

# A Review of Sensors for Explosive Detection

Dipali Ramdasi<sup>a</sup>, Dr. (Mrs.) Rohini Mudhalwadkar<sup>b</sup>

**Abstract**— The timely detection of explosives is a major concern in the present, for personal and homeland security. There are several proven methods like the Gas Chromatography or Mass Spectrometry, which are used very frequently for explosive detection. The main limitation of these equipments is their cost, huge size and laboratory based techniques. Small, portable instruments that give a low level of detection, even at the field, is the need of today. Researchers all over the world are working on this. This paper deliberately does not cover the conventional laboratory based methods. It provides consolidated information about explosive detection techniques with the polymer sensors, metal oxide sensors and Quartz Crystal Microbalance (QCM) sensors.

**Index Terms**— conductivity, explosive detection, fluorescence, metal oxide sensors, nitroaromatic, Polymer sensors, Quartz crystal microbalance, resonant frequency

## 1 INTRODUCTION

Terrorist attacks in different parts of the world are not new. The innovative ways in which explosives are used to carry out awful intentions are astonishing. The timely detection of explosives and making them inactive is a challenging task. Also, the low vapour pressure of explosives and their compounds poses a further challenge. Many times, trained canines (sniffer dogs) are used for explosive detection as they are the best proven method. It also proves that explosives have a specific vapour signature. If these vapours can be properly detected, identified and quantified, the explosive detection can be a comparatively easy task.

Currently, many methods are available for detection of explosives. In the spectroscopic methods, samples are drawn from the air into a spectrometer where they are ionised. The resultant ions are separated by electrical and magnetic fields according to mass charge ratio and detected and quantified. These methods display very high sensitivities and selectivities but are often expensive and require laboratory based equipment. The Ion mobility Spectroscopy [1], Mass Spectrometry [2], Infrared Spectroscopy[3] and Raman Spectroscopy[4] are some of the common spectroscopic methods used for explosive detection. Apart from this, Gas Chromatography, X - Ray techniques, Micro cantilevers and electrochemical sensors are also used for the detection of explosives.

This paper restricts its review to some non conventional but reliable methods for detection of explosives. Also, these methods are continuously being worked upon by researchers for enhancements in the results or to improve the level of detection. This paper reviews the fluorescence based polymer sensors, as well as the polymer sensors used for detection of explosives based on change in thermal conductivity. This paper also covers explosive detection using metal oxide sensors and Quartz Crystal Microbalance (QCM).

- Dipali Ramdasi is a faculty at Cummins College of Engineering, Pune, INDIA and is a research student at College of Engineering, Pune, INDIA E-mail: [dipali.ramdasi@gmail.com](mailto:dipali.ramdasi@gmail.com)
- Dr. (Mrs.) Rohini Mudhalwadkar is an Associate Professor at College of Engineering, Pune, INDIA E-mail: [rpm.instru@coep.ac.in](mailto:rpm.instru@coep.ac.in)

## 2 SENSORS USED FOR EXPLOSIVE DETECTION

### 2.1 Organic and Inorganic Polymer Sensors

The chemical and physical properties of polymers may be tailored over a wide range of characteristics. The use of polymers in a variety of sensors is increasing by the day [5]. Several polymers have been used to detect nitrogen based explosives by a variety of transduction schemes. Semiconductive organic polymers serve as extremely efficient conduits for the transport of induced excitations and it is this transport property that allows for the high sensitivity of these materials to trinitrotoluene (TNT) and dinitrotoluene (DNT), the primary explosives used in landmines. Detection relies on both electronic and structural interactions between the sensing material and the analyte. Quenching of luminescent polymers by electron deficient nitroaromatic explosives, such as trinitrotoluene, may be monitored to detect explosives. Resistive sensing using carbon black particles that have been coated with different organic polymers and deposited across metallic leads can also be used to detect nitroaromatic vapors in an electronic nose approach. Frequency changes in surface acoustic wave devices may be monitored to detect nitroaromatics after their adsorption into polymer coatings.

Sarah Toal and William Trogler [6] used Conjugated polymers for explosive sensing. Conjugated polymers are electron donors. Donor ability is further enhanced in their excited states. Excited state delocalization is important because exciton migration increases the frequency of interaction with a bound quencher, which contributes to enhanced detection sensitivity. Fluorescent organic and inorganic conjugated polymers have therefore been applied to the detection of nitroaromatic explosives in solution and in the vapor phase with detection limits in the parts-per-billion, and even parts-per-trillion, range have been observed. Fluorescence quenching is often achieved through an electron-transfer donor-acceptor mechanism. Electron deficient analytes, such as nitroaromatic explosives, can act as electron acceptors for photoexcited electrons of the polymers. Fluorescent organic polymers discussed in this paper [7] are Polyacetylenes [8], Poly(p-phenylenevinylenes) [9], Poly(p-phenyleneethynylenes) [10] and Polymeric porphyrins [11]. The fluorescent inorganic polymers discussed are Pol-

ysilanes, Polymetalloles and metallole-silane copolymers.

## 2.2 Fluorescence Based Polymers

Amplifying Fluorescent polymer (AFP) technique has been used by Massachusetts Institute of Technology to develop the sensor designed for detection of TNT. Conventional fluorescence detection normally measures an increase or decrease in fluorescence intensity that occurs when a single molecule of analyte interacts with a single fluorophore [12]. The binding of a single explosive molecule quenches only the chromophore to which the explosive molecule binds. AFP consists of fluorescing chromophores linked together in polymer chains. When stimulated by light of the correct wavelength, AFP will fluoresce or emit visible light. Explosive molecules will bind to the AFP and reduce the brightness of the fluorescence. A typical sensor probe is shown in figure 1. The inherent structure of the chromophore chain in AFP dramatically amplifies the quenching effect, resulting in ultra-low detection limits. The minimum detection limit for TNT is of approximately 1 femtogram ( $1 \times 10^{-15}$  grams). [12]

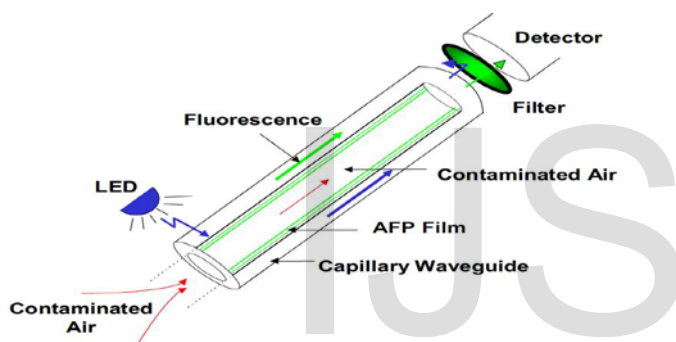


Fig. 1 Typical probe used in Fluorescence based sensor

The Fluorescence effect has also been utilized by Paul T. Charles et.al [13] in a different way. Fluorescence immunoassays employing monoclonal antibodies are directed against the explosive 2,4,6-trinitrotoluene (TNT). It is conducted in a multi-channel microimmunosensor which is prepared in poly (methyl methacrylate) (PMMA) using hot embossing from a brass molding tool. 39 parallel channels of size 25  $\mu$ m are embossed into PMMA. The channels are coated with a sol-gel film to generate a siloxane surface for antibody immobilization. Using a displacement immunoassay format, monoclonal antibodies directed against TNT are covalently immobilized in the microchannels via a heterobifunctional crosslinker. AlexaFluor-cadaverinetritrobenzene (AlexaFluor-Cad-TNB), which serves as the fluorescence reporter molecule is allowed to bind in the antibody binding sites prior to TNT exposure forming the sensing complex. In the presence of TNT, the antibody releases the fluorescence reporter molecule which is measured with a fluorescence detector downstream. The advantage of using this design and antibody immobilization protocol is an increase in the sensing surface area and the potential for high throughput applications. With this method, TNT was detected as low as 1 ng/mL.

## 2.3 Polymer sensors based on change in thermal conductivity

A.J. Matzger et.al [14] used arrays of polystyrene, polysulfone, polyvinylbutyl, polycaprolactone, polyvinylacetate, polymethylmethacrylate to observe responses to different analytes. These polymers are inexpensive, commercially available polymers. In this method, carbon black particles are coated with an organic polymer and deposited as a thin film across metallic leads. Due to the carbon black particles, electrical conductivity is imparted to the otherwise insulating organic polymer film. When vapours of the analyte are passed over these polymers, the analyte gets adsorbed to these polymers, resulting into swelling of the polymer. This changes the effective concentration of conducting carbon particles, resulting into change of resistance of these polymers.[14] By manufacturing an array of sensing elements, each with a different polymer or polymer blend coating, a characteristic signal from specific analytes can be obtained. Each polymer has a different response to an analyte depending on the partition coefficient of the analyte. Analytes which absorb to a greater extent cause a higher increase in film resistance. For nitroaromatic vapors, the rates of adsorption are slower than for other organics, though the array accurately distinguishes DNT, TNT, and toluene. Detection limits for DNT vapor in the low ppb range are observed. [14] This approach has been used in electronic noses.[15]

## 2.4 Metal Oxide Sensors

Metal-oxide gas sensors (such as tin dioxide, SnO<sub>2</sub>) are simple rugged devices that perform well with relatively simple electronics support. Metal oxide sensors exhibit a change in electrical properties when subjected to specific gases. When a metal-oxide crystal such as SnO<sub>2</sub> is heated at a certain high temperature in air, oxygen is adsorbed on the crystal surface and a surface potential is formed that inhibits electron flow. When the surface is exposed to reducible gases, the surface potential decreases and conductivity measurably increases. The relationship between the film's electrical resistance and a given concentration of gas is described by the following empirical equation: [16]

$$R_s = A[C]^{-\alpha} \dots\dots\dots(1)$$

where  $R_s$  is the sensor electrical resistance  
 A is a constant specific for a given film composition  
 C is the gas concentration  
 $\alpha$  is the characteristic slope of the  $R_s$  curve for that material and expected gas.

Metal-oxide devices change the resistivity as a function of the presence of reducible gases, and as such, they require an additional electronic circuit to operate. A response of a typical gas sensor is shown in figure 2 which illustrates the change in resistance with volume change in gas. Also the figure 3 shows the effect of change in atmospheric temperature on the change in sensor response. Thus, the sensitivity of the sensor depends on the following factors:

- a. Material of the sensor
- b. Temperature at which measurement is done
- c. Specific resistivity of the material
- d. Load resistance connected in the detection circuit
- e. Input supply given to the detection circuit

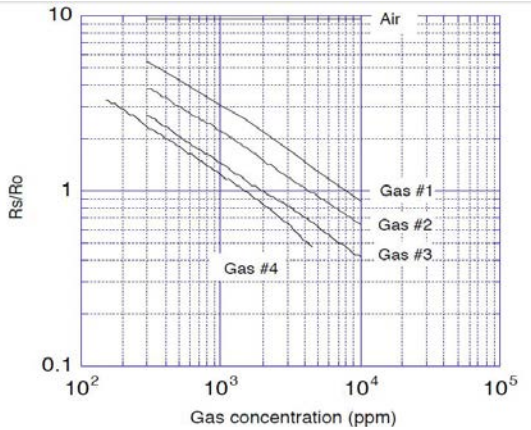


Fig. 2 Typical gas sensor output for different gases where Y axis shows the ratio of change in resistance to original resistance

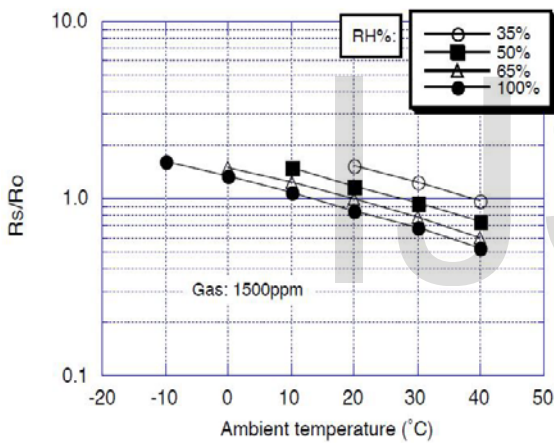


Fig. 3 Sensor response for change in ambient temperature where Y axis shows the ratio of change in resistance to original resistance

A typical arrangement is to design the sensor as one leg in a common wheatstone bridge circuit so that the changing resistance can be detected as an unbalancing of the potential drops observed across the bridge circuit. The negative temperature coefficient (NTC) thermistor with a linearizing parallel resistor is required to adjust the bridge balance point according to the sensor's temperature. Because the sensor behaves as a resistance whose value is controlled by gas species and gas concentration, the voltage drop across it is proportional to its resistance and a plot of voltage drop versus gas concentration is recorded. This method is applied to detect nitro-aromatic explosives. Occasionally, the rate of change of the conductivity is used to differentiate gases and concentrations.

K. Brudzewski et al. [17] devised a differential electronic nose composed of two metal oxide sensor arrays working in parallel. One of it forms the measurement array and the second works as

the reference array. Both arrays work in the same environmental conditions. The signals measured by these two arrays are subtracted from each other, producing a difference signal with reduced interference effects due to the changes in humidity or temperature of the environment. Twelve heated metal oxide gas sensors of Figaro series 2X-TGS are used to form the array.

The flow-air system for detection of the vapor explosive compounds is shown in figure 4. The streams of air are delivered to both chambers of gas sensor arrays from the odor acquisition place through the socket outlet. The measurement channel contains the vapor of explosive material, while the reference one has only the atmospheric air.

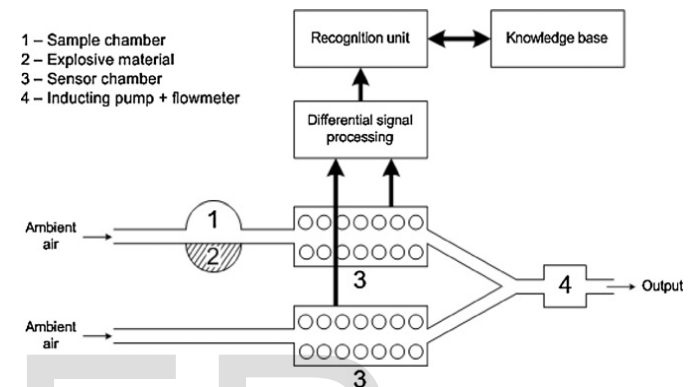


Fig. 4 Differential metal oxide arrays used for recognition of explosive materials.[17]

The corresponding signals registered by the appropriate sensors of both arrays are subtracted from each other by using the differential amplifier, then converted by A/D converter to the digital form and finally delivered to the computer interface for further processing, which leads to the recognition of smell. Signal Processing methods of Convolution, Auto Co-relation and Principal Component Analysis are used to enhance the difference between the differential signals of the setup at different sniffed explosive materials [17]. This method is able to differentiate the smell of TNT, PETN and RDX.

### 2.5 Quartz Crystal Microbalance (QCM)

The quartz crystal microbalance utilises the resonance frequency change due to changes in mass upon the crystal surface as a means to detect the presence of a substance of interest. This technique is further enhanced through coating the surface with various compounds which help provide specificity to this system. The signal transduction mechanism relies upon the piezoelectric effect. The decrease of the resonant frequency of a thickness shear vibrating quartz crystal resonator, having AT or BT cut, is proportional to the added mass of the deposited film and is given by the following equation[18]

$$\Delta f = - \frac{f_q^2 M_f}{N \rho_q S} \dots\dots\dots(2)$$

where  $f_q$  is the fundamental resonant frequency of the quartz

N is the frequency constant of the specific crystal

$\rho_q$  is the quartz density

S is the surface area of the deposited film and

Mf is the mass of the deposited film.

The sensitivity of the QCM for explosive vapours is given by:

$$\text{Sensitivity} = \frac{\Delta f}{C} \dots\dots\dots(3)$$

where  $\Delta f$  = variation in frequency

C = explosive vapour concentration in ppm

The sensitivity of QCM sensor is also dependent on the time for which it is exposed to explosive vapours and can be expressed as:

$$\text{Sensitivity} = \frac{\Delta f(\text{explosive})_t}{\Delta f(\text{explosive})_0} \dots\dots\dots(4)$$

where  $\Delta f(\text{explosive})_t$  = variation in frequency due to vapour exposure after fresh coating

$\Delta f(\text{explosive})_0$  = variation in frequency due to vapour exposure when coating is t days [19]

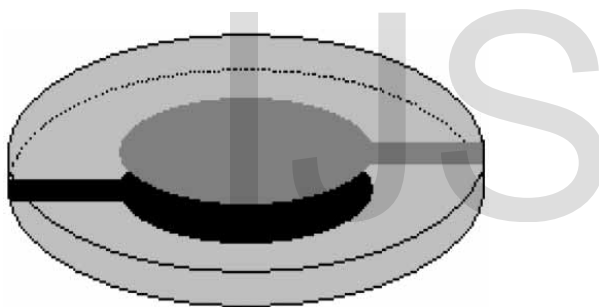


Fig. 5 Typical quartz crystal resonator [20]

A typical quartz crystal resonator is shown in Figure 5. Quartz is the most widely used material for the development of instruments containing oscillators due to its natural occurrence in the earlier days and due to its commercial availability. Nowadays, quartz crystals are synthetically grown. There are many ways to cut quartz crystal and each cut has a different vibrational mode upon application of a potential.[20]

Quartz is the most widely used material for the development of instruments containing oscillators due to its natural occurrence in the earlier days and due to its commercial availability. Nowadays, quartz crystals are synthetically grown. There are many ways to cut quartz crystal and each cut has a different vibrational mode upon application of a potential.

Larsson et al, developed a self assembled monolayer (SAM) and a detector gold biochip to detect TNT and its variants. The QCM method was used as one of the methods for monitoring the analog dissociation of the SAM. The detection limit for TNT was

within the 1-10  $\mu\text{g}/\text{litre}$  range.[21]

Cerruti et al, investigated the selective detection of TNT and DNT using QCM with a polymer-oligopeptide coating upon a gold chip capable of providing a stable and high density set of receptors with selective binding capabilities. This system was capable of providing real-time detection, in water, of TNT whilst the presence of DNT exhibited no resonance frequency change [22].

Lubczyk et al, combined several differently coated microbalances in an array to distinguish the peroxide based explosive TATP from chemically related compounds. Modified phenylene dendrimer, a cyclodextrin and a cholic acid derivative were the coatings used for the detection of TATP. This approach was then combined with high frequency QCM for a response time of a few seconds and detection limit of TATP in nitrogen at 1 ppm. [23]

Wang et. al developed a TNT sensor designed to measure the displacement of a TNT-specific antibody by QCM. This sensor combines high sensitivity of detection (0.1 ng/mL) with the ability to distinguish TNT from molecules with similar chemical properties. Particularly, the reliability of this method for the detection of TNT in dirty environments was investigated by using fertilizer solution and artificial seawater. Instead of measuring actual binding of TNT, the method described is based on the displacement of an anti-TNT antibody, which allows quantifying the concentration of TNT in solution with higher sensitivity. In addition, by utilizing the rate of antibody displacement, the detection time is significantly decreased from hours, which would be necessary to measure the frequency change at equilibrium, to minutes. A Langmuir kinetic model was used to describe the molecular interactions on the surface of the sensor and to establish a standard curve to estimate on-site TNT detection. [24]

Dilek Erbahar et. al described the use of QCM with specially designed pthalocyanines as sensitive materials for the detection of explosives in aqueous media. This work was specifically intended to detect explosives under water. The 4.95 MHz AT cut polished quartz crystals are used as transducers in their system. The level of detection for TNT is 0.5 ppm and for RDX is 5 ppm. [25]

### 3 DISCUSSION

The use of polymers in different sensing mechanisms is increasing. Due to advances in technology and synthesis methods, the flexibility in use of polymers can be exploited. With use of molecular imprinted polymers, the performance of these sensors may be improved. Polymer based sensors developed for explosive detection have been commercialized and are available in the international market. Though not much work is reported using metal oxide sensors, it is obvious that making use of these sensors for developing and evaluating mathematical models of sensors based on this technology opens up a research avenue for scholars. The QCM technique has been used primitively for measuring weights, though its use for explosive detection is a recent development. Also, studies done of MEMS and nanomaterials for explosive detection appears to be very promising.

## 4 CONCLUSION

The review of polymer based, metal oxide based and QCM based sensors for explosive detection is done in this paper with more efforts taken to cover recent developments. Some of the above mentioned techniques have been commercialized and are available as products. Research is an ongoing process and all these methods are also still under research. The field of micro-sensors and nanomaterials have developed a new avenue of research in the existing techniques. This paper thus gives a consolidated information on these three methods.

## REFERENCES

- [1] R.G. Ewing, D.A. Atkinson, G.A. Eiceman, G.J. Ewing, 'A critical review of ion mobility spectrometry for the detection of explosives and explosive related compounds', *Elsevier Talanta*, Vol 54, Jan 2001, pp 515-529
- [2] N.L. Sanders, S. Kothari, G. Huang, G. Salazar, R.G. Cooks, 'Detection of explosives as negative ions directly from surfaces using a miniature mass spectrometer', *Journal of Analytical Chemistry* Vol 82, 2010, pp 5313-5316
- [3] O.M. Primera-Pedrozo, Y.M. Soto-Feliciano, L.C. Pacheco-Londoño, S.P. Hernández-Rivera, 'Detection of high explosives using reflection absorption infrared spectroscopy with fiber coupled grazing angle probe/FTIR', *Journal of Sensor and Imaging*, Vol 10, 2009, pp 1-13
- [4] Hatab, N.A., Eres, G., Hatzinger, P.B., Gua, B. 'Detection and analysis of cyclotrimethylenetrinitramine (RDX) in environmental samples by surface-enhanced Raman spectroscopy' *Journal on Raman Spectroscopy*, Vol 41, 2010, pp 1131-1136.
- [5] Basudam Adhikari, Sarmishtha Majumdar, 'Polymers in sensor applications', *Elsevier*, Vol 29, Issue 7, July 2004, pp 699-766
- [6] Y. Liu, R. Mills, J. Boncella and K. Schanze, Langmuir, 'A Thin Film Fluorescence Sensor for Nitroaromatic Vapors based on a High Permeability Polyacetylene', *Langmuir* 2001, Vol 17, pp 7452-7455
- [7] C. Chang, C. Chao, J. H. Huang, A. Li, C. Hsu, M. Lin, B. Hsieh and A. Su, 'Fluorescent conjugated polymer films as TNT chemosensors', *Synth. Met.*, 2004, Vol 144, pp. 297-301
- [8] Jye-Shane Yang and Timothy M. Swager, 'Porous Shape Persistent Fluorescent Polymer Films', *Journal of American Chemical Society*, 1998, Vol 120, No. 21, pp 5321-5322
- [9] Samuel W. Thomas III, John P. Amara, Rebekah E. Bjork and Timothy M. Swager, 'Amplifying fluorescent polymer sensors for the explosives taggant 2,3-dimethyl-2,3-dinitrobutane (DMNB)', *The Royal Society of Chemistry Journal of Chemical Communication*, Aug 2005, 4572-4574
- [10] G. M. Murray, B. M. Arnold and D. S. Lawrence, US Pat. Appl., 2001077664, 2001
- [11] J. W. Gardner and J. Yinon, 'Electronic Noses & Sensors for the Detection of Explosives', NATO Science Series II: Mathematics, Physics and Chemistry - Vol. 159, Kluwer Academic Publishers, Netherlands, 2004, pp 29-37
- [12] FIDO Technical review, ICx Technologies
- [13] Paul T. Charles, Andre A. Adams, Peter B. Howell, Jr., Scott A. Trammell, Jeffrey R. Deschamps and Anne W. Kusterbeck, 'Fluorescence-based Sensing of 2,4,6-Trinitrotoluene (TNT) Using a Multi-channelled Poly(methyl methacrylate) (PMMA) Microimmunosen-
- sor', *Open access Journal on Sensors*, January 2010, Vol 10, pp 876-889
- [14] Matzger AJ, Vaid TP, Lewis NS. 'Vapor sensing with arrays of carbon black-polymer composites'. *Proc SPIE International Society of Optics Engineering*, 1999; Vol 3710, pp 315-20.
- [15] J. Yinon, 'Detection of Explosives by Electronic Noses', *Journal of Analytical Chemistry*, March 2003, pp. 99-105
- [16] 'Handbook of Modern Sensors' by Jacob Fraden, 3rd edition, 2004, Published by AIP press and Springer Verlag, pp. 503-505
- [17] K. Brudzewski, S. Osowski, W. Pawlowski, 'Metal oxide sensor arrays for detection of explosives at sub-parts-per million concentration levels by the differential electronic nose' *Elsevier Journal of Sensors and Actuators B: Chemical*, 2012, vol. 161, pp. 528-533
- [18] Vasile Mihai Mecea, 'From Quartz Crystal Microbalance to Fundamental Principles of Mass Measurements', *Taylor & Francis, Inc, Analytical Letters*, 2005, vol. 38: pp. 753-767
- [19] F. Parret, P. Montmeat and P. Prene, 'Detection of Explosives Vapors with a Portable Detector Based on Quartz Crystal Microbalance', *IEEE Sensors Conference Proceedings*, 2007, pp. 248-251
- [20] GAMRY Instruments Inc. Application Note, 'Basics of a Quartz Crystal Microbalance', Rev 1.2, 14 Feb 2012
- [21] A. Larsson, J. Angbrant, J. Ekeröth, P. Månsson, B. Liedberg, 'A novel biochip technology for detection of explosives - TNT: Synthesis, characterisation and application', *Elsevier Journal of Sensors and Actuators B: Chemical*, 2006, vol. 113, pp. 730-748
- [22] M. Cerruti, J. Jaworski, D. Raorane, C. Zueger, J. Varadarajan, C. Carraro, S. Lee, R. Maboudian, A. Majumdar, 'Polymer-oligopeptide composite coating for selective detection of explosives in water', *Journal of Analytical Chemistry*, 2009, vol. 81, pp. 4192-4199
- [23] D. Lubczyk, C. Siering, J. Lörger, Z.B. Shifrina, K. Müllen, S.R. Waldvogel, 'Simple and sensitive online detection of triacetone triperoxide explosive', *Elsevier Journal of Sensors and Actuators B: Chemical*, 2010, vol. 143, issue 2, pp. 561-566
- [24] Jinghui Wang, Mohammed AlMakhaita, Sibani Lisa Biswal and Laura Segatori 'Sensitive Detection of TNT using Competition Assay on Quartz Crystal Microbalance', *Journal of Biosensors and Bioelectronics*, vol. 3, issue:1
- [25] Dilek D. Erbahar, Ilke Gurol, Vefa Ahsen, Zafer Ziya Ozturk, Emel Musluoglu, Mika Harbeck, 'Explosives detection in sea water with phthalocyanine quartz crystal microbalance sensors', *Sensor Letters*, Vol. 9, pp. 1-4, 2011