

CASE STUDY:

University of Basel

University of Basel is a pioneer in designing analytical devices employing LEDs for detecting organic compounds in liquids and gases.

CHALLENGE

Benzene, toluene, ethylbenzene and xylenes, referred to as the BTEX compounds, are created during the processing of refined petroleum products and used in the production of paints, adhesives, cosmetics and pharmaceuticals. The primary man-made sources of BTEX into the environment are emissions from motor vehicles, refinery facilities, pipeline leaks, and surface spills. Exposure to these pollutants causes respiratory problems and cancer. The US Environmental Protection Agency (EPA) estimated that some five million Americans, not counting those with workplace exposures, face heightened cancer risks from benzene and 68 other carcinogens released into the air by the nation's oil refineries. Global environmental regulations are being tightened to ensure that exposure is kept to a minimum to reduce chronic and acute risks to the public. In 2014, the US EPA proposed monitoring and control of benzene concentration levels around the perimeter of all US oil refineries to reduce emissions of benzene and xylene by an estimated 5,600 tons per year.

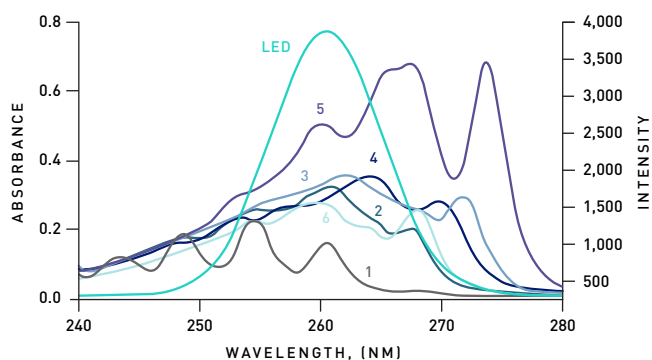
Standard protocols for detecting BTEX compounds have been developed, mostly on the basis of the gas chromatography and mass spectrometry (GC/MS) technique. This setup provides high reliability and sensitivity; however, it requires a highly skilled operator, is costly and has a major limitation in terms of field sensing due to the size and weight of the equipment. It is also time consuming due to analyte desorption and pre-concentration requirements and does not provide information on spatial and temporal variation of the analyzed gas concentration.

UV-Vis spectroscopic determination of BTEX is an attractive alternative since these compounds show strong absorption between 240 nm and 280 nm (Figure 1) that permit their identification and quantification after deconvolution of the spectrum. Optical systems are typically low maintenance and do not require consumables. They provide real-time data, in anywhere from few seconds to minutes to ensure real-time protection of workforce, environment and plant. If configured properly, they can also provide the distribution of emission plumes along the fence-line of a refinery, which in conjunction with wind data, can help locate specific emission sources.

**"HIGH INTENSITY DEEP UV LEDs
ENABLE THE DESIGN OF LOW COST
BTEX SENSORS. THE LOW POWER
CONSUMPTION OF THE LED ALLOWS
PORTABILITY AND BATTERY
OPERATION OF THE SENSORS."**

*Prof. Peter Hauser,
Department of Chemistry,
University of Basel.*

FIGURE 1



Emission spectrum of the deep UV-LED and absorption spectra of the BTEX species in isooctane: [1] benzene, [2] toluene, [3] o-xylene, [4] m-xylene, [5] p-xylene, [6] ethylbenzene [all 1.5 mM].]

Traditional UV-Vis detection methods in the UVC range (200 nm – 280 nm) use broadband emitters, such as deuterium lamps, as their primary light source, and monochromators for wavelength selection. Manufacturers select deuterium lamps due to their relatively high light output at deep UV wavelengths. However, these lamps require a very stable (and expensive) power supply to maintain their performance and a warm-up period of up to 30 minutes to allow the lamp to reach thermal equilibrium. For this reason, most lamps are left on while not in use so that the instrument is ready as needed—wasting much of the lamp’s useful life. Deuterium lamps are also bulky and have a large electrical power requirement (20–30 W). The resulting spectrometers are expensive, lack portability and require relatively frequent replacement of the light source.

The potential benefits of LEDs for UVC spectroscopy have been known for some time as the monochromaticity of LEDs eliminates the need for costly filters or monochromators. In addition, they can be powered with relatively inexpensive constant current drivers, have a smaller footprint and can use inexpensive silicon photodiodes for detection. This significantly reduces system complexity and cost.

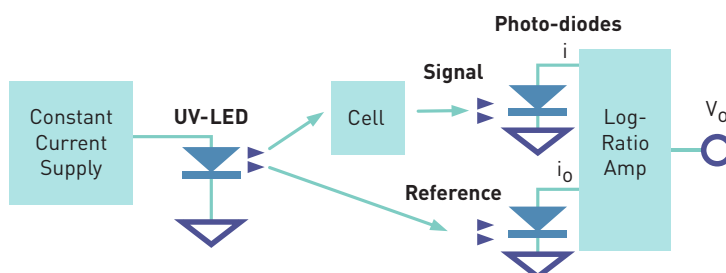
SOLUTION

The availability of high light output, long lifetime UVC LEDs from Crystal IS has enabled instrument designers to replace deuterium lamps with UVC LEDs for BTEX detection. These LEDs have relatively narrow emission bandwidths that can be matched with target wavelengths for detection and offer higher stability of light output, than deuterium lamps which enables lower detection limits.

University of Basel evaluated BTEX detection with a 260 nm Optan UVC LED. In their design, the light from the LED is split into two paths. The main portion of the light is directed through the absorption cell where the gases are introduced and then to a photodiode to generate the signal. Part of the light is also directly sent to a second photodiode to compensate for changes in the intensity of the UV LED and acts as the reference. The logarithm of the ratio of the signal and reference intensities is used to determine the UV absorbance of the compounds and thus, their concentration.



FIGURE 2



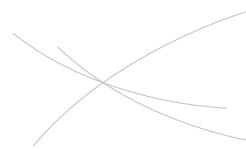
Schematic design of the BTEX sensor.

The performance of the sensor was first evaluated with the absorption measurement of vapors produced from each of the BTEX species. Key performance measures of sensors include noise, linearity of measurement and the detection limit. The peak-to-peak noise value over a period of 60 seconds was determined to be $40 \mu\text{AU}$ and limited by the electronic noise. The response was found to be linear for each species up to the highest concentration of 110 ppm measured and the correlation coefficients were determined to be 0.9990 or better. The good linearity confirms the adherence of the sensor response to Beer-Lambert's law as well as negligible levels of stray light and dark current on the photodiodes for the relevant absorbance range. The UVC LED-based sensor shows the highest sensitivity for p-xylene, while its sensitivity for benzene is lowest, and this is in agreement with the relative absorbances of the various compounds at 260 nm (Table 1). The detection limit of 1 ppm for benzene is better than the value of 13 ppm reported for benzene using a device based on a deuterium lamp and a monochromator and can be attributed to the superior stability of light of the LED source.

TABLE 1: DETECTION OF BTEX VAPORS

| Compound | Sensitivity ($\mu\text{AU/ppm}$) | LOD (ppb) |
|--------------|------------------------------------|-----------|
| Benzene | 60 | 1200 |
| Toluene | 150 | 660 |
| o-Xylene | 185 | 600 |
| m-Xylene | 170 | 610 |
| p-Xylene | 235 | 460 |
| Ethylbenzene | 165 | 610 |

"With new high intensity deep UV LEDs and a simple photodiode it was possible to construct a simple photometric sensor for the BTEX species," said Prof. Peter Hauser, Department of Chemistry, University of Basel. "The detection limit of the sensor was 10 times lower, compared to what was reported for earlier instruments employing a conventional deuterium lamp and monochromator, but not quite as good as those attained with the significantly more complex gas chromatographs. However, the low power consumption of the LED allows the construction of battery based portable instruments for less demanding applications."



Crystal IS **ADVANTAGE**

LEDs respond instantaneously, consume relatively little power and offer design freedom over traditional light sources. In addition, Crystal IS UVC LEDs deliver:

- >Excellent stability of light for lower detection limits
- >Superior spectral quality for measurement linearity over a wide concentration range
- >Little or no radiated heat, which is ideal for handheld applications



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