultaneously, many additional peaks appear in the chromatogram. **Figure 5(F)** is the t=80 min chromatogram which illustrates the rich and complicated chemistry occurring in the solution. No fewer than 15 individual peaks are noted in the chromatogram, with several of the peaks appearing as broad chromatographic bands. These broad bands may represent several closely related molecules that are not fully resolved in the chromatography. Interestingly, a peak (peak o) begins to appear at very large elution times (>1100 s). Apparently, the reaction of guaiacol in H_2O_2 + hν must lead to quite non-polar product. The importance of a sensitive absorption based chromatographic detector can now be fully understood. The analyst must instrumentally detect peaks eluting from the column in order to trigger fraction collection or data-dependent scans of mass spectrometers. The UV LED detector described within provides sufficient sensitivity for such analysis.

CONCLUSIONS

An ultraviolet light emitting diode (LED) has been used as a spectroscopic source to construct an absorption detector for liquid chromatography. The UV LED was observed to be > 4x more stable than a mercury lamp. The chromatography detector demonstrated noise equivalent absorption of 180 μAU, demonstration good sensitivity. The detector responded linearly with analyte concentration and allowed the sensitive detection of at least 15 reaction products that derived from the photochemical reaction of guaiacol in H_2O_2. The UV LED based detector can now find use in better characterizing complex reaction systems related to the formation of aerosol brown carbon (BrC).

DISCLOSURE STATEMENT

The authors declare that they have no competing conflicts of interest. This work does not involve study on humans or animals.

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