Benzene detection by absorbance in the range of 20 ppb-100 ppb
Application: Quality of indoor air

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Abstract

In the framework of a French Joint program COVADIS, an innovative system is developed for the simultaneous detection of benzene, toluene and xylenes in indoor air. The present work is mainly focused on the benzene detection. The detection is based on absorbance measurements over the 250 nm-300 nm range with a cooled spectrophotometer. The prototype includes an exposure chamber, which contains five sensors. The sensors are nanoporous disks, whose pore sizes are tailored to efficiently entrap the targeted pollutants. 20 ppb of benzene have been successfully detected within 40 minutes of exposure.

Keywords: Benzene ; Indoor air ; Sol-gel ; Optical detection ; Absorbance ; Nanoporous discs ; Volatile organic compound ; Gaz sensor.

1. Introduction

Benzene, toluene, and xylenes (BTXs) are volatile aromatic monocyclic hydrocarbons of significant health concern due to their toxicity. In particular, benzene is a well-known human carcinogen.

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Indeed, according to [1], the concentration of airborne benzene associated with an excess lifetime risk of $10^{-5}$ is 17 ug/m$^3$ ($\approx$ 5 ppb). Such concentration can be easily found in indoor air. Over the ppb concentration domain, there is no simple and direct method of measurements of these pollutants. Therefore, the development of a sensitive sensor easy to use, which can detect BTX in the ppb range is an important challenge. Other laboratories are working on similar devices with the same goal [2,3].

2. Detection principle

2.1 The nanoporous sensors

The sensors are nanoporous concave disks, which are produced via the sol-gel process (typical size : central thickness $\approx$ 0.5 mm to 1.0 mm, diameter $\approx$ 5.7 mm). Due to the high adsorption surface of the nanoporous materials (650 m$^2$.g$^{-1}$) and their pore size, the sensors can entrap efficiently the BTXs.

Once the benzene is entrapped into the sol-gel disks, the sensor absorbance increases due to the contribution of the benzene absorption. The sol-gel disks acts like benzene concentrators. For the benzene detection, the absorbance variation is analyzed at 254 nm.

2.2 Experimental set-up for the reader

The gas mixture to be analyzed flows between the disks, in a perpendicular direction to their cylinder axis. The detection unit is composed of a deuterium lamp and a cooled spectrophotometer (Fig. 1). The Deuterium lamp is a D-2000 from Ocean Optics. It typically delivers 250 $\mu$W/mm$^2$/nm at 250 nm. The cooled spectrophotometer is a QE 65000 from Ocean Optics. The entrance slit is 200 $\mu$m wide. The corresponding optical resolution is close to 6 nm.

![Fig. 1. Diagram of the detection system](image)

The experimental chamber, which contains 5 disks is modular (see Fig. 2). Other designs of disk holders to match other disk sizes, other geometries or more disks are possible. The disk holder is the intermediate part of the chamber.

![Fig. 2. (a) Modular chamber with 2 disk holders (b) Disk holder for 5 disks](image)
3. Protocol

3.1 Experimental protocol for the measurements

Firstly, the sensors are typically exposed during 40 minutes to a flow of synthetic air without benzene and then with few ppb of benzene with the same flow (i.e. 10 L/mm =10 000 sccm). During these processes, the absorbance variation is collected at 254 nm with a spectrophotometer (integration time around 1 second). The benzene effect is evaluated by subtracting the slopes of the transmitted light at 254 nm with and without benzene (Fig. 3).

![Transmitted light at 254 nm](image)

Fig. 3. Protocol to determine the variation of optical signal linked to a given benzene concentration. This variation is linked to the trapped benzene inside the sol-gel disks.

3.2 Sensor preparation

Before applying the experimental protocol previously described, a stabilization phase of the transmitted light at 254 nm through the sensors is essential. The lamp stabilization is not discussed in this paper. The first stabilization phase without gas flow lasts typically between 8 and 10 hours (phase 1). The second phase occurs when the disks are exposed to a synthetic air flow (phase 2). During the phase 2, firstly a rise occurs and then a decrease (see Fig. 4). In this paper, the benzene detection begin at the end of the phase 2, when the slope becomes linear. Phase 1 and phase 2 could be carried out simultaneously.

![Sensor preparation](image)

Fig. 4. Sensor preparation before using the sensors for benzene detection
phase 1 : without gas flow, 8 to 10 hours duration ; phase 2 : with synthetic air flow at 10 L/mm, typically 2 hours duration

4. Experimental results : benzene calibration curve

By changing the concentration of benzene in the calibrated gas mixtures, a calibration curve is obtained (Fig. 6b). The benzene concentration is evaluated by subtracting the slopes of the transmitted light at 254 nm with and without benzene (Fig. 6a). A benzene detection of 20 ppb has been successfully
achieved. According to these experimental conditions, it can be estimated, that a slope larger than “-0.1 a.u s⁻¹” (i.e. inferior to -0.1 a.u s⁻¹) are not significant to warn the presence of benzene.

Fig. 6. (a) Transmitted light at 254 nm under various benzene concentrations (10 L/mm) (b) Calibration curve with a set of 5 disks

5. Conclusion and perspectives

This detection set-up, including five sol-gel disks for the trapping of the pollutants, allows the detection of 20 ppb of benzene typically within 2 hours (without taking into account the stabilization phases). The stabilization phase under UV might be done collectively before using the sensors. Therefore, only a stabilization of 2 hours under synthetic air flow has to be achieved before launching a concentration measurement. Presently, a bottle of clean air (10 liters pressurized at 200 bars) is necessary for one concentration measurement in using a 10 L/mm flow.

Many difficulties remain to produce a commercial product. First of all, system and sensor repeatabilities have to be stabilized to lead to a generic calibration curve. More work are undergone to solve these problems and to evaluate the trapping efficiency of the sol-gel disks for toluene and xylenes.

Acknowledgements

This work was performed in the framework of a French joint program COVADIS under the auspices of Lyonbiopôle, Axelera and Advancity within the 9th FUI project call. A part of this project is financed by OSEO and various territorial collectivities (Rhône Alpes region, Grenoble city, ...). The authors would like to thank B. Schaerer for the drawing.

References

[1] WHO Guidelines for indoor air quality: selected pollutants, ISBN 978 92 890 0213 4
[2] “ppb level benzene gas detection by portable BTX sensor based on integrated hollow fiber detection cell”, S. Camou, T. Horiuchi, T. Taga, IEEE sensors 2006, Daegu, Korea, 22-25 October 2006
[3] “Portable Aromatic VOC Gas sensor for onsite continuous air monitoring with 10-ppb benzene detection capability”, T. Horiuchi, Y. Ueno, S. Camou, T. Haga, A. Tate, NTT Technical review. (https://www.ntt-review.jp/archive/ntttechnical.php?contents=ntr200601030.pdf)