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Selection of a sensitive material for the detection of explosive, application to the detection of traces of TNT

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Abstract:
For the development of fluorescent sensors, one of the key points is choosing the sensitive material. Here, we aim at evaluating, under strictly identical experimental conditions, the performance of three materials for the detection of dinitrotoluene (a volatile marker of trinitrotoluene) through various parameters: response time, fluorescence intensity, sensitivity, reversibility, reaction after successive exposures and long-term stability. This first study rendered it possible to select a conjugated molecule as the best sensitive material for the development of a lab-made prototype. In a second part, the material is used for the detection of vapours emitted from swabs tainted with TNT.

Key words: Detection, explosives, fluorescent material, chemical sensors, sampling

Introduction

The increased use of explosives in terrorist activities has created a demand for a continued innovation in the detection of these agents. To this aim, the detection of nitroaromatic compounds (NAC) using chemical sensors has been the major goal of our team for almost a decade. Fluorescent sensors especially seem to satisfy requirements in terms of reliability, cost and handling ability. In this field, an optical device based on the capability of various materials to detect explosives vapours, particularly nitroaromatics compounds such as trinitrotoluene TNT and dinitrotoluene DNT, has been developed [1]. TNT is one of the most commonly used explosives for military applications and DNT has a significant part in the chemical signature of this target compound [2].

The goal of this paper is first to select a fluorescence sensitive material adapted for the detection of nitroaromatic explosive vapours. Three various materials have been first selected (cf. Tab. 1). In the second part of this study, the selected material is used for the detection of ultra-traces of TNT. The detection of explosive is often performed from swabs tainted with particles of explosives on their surface[3-5]. In order to evaluate the sensitivity of our fluorescent sensor in such conditions, an oven has been developed to desorb vapours from swabs and transport them to the sensor.

Experimental part

Fluorescent prototype:
The prototype used for the detection by fluorescence is presented in *Fig. 1*. It has been described in detail elsewhere [6].

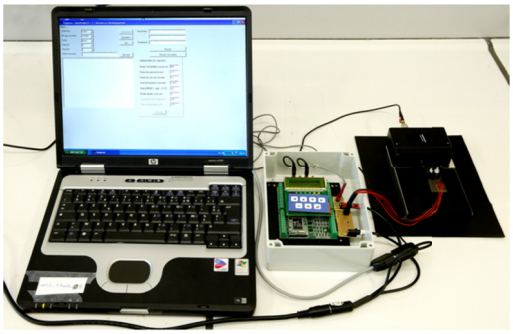


Fig. 1: Photography of the fluorescent detector

For the fluorescence measurements, each material was deposited on the entire surface of a glass substrate (microscope slides, 75 mm × 25 mm × 1 mm) by spin-coating (Braive Instrument's spin-coater at 600 rpm) from a chloroform solution during 60 s of drying. The concentrations were determined in order for the fluorescence signal to be contained between 3 and 10 V in the prototype.

Description of the sensors tests:
The three materials were evaluated for the detection of vapours under dry synthetic air and real ambient air. During a typical experiment, the material was exposed to air (synthetic or ambient), organic vapours diluted in air

(synthetic or ambient) for 10 min and then to air again (synthetic or ambient) with a flow rate of 20 L/h.

Description of the oven and the tests with swabs:

The oven is shown in *Fig. 2*. Swabs were elaborated from pieces of PTFE.

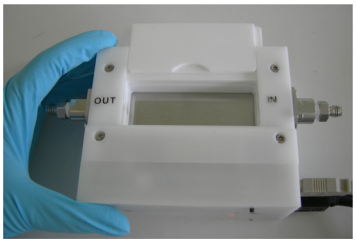


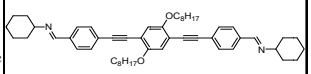
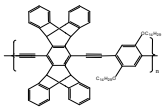
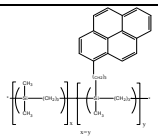
Fig. 2: Photography of the oven

The swab tainted with explosive was elaborated as followed: 10 µL of a solution of TNT in acetone were dropped on the surface of the PTFE and then dried. The experiments of detection have consisted in recording the response of the sensors when exposed to the vapor of the swab when heated at 140 °C in the oven. The flow rate was 20 L/h.

Choice of the best sensitive material

The design of a sensor requires several steps. One of the key points is the choice of the sensitive material. Here, we first evaluate, in strictly identical conditions, various performance parameters of the three materials [7-9] (cf. Tab. 1) for the detection of DNT as a volatile impurity of TNT: fluorescence intensity, response time, sensitivity, reversibility, reaction after successive exposures and long term stability.

Tab. 1 : Presentation of the three fluorescent materials [8-10] studied in this work

Sensitive material	Chemical structure	Nature	Main characteristics
Material 1: π-conjugated phenylene-ethylene diimine		Molecule / Oligomer	Non Porous, π-conjugated
Material 2: polypentiptycene		Solid polymer	Porous, π-conjugated, fluorescent quenching amplification effect
Material 3: fluorescent polycarbosilane		Viscous liquid polymer	Viscoelatic properties, high gas permittivity

To demonstrate the feasibility of the fluorescent sensor, each material was first tested in the presence of DNT (30 ppb_v). The obtained detection signals are shown in *Fig. 3*.

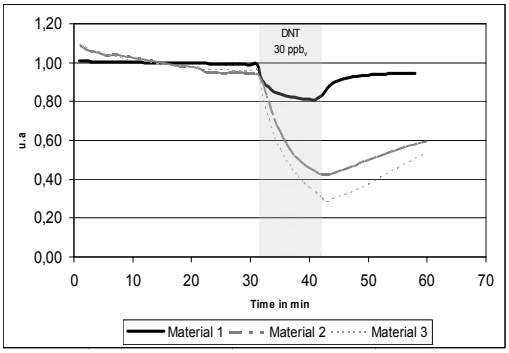


Fig. 3: Example of signal detection by fluorescence upon exposure to 30 ppbv of DNT for 10 min

All the previous criteria are shown in Tab. 2, a ranking of the materials was proposed. Material 2 was very sensitive but the intensity of fluorescence as well as the reversibility was poor. Material 3 was also very sensitive, but the response time as well as the reversibility was far from optimal. Material 1 enabled a safe and reproducible detection since this material exhibited the best reversibility. Its only drawback concerned the weaker sensitivity compared to materials 2 and 3. Nevertheless, the limit of detection was estimated at ca 12 ppb_v, which was sufficient for our application. The excellent reversibility led to a long-term stability of the sensor and thus reduced the maintenance cost of the detector. For this reason, material 1 was selected for further investigations.

Performances	ranking		
	Material 1	Material 2	Material 3
Intensity of fluorescence	+++	+	++
Response time	+++	++	+++
Response amplitude	+	+++	+++
Linearity of the response for low concentration	+++	++	++
Reversibility	+++	++	++
Behavior after several exposures	+++	+	++
Global performances	+++	+	++

Tab. 2 : Performances summary with ranking of materials

Application to the detection of traces of TNT

We have checked that no signal was observed when the previous procedure was applied to:

- The oven with 10 µg onto a swab (T = room temperature)
- The oven with a swab cleaned with acetone (T = 140°C)

A typical response obtained with 10 µg of TNT is shown in *Fig. 4*. The decrease of the fluorescence was very large and significant. We could notice that the reversibility was poor. The oven was thus well-adapted to extract vapours from a tainted swab.

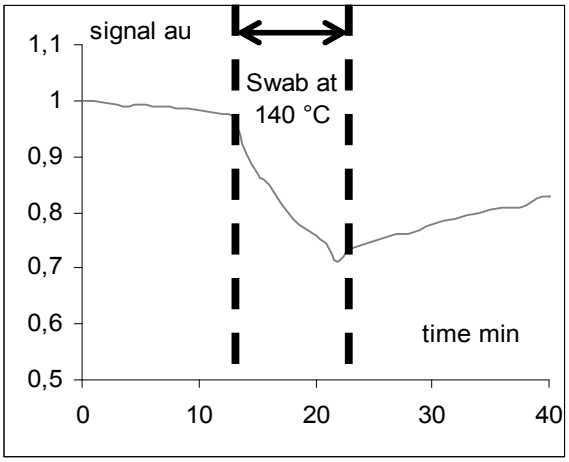


Fig. 4: Response of the sensors to 10 µg of TNT

Fig. 5 represents the average percentage of fluorescence quenching we obtained for several amounts of TNT, each bar is representative of 4 different experiments performed with various swabs and various sensitive films. A reliable detection occurred when the percentage was up to 7.5% [6]. Thus, the limit of detection of the sensor was closed to 500 ng.

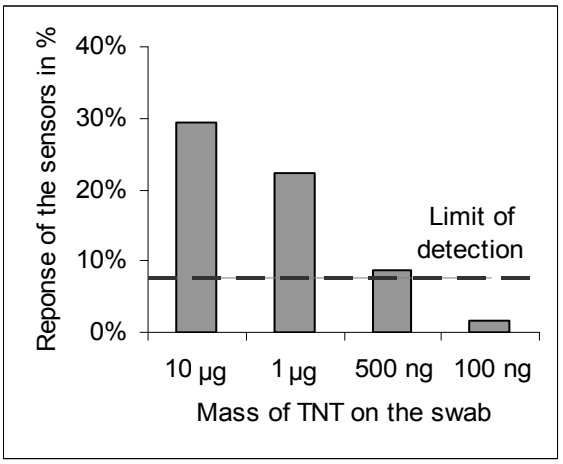


Fig. 5: Responses of the sensors to various mass of TNT

Conclusion

One of the objectives of our research group is to develop a fluorescence detection prototype [1] which detects vapors from nitroaromatic compounds. In this context, the present study concerning the choice of the best sensitive material was realized. The three materials selected for their various structures presented large responses towards DNT. Nevertheless, only the π-conjugated phenylene-ethynylene diimine conjugated exhibited an excellent reversibility, which conferred a large advantage to this material rendering possible its use without servicing or calibration between two exposures. Moreover, the performances of this chemical were in line with our objectives in terms of fluorescence intensity, response time, sensitivity and selectivity. It was also shown to be an efficient sensitive material for the detection of ultra-traces of TNT. The sensor has detected vapors of TNT emitted from the thermal desorption of a tainted swab. The sensitivity was closed to 500 ng of TNT.

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References

[1] T. Caron, S. Clavaguera, M. Huron, P. Montméat, E. Pasquinet, J. P. Lère-Porte, F. Serein-spirau, F. Perraut, and P. Prené, *Chemical Engineering Transactions* 23, 25-30 (2010); doi: 10.3303/CET1023005

[2] P. A. Pella, *J. Chem. Thermodynamics* 9, 301-305 (1977); doi: 10.1016/0021-5614(77)90049-0

[3] D. Perret, S. Marchese, R. Gentili, R. Curini, A. Terracciano, E. Bafile, and F. Romolo, 68, (2008); doi: 10.1365/s10337-008-0746-8

[4] A. Popov, H. Chen, and O. Kharybin, *Chemical Communication* 15, 1953-1955 (2005); doi: 10.1039/b419291

[5] J. Yinon, "Forensic and Environmental detection of explosives, Chap. 2," ed: wiley, 1999.

[6] T. Caron, M. Guillemot, P. Montméat, F. Veignal, F. Perraut, P. Prené, and F. Serein-spirau, *Talanta* 81, 543-548 (2010); doi: 10.1016/j.talanta.2009.12.040

[7] J. S. Yang and T. M. Swager, *Journal American Chemical Society* 120, 5321-5322 (1998); doi: 10.1021/ja9742996

[8] E. Pasquinet, P. Montméat, L. Hairault, R. Amedee, F. Guida, B. Boutevin, and F. Ganachaud, France Patent FR2929283 (2009).

[9] S. Clavaguera, O. Dautel, L. Hairault, C. Méthivier, P. Montméat, E. Pasquinet, C. M. Pradier, F. Serein-spirau, S. Wakim, F. Veignal, J. Moreau, and J. P. Lère-Porte, *Journal of Polymer Science, Part A, Polymer Chemistry* 47, 4141-4149 (2009); doi: 10.1002/pola.23474

[10] J. S. Yang and T. M. Swager, *Journal American Chemical Society* 120, 11864-11873 (1998); doi: 10.1021/ja982293q