



DRAFT MIGRATE-XX

OPTICAL DETECTION OF BTEX: REVIEW OF DIFFERENT TECHNIQUES

Sulaiman Khan¹, Stéphane Le Calvé^{2,3}, David Newport¹

¹Department of Mechanical Aeronautical & Biomedical Engineering, University of Limerick

Sulaiman.khan@ul.ie, David.newport@ul.ie

²University of Strasbourg, Institute of Chemistry and Processes for Energy, Environment and Health (ICPEES), Group of Atmospheric Physical Chemistry, Strasbourg France

slecalve@unistra.fr

³In'Air Solutions, 1 rue Blessig, 67000 Strasbourg

KEY WORDS

Interferometry, spectrophotometry, Optical sensors, UV Vis absorption cells, Gas sensors

ABSTRACT

Introduction

On average a person spends 80%-90% in indoor environments where exposure to various indoor air pollutants is inevitable [1]. Among these air pollutants, Benzene, Toluene, Ethylbenzene and Xylene (BTEX) can pose a serious threat to human health. Among BTEX, benzene is toxic and classified as carcinogenic [2,3]. In 2013, the EU proposed a maximum exposure limit value of 5 $\mu\text{g}/\text{m}^3$ (1.6 ppb) for benzene in public indoor spaces [4,5] and this will be decreased down to 0.64 ppb in 2018 [6]. For *in situ* continuous monitoring of BTEX, a detection technique which is high sensitive and selective, portable and have a capability of miniaturization is needed. This paper considers alternative optical approaches to the detection of air borne BTEX.

BTEX Detection Techniques: Optical Detection

Currently different technologies are available for BTEX detection. A detailed comparison is shown in Table 1 and figure 1. Optical gas sensors have features of high sensitivity and selectivity, non-destructive, respond quickly and are less prone to drift. They are inherently reliable and have zero cross-response from other gases. Numerous optical gas-sensing techniques have been developed and can be categorized into direct spectrometry and reagent/film mediated optical sensors. Different optical configurations are used for sensing application from free-space sensors to fiber based configurations to optical waveguides [7].

In direct sensors, the analyte is detected directly based on the measurement of intrinsic properties like absorption spectra e.g., spectrophotometry. In reagent/film mediated sensor, a change in the optical response of an intermediate agent is used to monitor the analyte. S.K.Sulick *et al.* reported this type of sensor using a disposable colorimetric sensor array made from a diverse set of chemical responsive colorants. It is portable and has good sensitivity (limit of detection 0.2 ppm for benzene)[8]. Interferometry based gas sensors can be considered as film-mediated optical sensors. This paper considers both spectrometric and interferometric based detection techniques for BTEX.



Table 1. Comparison of different sensing techniques for BTEX detection

| Method/Technique | | LOD | Advantages | Limitations | Ref. |
|---------------------------------|-------------|-------------------|--|---|------|
| Metal Oxide Semiconductor (MOS) | | 10 ppb | Low cost. Quick Time response. Acceptable life time. Easily to integrate. | Relative low selectivity and sensitivity. High operating temperature. Zero drift and aging effect. Interference from humidity and temperature. | [9] |
| Electro Chemical | | 0.5 ppm | Relative sensitive. Reliable. | Zero drift. Restricted life and Aging. Cost. | [10] |
| PID | | 1.2 ppt – 1.4 ppt | High sensitivity. Quick response. Portable . | Lower selectivity, all the gases with IP equal or lower the photon may be detected. Complex electronics. Cost. | [11] |
| μ-GC | | 15 ppb | High sensitivity. High selectivity. | High cost and size Complex analytical setup and fabrication. | [12] |
| Piezoelectric | QCM | 1.2 to 2.1 ppm | Excellent sensitivity. Portable. Good dynamic range. | Large measurement noise. Weak selectivity. Zero drift and cross reactivity. Interference from humidity and temperature. | [13] |
| | SAW | 100ppb | | | [14] |
| | Tuning fork | 4 ppb-1000 ppm | | | [15] |

Spectrophotometry

Spectrophotometry based gas sensors offer a reliable and gas specific approach for BTEX detection. It relies on the intrinsic properties of gases i.e., unique absorption spectra (fingerprints) at specific wavelength. The absorption level follows the Beer Lambert law. The sensitivity is highly dependent on the optical path length which is defined by the design of absorption cell. The absorption cell can be single pass, multiple pass or a resonant cavity. For single pass cells, optical path lengths up to 1 m can be achieved but drawbacks are limited sensitivity and optical losses. In multiple pass cells, mirrors are used which allow longer optical path lengths. It is relative sensitive but have limited spectral bandwidth and high sensitivity towards external vibrations [16].

Horiuchi *et al.* reported BTEX sensor based on integrated single pass absorption cell [17]. Absorption cell of length 2 cm coated with platinum was used and detection limit of 25 ppb for benzene was achieved. The LOD was improved to 1 ppb by using a hollow fiber of length 12 cm with wall coated aluminum [18]. There is a good potential of improving the sensitivity to sub ppb by designing absorption cell that is capable of miniaturization and have the least optical losses possible.

A Hollow Core Waveguides (HCW) offer an alternative to absorption cell and have been applied for spectrometry and sensing applications [19]. The use of HCW provides a distinct advantage of combining a compact gas cell with an efficient radiation guide for the measurement of small gas concentration. A compact light weight spectrophotometer can be developed by using chip scale HCW. However the major limitation is the lack of low optical loss waveguide design. Recently a novel HCW design is developed by Weijian *et al.* made from two planar, parallel, silicon-on-insulator wafers with subwavelength gratings for IR applications [20]. This design has a distinct advantage of efficiently guiding light (optical losses 0.37 dB/cm) without sidewalls for a 9 μm waveguide, which allow the inflow and outflow of gases from the side. Silicon has low band energy and absorbs UV-visible radiations (1.1eV) which limits its application for BTEX detection. A material with high band energy i.e., Aluminum Nitride, Gallium Nitride and Silicon carbides can be a viable option to replace silicon [21]. The multilayer fabrication of high band energy material can be technical challenge for our design.

Interferometry

Interferometry based detector for BTEX is a film-mediated optical sensor. Interferometric based measurement techniques are very sensitive and have been utilized for pressure, temperature and concentration measurements [22,23]. Martinex *et al.* used Pohl interferometry setup using PDMS thin layer as a sensing film for VOCs detection [24]. A setup has very limited sensitivity of 1500 ppm. Razak *et al.* used polyacrylate resin layer as a sensing layer in the waveguide and obtained a detection limit of 8 ppm [25]. Xiangping *et al.* applied interferometric configurations i.e., Faby-Perot (FP) and Sagnac interferometer (SI) with PDMS as sensing film for detection of VOCs [26]. A sensitivity of 9.02×10^{-4} nm/ppm and 1.17×10^{-3} nm/ppm was achieved using SI and FP interferometer respectively.

Karthik et al. also used FP interferometer with PDMS as sensing film integrated with μ GC and detected toluene down to 25 ppb [27].

Planned Work

Michelson interferometer is developed for the measurement of BTEX concentration. PDMS is used as a sensing film which has the property of swelling and/or change of refractive index, when interact with BTEX. The schematic is shown in figure 2. The sensing film is attached onto the mirror which is exposed to BTEX. The interference of reflected beam I_r and I_s produce fringes pattern on the screen. The changes in the fringes are monitored to measure the concentration of the BTEX.

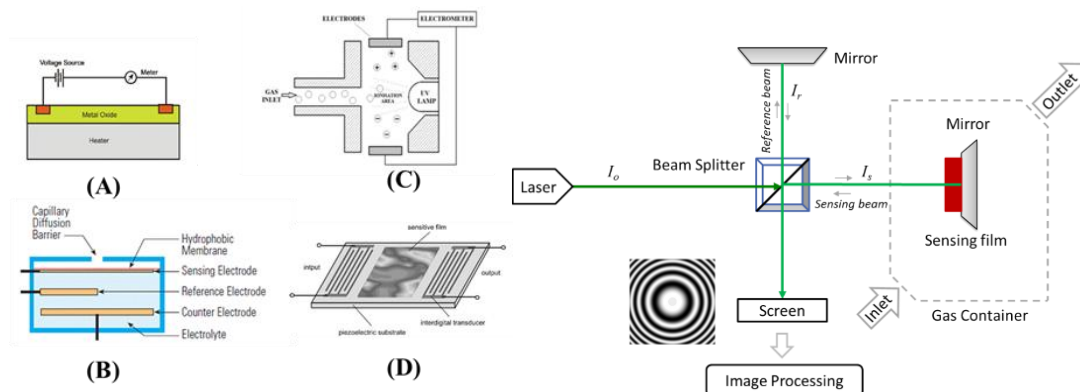


Figure 1. Different BTEX detection Techniques: (A) MOS (B) Electrochemical (C) PID (D) Piezoelectric sensors.

Figure 1. Schematic of Michelson Interferometer for BTEX detection

Acknowledgements

This ITN Research Project is supported by European Community H2020 Framework under the Grant Agreement No. 643095 (H2020-MSCA-ITN-2014) .

References

- 1 N. E. Klepeis, W. C. Nelson, W. R. Ott, J. P. Robinson, A. M. Tsang, P. Switzer, J. V Behar, S. C. Hern and W. H. Engelmann, .
- 2 P. Schneider, I. Gebefügi, K. Richter, G. Wölke, J. Schnelle, H.-E. Wichmann and J. Heinrich, *Sci. Total Environ.*, 2001, **267**, 41–51.
- 3 D. Pyatt and S. Hays, *Chem. Biol. Interact.*, 2010, **184**, 151–164.
- 4 A. Cicolella, *Rev. Mal. Respir.*, 2008, **25**, 155–163.
- 5 Décret n° 2011-1727 du 2 décembre 2011 relatif aux valeurs-guides pour l'air intérieur pour le formaldéhyde et le benzène|Legifrance.
- 6 R. Nasreddine, V. Person, C. A. Serra and S. Le Calvé, *Sensors Actuators, B Chem.*, , DOI:10.1016/j.snb.2015.09.077.
- 7 J. Hodgkinson and R. P. Tatam, *Meas. Sci. Technol.*, 2013, **24**, 12004.
- 8 H. Lin, M. Jang and K. S. Suslick, *J. Am. Chem. Soc.*, 2011, **133**, 16786.
- 9 M. Leidinger, M. Rieger, T. Sauerwald, C. Alépée and A. Schütze, *Sensors Actuators B Chem.*, 2016, **236**, 988–996.
- 10 P. K. Sekhar and K. Subramaniyam, *ECS Electrochem. Lett.*, 2014, **3**, B1–B4.
- 11 H. Zhu, R. Nidetz, M. Zhou, J. Lee, S. Buggaveeti, K. Kurabayashi and X. Fan, *Lab Chip*, 2015, **15**, 3021–3029.
- 12 T. H. Tzeng and E. Al, *IEEE J. Solid-State Circuits*, 2016, **51**, 259–272.
- 13 A. Mirmohseni and V. Hassanzadeh, *J. Appl. Polym. Sci.*, 2001, **79**, 1062–1066.
- 14 F. Bender, F. Josse, R. E. Mohler and A. J. Ricco, in *European Frequency and Time Forum & International Frequency Control Symposium (EFTF/IFC), 2013 Joint*, IEEE, 2013, pp. 628–631.
- 15 C. Chen, K. Driggs Campbell, I. Negi, R. A. Iglesias, P. Owens, N. Tao, F. Tsow and E. S. Forzani, *Atmos. Environ.*, 2012, **54**, 679–687.
- 16 K. C. Cossel, E. M. Waxman, I. A. Finneran, G. A. Blake, J. Ye and N. R. Newbury, *J. Opt. Soc. Am. B*, 2017, **34**, 104.
- 17 T. Horiuchi, Y. Ueno, S. Camou, T. Haga and A. Tate, *NTT Tech. Rev.*, 2006, **4**, 30–37.
- 18 S. Camou, T. Horiuchi and T. Haga, *Proc. IEEE Sensors*, 2006, 235–238.
- 19 C. M. Frey, F. Luxenburger, S. Droege, V. Mackoviak and B. Mizaikoff, *Appl. Spectrosc.*, 2011, **65**, 1269–1274.
- 20 W. Yang, J. Ferrara, K. Grutter, A. Yeh, C. Chase, Y. Yue, A. E. Willner, M. C. Wu and C. J. Chang-Hasnain, *Nanophotonics*, 2012, **1**, 23–29.
- 21 M. N. Yoder, *IEEE Trans. Electron Devices*, 1996, **43**, 1633–1636.
- 22 B. Szulczyński and J. Gębicki, *Environments*, 2017, **4**, 21.
- 23 J. Garvey, D. Newport, F. Lakestani, M. Whelan and S. Joseph, *Microfluid. Nanofluidics*, 2008, **5**, 77–87.
- 24 C. Martínez-Hipatl, S. Muñoz-Aguirre, G. Beltrán-Pérez, J. Castillo-Mixcóatl and J. Rivera-De la Rosa, *Sensors Actuators, B Chem.*, 2010, **147**, 37–42.
- 25 R. Kadir, A. Yimit, H. Ablat, M. Mahmut and K. Itoh, *Environ. Sci. Technol.*, , DOI:10.1021/es8034297.
- 26 X. Ning, J. Yang, C. L. Zhao and C. C. Chan, *Appl. Opt.*, 2016, **55**, 3543.
- 27 K. Reddy, Y. Guo, J. Liu, W. Lee, M. K. Khaing Oo and X. Fan, *Lab Chip*, 2012, **12**, 901.