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Detection of explosive vapors: development and performances of a fluorescence sensor

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This paper describes a device dedicated to the detection of nitroaromatic explosives consisting of a portable detector based on a specific fluorescent material. The developed sensor was able to detect ultra traces of explosives, such as trinitrotoluene (TNT) or its derivate 2,4-dinitrotoluene (DNT), in ambient air.

1. Introduction

One strategy of law enforcement against terrorism is to develop reliable, sensitive and specific systems for the detection of explosives in luggage, vehicles and soils. In this context, the present study describes the development of an optical device which combines all the expected properties, and is based on the capability of pi-conjugated fluorescent materials to interact especially with explosives vapors, in particular trinitrotoluene derivates (TNT, DNT…)[1,2]. The principle of the detection is based on the inhibition the fluorescence of a fluorescent thin film when nitroaromatics absorb onto the surface [3] .
First, the development of the sensitive material suitable for the application will be discussed. The second part will concern the portable detector and the evaluation of its performances.

2. Experimental

Except TNT and the sensitive compound which were homemade, chemicals were purchased from Aldrich Chemical Co. Inc. and used as received.

2.1 Sensitive compound

The selected material was a π-conjugated phenylene-ethynylene diimine "**A**" its chemical structure is given in figure 1.

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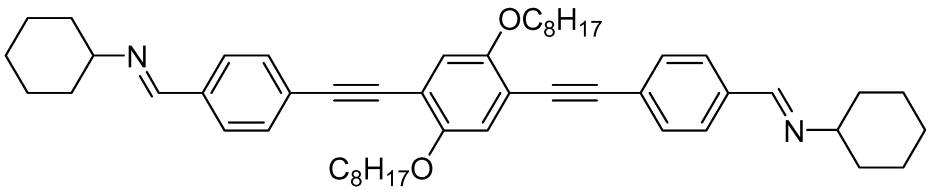

*Figure 1: sensitive material, **A***

This compound exhibited a high level of fluorescence (pi-conjugated) and an electron donor aromatic ring which could strongly interact with electron acceptor aromatic ring of TNT or DNT. The synthesis was described in our previous work [4]

2.2 Thin films

The sensors were elaborated with a thin film of A on a glass substrate (Heathrow Scientific microscope slides 75x25x1 mm). In order to identify the best elaboration process for the detection, various deposition methods have been investigated:

- Spin coating: Braive instrument
- Spray coating : Dosage 2000
- Sublimation : EDWARDS Auto 306
- Ink jet printing : Silliflow instrument
- Dip coating : home made instrument

THF was used as solvent when necessary. A Perkin-Elmer Lambda 35 spectrometer was used to determine the optical properties of the films. To compare all the deposition methods, the optical densities of the films (λ= 415 nm) were fixed at about 0.2.

2.3 Detector

The transduction and detection techniques have been previously developed for a biosensors array [5] and were here adapted for a single chemical gas sensor. A schematic of the setup is depicted in figure 2. The Fluorescence was guided in the slide by total internal reflection and was directly collected at the end-face by a photo-multiplier tube (H8249-101, Hamamatsu). The detector have been interfaced with a bandpass filter (400ALP/E, Omega Optical) and a high pass colored filter (OG570, Schott) to suppress the remaining excitation radiation. The high collection efficiency of the transducer rendered the use of imaging optics unnecessary, thus increasing the robustness, compactness, and simplicity of the system.

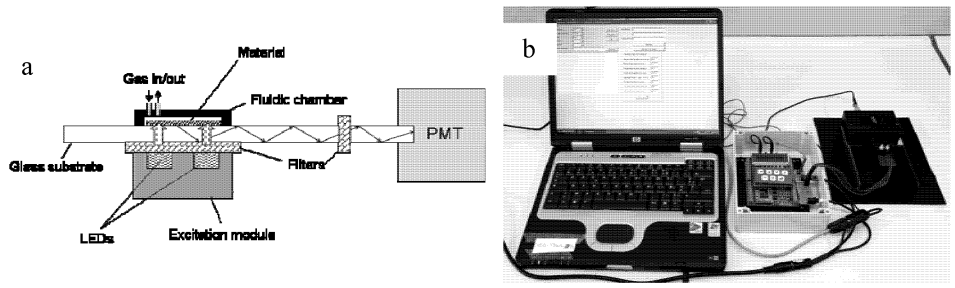

Figure 2: a) Transduction technique and b) Portable detector

The transducer was embedded into a home-made fluidic reaction chamber fabricated in aluminum and coated with black PTFE. The flow channel was 6 mm in width, 0.130 mm in height, and 46 mm in length. The sample successively passed the areas #1, #2, #3, and #4. The fluidic circuitry was composed of ⅛'' PTFE tubes, and the whole prototype was 40 cm × 30 cm × 16 cm. presents a photography of the prototype.

The portable system (figure 2b) was controlled with a single-board computer (BL2120 Smartcat, Z-World, USA) that had been programmed using Dynamic C® language. . The developed software was able to display real-time graphics and to select experimental parameters such as PMT settings and the measurement frequency.
For explosives tests, specific testing bench were developed (see figures 3 and 4).
The first one was devoted to the comparison of the response of each deposition method with regard to the response of the sensor when exposed to 120 ppbv DNT in dry air [6].
All experiments were performed at 20+/-2°C, the flow was 20 L/h.

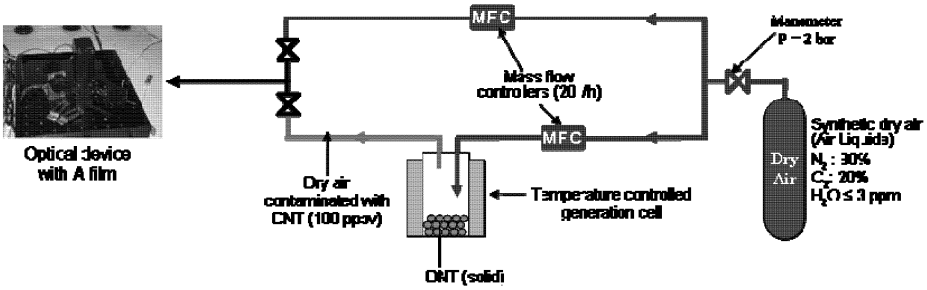

Figure 3: Testing bench for dry air experiments

In order to qualify the system under real ambient air, different analytes placed in 20mL vials were tested. The sampling was achieved by placing the gas inlet above the opened vial. The tested analytes were: DNT, TNT, methylene chloride, méthyléthylcétone (MEK), toluene, and domestic vapors : Scorpio perfume, Lacoste perfume, laundry detergent, sun screen.

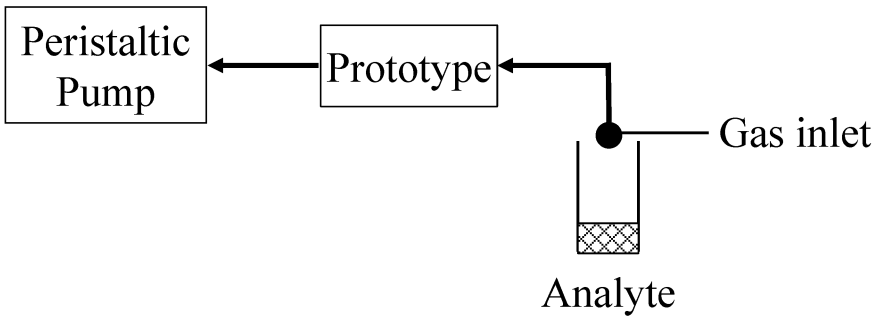

Figure 4: Testing bench for explosives and interfering compounds experiments

3. Results

3.1 Choice of the deposition method

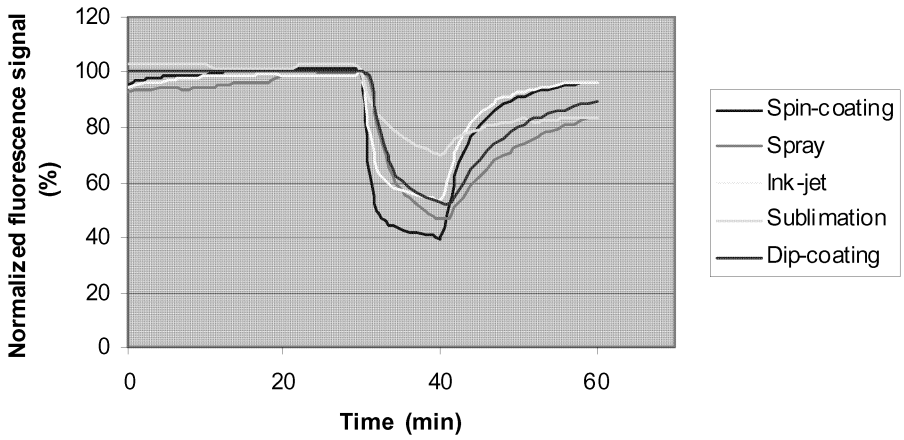

Figure 5: Effect of the method of deposition of 'A' on the response of the sensor to DNT (abs # 0.2, HR<2%))

The Reponses of the various films are plotted in figure 5. For each film, the fluorescence was largely decreasing in presence of vapors of DNT. This clearly indicated that the material was very sensitive to nitroaromatics vapors. The reversibility of the detection process was slower than the adsorption process.
Spin and Spray coatings exhibited the largest responses while the sublimation process lead to the shortest one, an intermediate value was observed in the case of ink jet printing.

We have decided to select spin coating as the reference method for sensor elaboration because it led to the largest response to DNT and exhibited the best reproducibility.

Further experiments were performed with a spin coated film of absorbance 0.2.

3.2 Performances of the detector

The responses of the detector to DNT and TNT (120 and 5 ppbv) and various vapours (> 10000 ppmv) are plotted in figure 6.

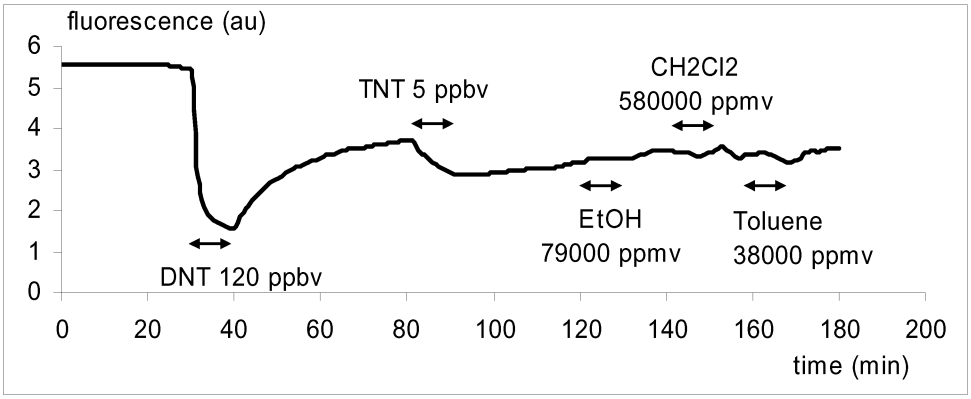

Figure 6: Sensor responses to various vapours (HR = 30 %)

TNT and DNT led to significant signals while no significant effect was observed with non explosive solvents. No effect was also observed when domestic vapors were used as interfering compounds.
The device was thus very sensitive and selective to TNT or DNT vapors. After 10 min, the response was 70 % under DNT and 30 % under TNT. The limit of detection of the device could be extrapolated to 10 ppbv of DNT and 1 ppbv of TNT in a real atmosphere with a response time of 10 minutes.
The device was also very selective towards nitroaromatics vapors since other volatile compounds did not lead to significant effects on the fluorescence of the sensor.

The sensor was thus able to detect the presence of explosive in complex atmospheres.

4. Conclusion

We have developed a portable detector dedicated to the identification of vapors traces of nitroaromatic explosives. The sensors exhibited large sensitivity towards TNT or derivative compounds. With its excellent selectivity as well, the detector matches the ain requirements for the identification of suspect luggage, the clearing of battlefields or forensic analyses.

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