Generation of Polluted Atmospheres for the Calibration of QCM Gas Sensors

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Abstract

One of the major requirements for developing sensitive and selective detectors based on chemical gas sensors is to generate calibrated polluted atmospheres. In this paper a generation method of volatile organic compounds and explosive vapours is presented. The work was focused on the generation of 4-nitrotoluene (NT), 2,4 and 2,6 dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), toluene and nitromethane vapours. The methodology described in this study was applied to determine the detection limit of a Quartz Crystal Microbalance (QCM)-based sensor.

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1. Introduction

The use of devices for explosive detection has increased worldwide for preventing terrorist activities. Many developments are focused on the detection of vapour traces, such as electrochemical sensors, mass sensors (SAW, QCM), optical sensors (based on photoluminescence, fluorescence, terahertz spectroscopy, etc.) or microelectromechanical systems (MEMS).

Because of the variety of explosive compositions available whose vapour pressure is often low, the task of detection of traces is quite difficult. This is why accurate calibration and standard tests are needed for the development of such sensitive detection devices.
In this work, a continuous-flow trace vapour source was designed and evaluated in terms of temperature dependence and stability. The generation cell was used for the determination of the detection limits of a QCM-based device when exposed to the vapours.

2. Experimental

The setup shown in figure 1 was used to generate the target vapours. A double wall cell made of borosilicate glass was used to provide thermal stability. The temperature of the cell was regulated using a Thermo Neslab RTE 111 Bath/circulator in the -10° C to +25° C range.

The vapor generation and detection tests were composed of two lines supplied with dry synthetic air (Air liquid synthetic air, Alphagaz Air 1). On the first line, the air was unaltered in order to provide the sensor with clean air and obtain the system base line. On the second line, the air passed through the vapor generation cell containing 1 g of the considered analyte. Then, the chosen flow was distributed either to the sensor (for detection tests) or to the trapping device for concentration measurements.

In the case of high vapour pressure compounds such as toluene and nitromethane, the generated concentration was evaluated by a gravimetric method. The concentrations of the vapours emitted by the compounds exhibiting a low vapour pressure (NT, DNT and TNT) were measured via a liquid/gas extraction in a bubbler containing acetonitrile or methanol, followed by analyses with High Performance Liquid Chromatography (HPLC) or UV spectroscopy. The gas sensor was a 9 MHz QCM coated with a substituted Zinc phthalocyanine, PcZn(Ooct)₈ [1]. The detection measurements were performed at 25°C.

3. Results and discussion

3.1. Generation of the vapours

The concentrations of the generated vapours are presented in figure 2 (a) versus the temperature of the generation cell. The variation of the concentration of the vapours was shown to be consistent with the Clausius-Clapeyron relation [2, 3]. A decrease in temperature led to a decrease of the vapours concentration, especially in the case of low vapour pressure compounds such as DNT and TNT.
The stability of the delivered concentrations was also examined (see figure 2 (b)). Average concentrations of toluene vapours of 16300 +/- 800 ppmv were generated at 15°C for a period of 2 months. These results provided evidence for the control of the vapours concentrations in the chosen configuration of the generation device.

![Figure 2](image1)

**Fig. 2.** (a) Evolution of the concentration of the vapours with the temperature of the generation cell at a flow rate of 20 L/h

Toluene + ; Nitromethane ▲ ; DNT × ; TNT ○ ; NT ◊ ; (b) Frequency variations measured with the QCM sensor in presence of toluene vapours

### 3.2. Detection of the vapours with the QCM sensor

The frequency shifts of the coated QCM presented in figure 3 were measured at varying concentrations of DNT and nitromethane vapours. A Langmuir model was chosen for the description of the adsorption process [4].

![Figure 3](image2)

**Fig. 3.** Frequency variations measured with the QCM sensor in presence of (a) DNT vapours ; (b) nitromethane vapours
The detection limits of the QCM sensor in presence of all of the vapours generated in this study (see table 1) were extrapolated at a frequency shift of 20 Hz, which is the quantification limit. No detection of the TNT vapours could be observed, which is due to the lack of sensitivity of the QCM sensor at such weak vapour concentrations. On the contrary, a previous study showed that concentrations of TNT as low as 1.5 ppbv could be detected with a fluorescent sensor based on a Phenyleneethynylene π-conjugated compound [5]. This material was found to be very sensitive and highly selective towards nitroaromatic compounds.

In the present work, the QCM sensor was shown to be much more sensitive to DNT or NT vapours than to the vapours emitted by toluene or nitromethane. A sensitivity as high as 2 Hz/ppb was obtained in presence of DNT vapours while a low sensitivity of 3x10^-5 Hz/ppb was measured in presence of nitromethane vapours. This result provided evidence of the strongest affinity of the PcZn(Ooct)₈ sensitive material for the nitroaromatic compounds.

Table 1. Detection limits of the QCM sensor

| Compound     | Detection limits |
|--------------|------------------|
| NT           | 1 ppmv           |
| DNT          | 7 ppbv           |
| TNT          | No detection     |
| Nitromethane | 400 ppmv         |
| Toluene      | 500 ppmv         |

4. Conclusion

In this study, a dynamic method based on evaporation was chosen for its ability to produce stable concentrations of vapours. It was shown that controlled concentrations could be generated, whatever the vapour pressure of the compound. A detection limit of the QCM sensor as low as 7 ppbv in presence of dry DNT vapours was determined. Future work will be dedicated to the measurement of the sensitivity of the gas sensors in presence of humidified vapours. The selectivity of the sensor in presence of a mixing of vapours will also be explored.

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