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PHOTOMULTIPLIER TUBES FOR APPLICATION OF TOLUENE DETECTION USING DEEP-UV ABSORPTION SPECTROPHOTOMETRY

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KEY WORDS

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ABSTRACT

Nowadays there is an increasing demand for monitoring indoor air quality due to presence of harmful pollutants. Among other air-borne pollutants, Volatile Organic Compounds (VOCs) are generated from daily use products used in cleaning, cooking, polishing and painting etc. Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) are aromatics compounds considered to be some of the hazardous VOCs. Toluene is a colourless compound having a sweet pungent odour with density and boiling point of 0.866 g-cm^{-3} and 110.7 ^{o}C respectively. In indoor spaces, it is generated from daily-use items like cleaning products, paints, perfumes, polishing and smoking and in outdoor it is emitted mostly from automobiles [1]. Acute exposure to toluene can affect the kidney, liver, skin and central nervous system [2]. There are increasing strict regulations about the exposure limits of BTEX. For example, the American Conference of Governmental Industrial Hygienists (ACGIH) have defined the threshold limit value (TLV) of 50 ppm for toluene for an 8-hour exposure [3]. Monitoring of airborne BTEX at sub-ppm range needs a sensitive and selective detection technique.

Optical detection methods are sensitive and non-invasive detection methods, have minimal drift issues and have a rapid time response. Amongst these methods, absorption spectrophotometry is a direct and inherently selective measurement technique based on the unique fingerprints (absorption spectra) of the molecules at a specific wavelength. UV absorption spectrometry is a well-known analytical technique and has been applied to a number of applications in analytical chemistry, biochemistry and biomedical due to its simplicity, flexibility, low cost and convenience [4]. BTEX molecules absorb strongly in deep-UV range (i.e. 250-270nm) facilitating detection using absorption spectrophotometry [5].

There is an increasing demand for miniaturized analytical devices to realize analytical data with high sensitivity, low sample consumption, portability and low power consumptions. The latest advancement in microfluidics, optoelectronics and optofluidics facilitate the development of portable deep UV spectrophotometers for gas sensing applications. Recently deep-UV LEDs have been developed which provide a portable and quasi-monochromatic source with stable output, minimal intensity drifts, low cost, long lifetime (10^4 hours) and low heat generation [6].

There are limited detectors options for the deep-UV application. Recently our team demonstrated the application of mini-spectrometer for the detection of toluene and a detection limit of 12.45ppm was achieved [7]. In the present work, we have studied the application of photomultiplier tubes (PMT) for toluene detection using aluminium hollow-core waveguides as a gas cell.

Photomultiplier tube (PMT) is a versatile sensitive and ultra-fast response device. It has a large detection area and can detect low-intensity levels of light. A typical PMT consists of a photo-emissive cathode (photocathode), focusing electrodes, an electrons multiplier and electron collector (anode) enclosed in a vacuum chamber as shown in Figure 1. Light enters a PMT and generates an output signal through the following process: (1) Light passes through the input window; (2) Light excites electrons in photocathode which results emission of photo-electrons into a vacuum; (3) Focusing electrode accelerates and focusses the electron into the first dynode where they are multiplied by the emission of secondary electrons. This secondary emission is repeated at each of the successive dynodes; (4) The multiplied secondary electrons from the last dynode are finally collected by the anode.

One of the challenges in design of deep-UV spectrophotometer is the selection of the material for the gas cell due to compatibility constraints of deep-UV with a number of materials. A hollow-core waveguide (HCW) is an attractive option and can be employed as a miniature gas cell, guiding radiation for measurement of small gas volumes. A leaky-mode transmission is an attractive option for deep-UV due to ease in fabrication and integration with other spectrometry components. The optical transmission in leaky-mode depends upon the metallic or dielectric coating deposited on the inner wall of metal, polymer or glass tubing. Among the different coating materials like silver, Aluminum has an efficient transmission with relatively minimal losses [8].

Materials and methods

An Aluminum HCW was employed as a gas cell, coupled with a source and detector *via* optical fiber (range 200-1100nm, Ocean Optics USA) as shown in Figure 2. The gas cell was thermally insulated to avoid thermally induced noise. A deep-UV LED (Mightex System, USA) with peak wavelength 260nm and power range 45-80 µW was used as a source. A constant current was supplied to the LED to ensure a stable signal. A low-powered photomultiplier tube (Hamamatsu Japan) was employed as a detector with an operating wavelength range of 230-700 nm. The optics and fluidics connections were realized through 3D-printed connectors using Acrylonitrile Butadiene Styrene (ABS). All the components were aligned using optical bread-board to minimize the shifts due to mechanical movements.

Different concentrations of toluene were generated using nitrogen and toluene cylinders (100 ppm ± 2%, Air Products, France) connected with mass flow controllers (Bronkhorst, Netherland) with a full-scale range of 20ml/min±0.5% and 10 ml/min±0.5% respectively. The data were acquired using a custom script at a sampling rate of 1.0 S/sec and post-processing of data was performed using Matlab.

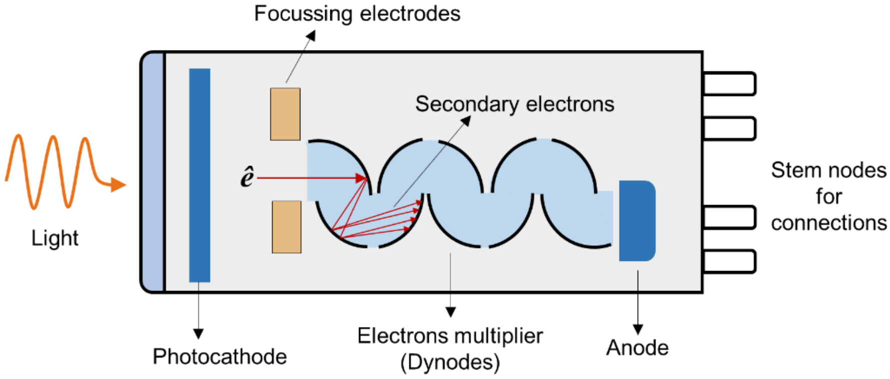

Figure 1. Schematics of photomultiplier tube.

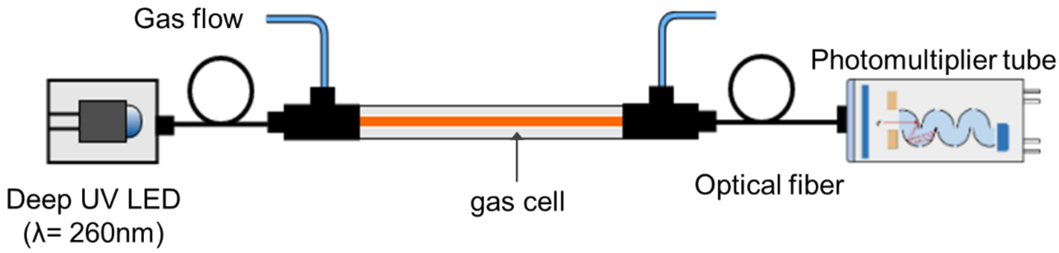

Figure 2. Schematic of experimental setup. Aluminum HCW is employed as a gas cell, coupled with UV LED and PMT via optical fibre.

Results and discussion

Different concentrations of toluene in nitrogen were generated and injected into the gas cell with a total flow of 20 ml/min. Nitrogen and toluene were injected for 3 min to obtain a stable signal for reference and test data respectively. The absorbance was calculated according to the Beer lambert law using the average value of intensity over the duration of injection. The intensity values obtained for different concentration is shown in Figure 3. The intensity values decrease with the increase of toluene concentration. A peak appears at the time of changing the flow from nitrogen to toluene and vice versa which can be attributed to the change of the value position. Two gas cells of optical path of 25 cm and 50 cm with volume of 0.78 ml and 1.57 ml respectively were tested for a concentration of 20 ppm to 1.25ppm. Both gas cells show a good linearity with R values of 0.991 and 0.997 for 25 cm and 50 cm respectively. The corresponding calibration curves are shown in Figure 4. Sensitivities of 2.01×10^{-1} mA·U/ppm and 9.68×10^{-1} mA·U/ppm were calculated for 50 cm and 25 cm gas cell respectively with a limit of detection of 1.33 ppm and 4.08 ppm respectively. The proposed design has low volume (786 µl) compare to the previous work (1257 µl) [9], which can be employed with µGC to improve the sensitivity.

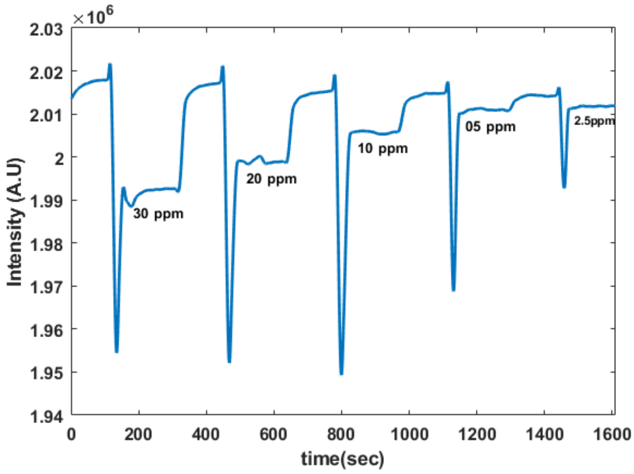

Figure 3. Variation of intensity with different concentration of toluene for the gas cell of 50 cm.

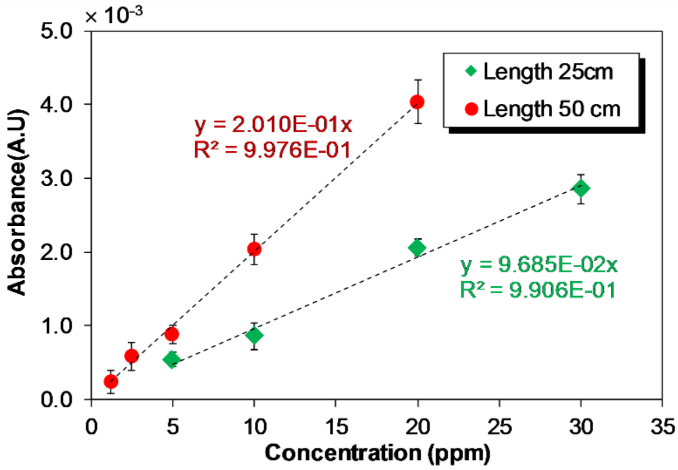

Figure 4. Calibration curves for toluene concentration ranging between 2 and 30 ppm using optical gas cell of length 50cm (red) and 25cm (green).

Conclusion and future scope

In this work, the application of photomultiplier tube coupled with deep-UV LED has been investigated for toluene detection. Aluminium based HCW with optical path lengths of 25 cm and 50 cm were tested. The setup was tested for concentrations from 2.5-20ppm and a good linearity and sensitivity was obtained. A limit of detection of 1.33 ppm was estimated for a gas cell with an optical pathlength of 50cm. The proposed design has the potential to be used for sensitive and selective detection of BTEX by integrating it with µGC equipped with a pre-concentrator owing to its low volume gas cell (786 µl). Finally, the design can be also adapted and employed for detecting a number of organic or inorganic molecules, for instance ozone, BTEX, NO_2 and SO_2.

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