Development of a sensors array based on quartz crystal microbalances for the explosives detection

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Abstract

Q Quartz crystal microbalances are interesting for the environmental safety guarantee because of their capability for the detection of vapour adsorptions. Unfortunately, they often exhibit a poor selectivity; that is why many studies deal with sensors arrays. Here, we focus on the detection of different explosives (nitroaromatics, peroxides or nitrate esters) with a sensors array based on 8 microbalances.
Keywords: Gas sensors, explosives detection, microbalances

1 Introduction

Explosives detection has been an important investigation topic since the fight against terrorist attacks has been strengthened. Accordingly, one strategy of law enforcement agencies is to develop efficient, portable and low cost explosive detection devices.
The quartz-crystal microbalances (QCM) are one of the most promising device [1-5]. When a QCM is used as a chemical gas sensor, the vibration frequency of an oscillating piezoelectric crystal is decreased by the selective adsorption of a gaseous compound on the crystal coating [6].
Because of the wide range of energetic materials and the huge differences in their physical and chemical properties, several detection devices detect only certain molecules of explosives and fail to detect others. For example, many detection devices readily detect conventional explosives made of nitro-organics compounds, but fail to detect explosives made of non-nitrogeneous compounds.
To this purpose, an emerging subject of interest is the use of sensors arrays for the detection of several kinds of hazardous chemicals: explosives, explosives synthesis impurities and explosives taggants.
The performances of several organic coatings for the detection of compounds from these three families will be discussed, particularly their selectivity with respect to different interfering solvents.

2 Experimental

The piezoelectric crystals used in this work are 9-MHz AT-cut quartz crystals [7].The detection performances of coated QCM were tested with 7 different vapours reported in table 2.1: 2,4-dinitrotoluene (DNT), p-nitrotoluene (p-NT), dimethyldinitrobutane (DMNB), nitromethane (CH_3NO_2), ethylene glycol dinitrate (EGDN), triacetone triperoxide (TATP), and hydrogen peroxide (H_2O_2). The two first are impurities of trinitrotoluene, nitromethane and DMNB are explosives taggants, EGDN is both an explosive and a taggant of SEMTEX, and TATP is an explosive commonly used by terrorists. In addition, 4 interfering compounds were chosen as representatives of various kinds of interfering solvents: ethanol, dichloromethane (DCM), toluene and methylethylketone (MEK).

Table 2.1: Physico-chemical characteristics of every tested vapour [8]

	DNT	**p-NT**	**CH_3NO_2**	**EGDN**	**TATP**	**DMNB**	**H_2O_2**	**Ethanol**	**DCM**	**Toluene**	**MEK**
M (g/mol)	182	137	61	152	222	176	34	182	137	152	222
Pvap at 25°C (ppm)	0.29	79	47 10^4	100	/	2.7	/	7.7 10^4	56 10^4	37 10^4	12 10^4

The materials selected as QCM coating already exhibited good sensitivity to nitroaromatic vapours. Selected materials were: a phtalocyanine, polymers (a polysiloxane, an organic polymer, a polycarbosilane), a cavitant molecule, a salt and colloidal silica.
Each material deposition was carried out by spray-coating, on both side of the quartz, except colloidal silica which was dip-coated. It resulted in a decrease of 10 kHz in the crystal frequency.
Detection experiments were performed under a constant flow of dry air at 20L/h. The microbalance frequency is registered during first 30 min of stabilisation under dry air, then 10 min exposition, and again 30 min under dry air.

3 Results and discussion

The variation of the microbalance frequency and the curve shape is characteristic of each vapour nature.
Among all materials, three compounds appeared to be sensitive to all vapours tested: phtalocyanine, colloidal silica, and an organic polymer.
As an example, figure 3.1 reports the variation of the frequency as a function of time for the microbalance coated with phtalocyanine.

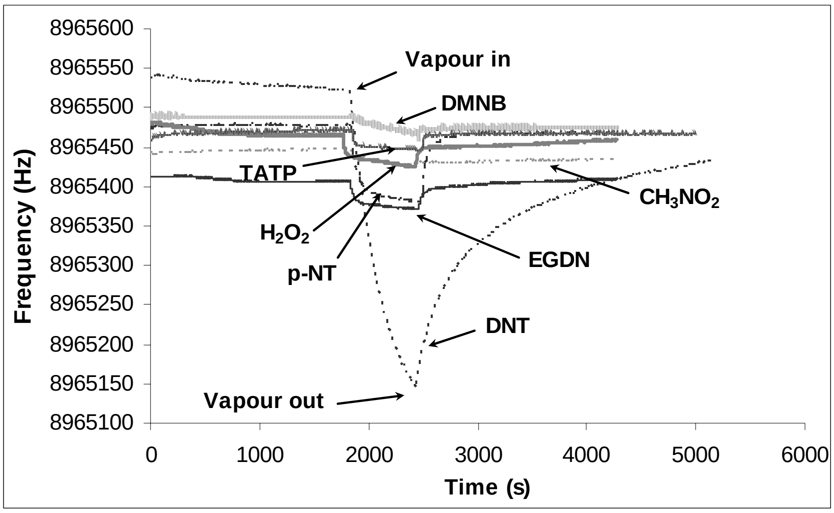


Figure 3.1: Effects of 10 min exposure on the 9 MHz phtalocyanine coated quartz.

The decrease of frequency when vapour is sent on the coated quartz corresponds to molecules adsorption at the surface coating. The greater is the variation, the more sensitive is the material.

Table 3.1 reports the values of frequency variation (Δf) for each compound.

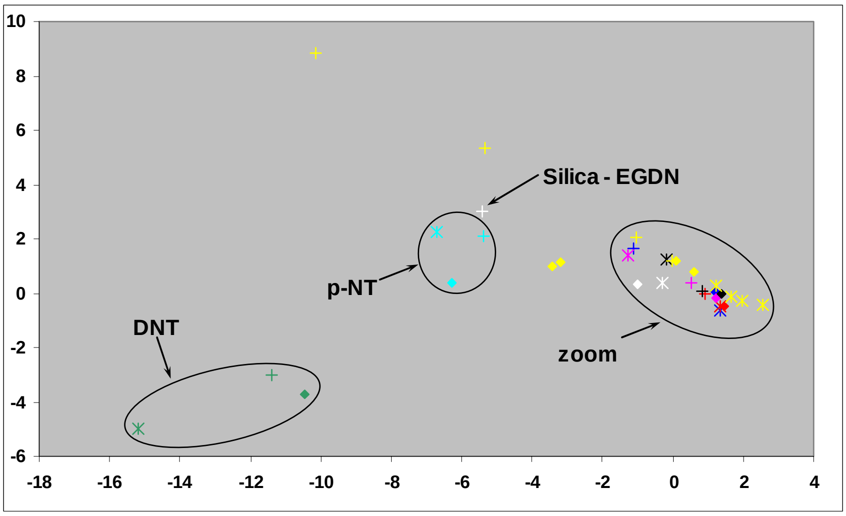
Three different curve shapes are observed:

1. An exponential shape for DNT detection. In that case, the time to recover a stable frequency is much longer than for the other vapours.
2. An exponential shape for p-NT, EGDN, TATP and H_2O_2 detection with a lower time constant than in case 1.
3. A “linear” shape for DMNB and CH_3NO_2 detection.

Table 3.1: Shift in phtalocyanine-coated QCM frequency

	Δf (Hz)
DNT	381
p-NT	96
CH_3NO_2	25
DMNB	22
EGDN	36
TATP	25
H_2O_2	40

The selectivity of each material can be evaluated by CAP, in terms of different shapes and different frequency variations (figure 3.2).



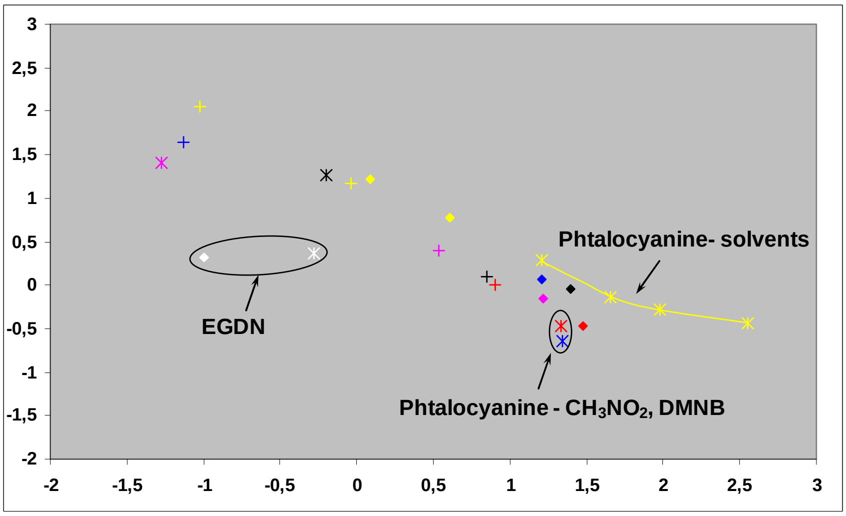


Figure 3.2: (a) CAP (cyan: p-NT, green: DNT, white: EGDN, black: TATP, blue: CH_3NO_2, red: DMNB, pink: H_2O_2, yellow: solvents; +: colloidal silica, ◊: organic polymer, ✳: Phtalocyanine.
(b) zoom.

From these results it appears that DNT and p-NT are clearly identified by the three materials. It is also the case for EGDN, except with silica, which response is close to p-NT one.
Phtalocyanine gives a good response for TATP and H_2O_2 but not for CH_2NO_3 and DMNB who are in the same area of the CAP. The phtalocyanine response for solvents is clearly identifiable as they are on the same line as shown on the figure 3.2.b. Organic polymer gives close responses for the detection of TATP, H_2O_2, DMNB and CH_3NO_2. CH_3NO_2 is clearly detected by silica whereas it is not possible to separate its answer for H_2O_2, TATP and DMNB.

4 Conclusion

Various materials were tested as sensitive coating for explosives and taggants detection. From CAP, it appears that the most sensitive and selective one is phtalocyanine. However the use of three sensitive layers allows a better separation of responses and permits to identify exactly which compounds is present in the atmosphere.

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