Review

Sensors—An effective approach for the detection of explosives

Suman Singh *

Central Mechanical Engineering Research Institute, M. G Avenue, Durgapur, 713209 West Bengal, India

Abstract

The detection of explosives and explosive related illicit materials is an important area for preventing terrorist activities and for putting a check on their deleterious effects on health. A number of different methods, based on different principles, have been developed in the past for the detection of explosives. Sensors are one of those methods of detection which have capability to mimic the canine system and which are known to be the most reliable method of detection. The objective of this review is to provide comprehensive knowledge and information on the sensors operating on different transduction principles, ranging from electrochemical to immunosensors, being used for the detection of explosives as they pose a threat for both health and security of the nation. The review focuses mainly on the sensors developed in the recent 5 years and is prepared through summary of literature available on the subject.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Explosives; Explosive related compounds (ERC); Sensors

Contents

1. Introduction

An explosive is defined as a material (chemical or nuclear) that can be initiated to undergo very rapid, and self-propagating decomposition resulting in the formation of more stable material, liberation of heat or the development of sudden pressure effect.

Based on structure and performance, explosives have been classified into many types (Scheme 1). Basically, explosives are classified as low and high explosives and both types are further classified into different forms. Low explosives or propellants burn at relatively low rates ($cm\,s^{-1}$), whereas high explosives detonate at velocities of $km\,s^{-1}$. Low explosives include propellants, smokeless powder, black powder, pyrotechnics, etc. The chemical reaction propagates with such a rapidity that the rate of reaction in material exceeds the velocity of sound. High explosives have again been sub-divided into two groups according to their function in the explosive train, i.e. primary explosives and secondary explosives. Primary explosives, which include lead azide and lead styphnate, are highly susceptible to initiation and are often referred as 'initiating explosives' because they can be used to ignite secondary explosives. Secondary explosives, which include nitroaromatics and nitramines are much more prevalent at military sites than primary explosives. Secondary explosives are often used as main charge or bolstering explosives because they are formulated to detonate only under specific circumstances. Secondary explosives can be loosely categorized into melt-pour explosives which are based on nitroaromatics, such as trinitrotoluene (TNT), dinitrotoluene (DNT) and plastic-bonded explosives which are based on a binder and crystalline explosive, such as hexahydro-1,3,5 trinitroazine (RDX). Plas-

tic explosive means an explosive material in flexible or elastic sheet form, formulated with one or more high explosives which in their pure form have a vapor pressure less than 10^{-4} Pa at a temperature of 25 °C. Such explosive is formulated with a binder material and the so formed mixture is malleable and flexible at normal room temperature. The energetic materials used by military as propellants and explosives are mostly organic compounds containing nitro (NO_2) groups. The three major classes of these energetic materials are nitroaromatics (e.g. TNT), nitramines (e.g. RDX) and nitrate esters (e.g. nitrocellulose and nitroglycerine). However, there are six principle chemical categories of explosives (Table 1) [1].

Continuous measurement of explosives is preferred as it provides an appropriate feedback during the characterization or remediation of contaminated sites and offers rapid warning in case of contamination by previous disposal methods like during manufacturing, storage and demilitarization of weapons. Not only this, identification and quantification of explosives has constituted an emerging and important topic of interest due to their relevant role in security threat. It has been widely discussed that the detection of explosive compounds is a highly significant task in forensics, antiterrorist activities and global de-mining projects. Accordingly, extensive efforts have been devoted to the development of innovative and effective sensors, capable of monitoring explosives both in time and location. Asbury et al. [2] have pointed out the importance of analysis of explosives in two different fields. One is the threat of an illegal use of these compounds against the security of the nation and to cause the chaos in the nation, thus encouraging the terrorist activities. As the threat of terrorism is increasing, the demand for reliable and rapid methods for screening luggage is also increasing. The effective scanning for explosives in objects of various sizes, ranging from small postal parcels to large containers and trucks is now becoming an important aspect of counter-terrorism activities. All these problems have led to the major efforts in developing explosive detection systems. And, the other threat is growing concern about health risks associated with the release of explosives into the environment from military sites and former ammunition plants. An important characteristic of nitroaromatic compounds is their ability to rapidly penetrate the skin. They can cause the formation of methemoglobin on acute exposures and anemia on chronic exposures. 2,4,6-Trinitrotoluene (TNT) explosive can readily enter groundwater supplies and has been classified as toxic at concentrations above 2 ng ml^{-1} by the Environmental Protection Agency [3] as it presents harmful effects to all life forms [4]. It causes liver damage and aplastic anemia.
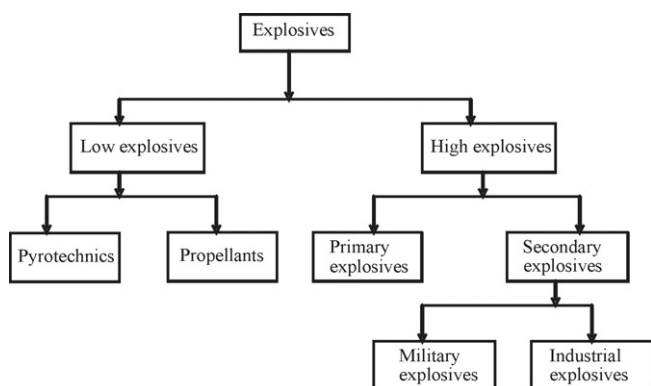
Scheme 1. Classification of explosives based on structure and performance.

Table 1
Six principle chemical categories of explosives

S. no.	Compound class	Example	Symbol	Formula	Commonly found in following
(1)	Aliphatic nitro	Nitromethane	–	CH_3NO_2	
		Hydrazine nitrate	–	$H_5N_3O_3$	Rocket fuel and liquid component of two part explosive
(2)	Aromatic nitro (C—NO$_2$)	Nitrobenzene	NB	$C_6H_3NO_2$	
		Nitrotoluene	NT	$C_7H_7NO_2$	
		2,4,6-trinitrotoluene	TNT	$C_7H_5N_3O_6$	Composition B with equal part of RDX, Pentolite with equal part of PETN
		2,4-dinitrotoluene	DNT	$C_7H_6N_2O_4$	
		2,4,6-trinitrophenol	TNP	$C_6H_3N_3O_7$	
(3)	Nitrate ester (C—O—NO$_2$)	Nitroglycerine	NG	$C_4H_5N_3O_9$	Certain dynamites and pharmaceutical.
		Ethylene glycol dinitrate	EGDN	$C_2H_4N_2O_4$	Some dynamites
		Pentaerythitol tetranitrate	PETN	$C_5H_8N_4O_{12}$	Detonating cord, Detasheet, Semtex with RDX
		Nitrocellulose	–	$[C_8H_{13}N_3O_{11}]n$	'guncotto', main component of Single based smokeless powder
		Nitrocellulose and NG	–	$C_6H_7N_3O_{11}$ and $C_3H_5N_3O_9$,	Double based smokeless powder
		Nitrocellulose, NG and nitroguanidine	–	$C_6H_7N_3O_{11}$ $C_3H_5N_3O_9$, and $CH_4N_4O_2$	Triple based smokeless powder
(4)	Nitramines (C—N—NO$_2$)	Trinitro-triazacyclohexane	RDX	$C_3H_6N_6O_6$	C-4, tetrytol-millitary dynamite with TNT
		Tetranitro-tetrazacyclooctane	HMX	$C_4H_8N_8O_8$	Her Majesty's explosive
		Tetranitro-N-Methylaniline	Tetryl	$C_7H_5N_5O_8$	
(5)	Acid salts (NH$_4^+$)	Potassium nitrate	–		Black powder with sulphur and charcoal
		Ammonium nitrate	–	$H_4N_2O_3$	Ammonium nitrate fuel oil (ANFO) w/fuel oil, nitro-carbo-nitrates (NCN) with oil
(6)	Peroxides (C—O—O—C) or primary explosives	Hexamethylene triperoxide diamine	HMTD	$C_6H_{12}N_2O_6$	
		Triacetone triperoxide	TATP	$C_3H_6O_6$	

Deaths from aplastic anemia and toxic hepatitis were reported in TNT workers prior to 1950s [5,6]. Other occasional effects include leukocytosis or leukopenia, peripheral neuritis, muscular pains, cardiac irregularities, renal irritation and bladder tumors [7–9]. These compounds are generally recalcitrant to biological treatment and remain in the biosphere, where they constitute a source of pollution due to both toxic and mutagenic effects on humans, fish, algae and microorganisms. The vapor or dust can cause irritation of mucous membranes resulting in sneezing, cough and sore throat. However, relatively few microorganisms have been described as being able to use nitroaromatic compounds as nitrogen and/or carbon as energy source [10–12]. To face these problems, there is an urgent need for instrumentation that can detect commonly used explosives at trace levels, with a high degree of accuracy, within a small timeframe and without significant cost.

The detection of explosive compounds is a highly significant task, which could help in reducing the continued fatalities from land mines among civilians as well as tracking and locating explosive materials. But since the explosives are composed of many chemicals with different volatilities and have extremely low pressures (e.g. TNT, RDX, HMX, Tetryl and PETN), their detection is a very complicated task. Moreover, terrorists pack explosives in the materials, which further block the escape of vapors. As reported in literature, the effective vapor pressure can be reduced by a factor of 1000 by sealing in plastics [13,14]. Vapor pressure of some of the explosives along with some other chemical and physical properties is given in Table 2 [15–19].

Aside from physical inspection by government agents, inspections are done using fixed instrumentation, portable instrumentation and sniffing dogs. Depending on the particular situation, one or more of these techniques are used. The most effective and efficient method of detecting explosives in current use is sniffing dog. Recent studies have shown that sniffing dogs do not just react to a particular chemical smell, but to a combination of many smells that make up an explosive or narcotic [1,15]. But dogs also suffer from some limitations like high cost of maintaining and training them, require skilled handler, their inability to work round the clock, behavioral and mood variations. In spite of spectacular progress in the real time detection of explosives, the issue still remains one of the challenging tasks. Researchers are working hard to find ways of improving the current technologies as well as trying to develop new detection methods, which will be user-friendly and will allow speed, reliability, selectivity and sensitivity.

2. Methods of detection

Detection gives an indication/alarm for the presence of target or some target-related material. Detection can be achieved via available instruments but most of the instruments used are either big in size or too sophisticated to handle or lack sensitivity. Also, traditional methods involve on-site sample collection and transportation of the sample to a certified laboratory for its analysis by highly trained scientists. So, to ensure accurate, fast and economical monitoring or detection of explosives/explosive related material, there is a need to develop portable, easy to operate and low cost sensors. Based on the origin of obtainable signals, most commonly used sensors for the detection of explosives can broadly be classified as: (1) electrochemical sensors, (2) mass sensors, (3) optical sensors and (4) biosensors. The categorization of these sensors is based primarily on the principal physics and operating mechanisms.

In this review article, an attempt has been made to accumulate the research done in past 5 years in the area of development of sensor based methods for the detection of explosives either as hidden material or as a contaminant of water and soil.

2.1. Electrochemical sensors

Electrochemical sensors include those sensors, which detect signal changes caused by an electric current being passed through electrodes that interact with chemicals. They can be categorized into three groups: (1) potentiometric (measurement of voltage), (2) amperometric (measurement of current) and (3) conductometric (measurement of conductivity). This approach differs from other electrical methods in the sense that the measurement involves chemical modification of explosives or their degradation products. This method promises some specificity. The fundamental requirement of electrochemical method is a mobile electrolyte to maintain charge balance once an electron is removed or injected into the chemical being detected. The inherent redox properties of nitroaromatic explosives make them ideal candidates for an electrochemical detection.

Table 2
Vapor pressure of some explosives along with some other chemical and physical properties (Refs. [15]–[19])

Explosive	Molecular weight	Melting point (°C)	Boiling point (°C)	Vapor pressure at 20 °C (Torr)
Nitromethane	61.04	−29	100–103	2.8×10^{-1}
2,4,6-Trinitrotoluene (TNT)	227.13	80.1–81.6	240 (explodes)	1.1×10^{-6}
2,4,6-Trinitrobenzene (TNB)	213.11	122.5	315	2.2×10^{-4}
Pentaerythritol tetranitrate (PETN)	316	141.3	190 (decomposes)	3.8×10^{-10}
Ethylene glycol dinitrate (EGDN)	152.06	22	114 (explodes)	2.8×10^{-2}
Nitroglycerine (NG)	227	13.2	–	2.6×10^{-6}
Tetranitro-triazacyclohexane (RDX)	222.26	204.1	(Decomposes)	4.1×10^{-9}
Tetranitro-N-methylamine (Tetryl)	287.14	129.5	187 (decomposes)	5.7×10^{-9} @ 25 °C
Ammonium nitrate	80.04	170	210 (decomposes)	5.0×10^{-6}
1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane (HMX)	296.16	276–280	(Decomposes)	3.3×10^{-14}
Picric acid (2,4,6 trinitrophenol)	229.11	122	300	5.8×10^{-9}

A mobile, remote controlled and underwater electrochemical sensing system is reported for detecting TNT in marine environment [20]. This submersible, pulsed-voltammetric, three-electrode electrochemical sensor is mounted to a remotely operated surface vehicle with vision detection capability. Square wave voltamogram was used for scanning. The detection scheme is based upon a stepwise reduction of nitro aromatic groups on the explosive molecule first to hydroxylamines and then followed by the conversion of hydroxylamines into amine groups. The reduction potentials provide selectivity to the method for a specific explosive and the current required per unit time determines the concentration of the targeted explosive in an aqueous media. Successful field test data have been obtained which are comparable to those measured with laboratory instruments. Genetically engineered nitroreductase has also been utilized to develop an amperometric bioelectrochemical sensor for the detection of explosives [21]. The results demonstrate the detection levels in the parts per trillion (ppt) range. Masunaga et al. [22] tried to detect aromatic nitro compounds like DNT and TNT as explosive charges using surface-polarization controlling method that measures electrochemical impedance of an electrode surface where explosive compounds adsorb. Detection limits of sub μM level could be achieved with the system. Furthermore, in order to improve specificity and sensitivity to aromatic nitro compounds, the electrode surface was modified with anthracene as arene that makes charge-transfer complex with aromatic nitro compounds. This method finds its application in making sensors for landmine detection.

Screen printed thick film electrodes have also been utilized for fabricating voltammetric sensors for the measurement of TNT and RDX [23]. Detection limit of this electrochemical system is enhanced remarkably by coupling it with a solid-phase extraction (SPE) protocol using Empore SDB-RPS membranes. This work led to the development of a new method to examine, use and optimize screen printed carbon electrodes for the detection of TNT, RDX and metabolites from various matrices. Attempts have also been made to remove TNT using horseradish peroxidase enzyme [24]. The reaction takes place in an electrochemical packed bed flow reactor operating in circulating batch mode with the help of in situ generated hydrogen peroxide. HRP immobilized on reticulated vitreous carbon electrode was used as working electrode, which is capable of catalyzing the oxidation and detoxification of 44 μm of TNT in aqueous solution under optimized conditions. Ly et al. [25] used a mercury film (MF) prepared by an electrochemical deposition on a glassy carbon electrode (GCE) for the analysis of RDX using square-wave stripping voltammetry. Two linear concentration ranges were observed: one in lower RDX concentration range of 0.2–10 mg l^{-1} and the other in higher RDX concentration range of 10–100 mg l^{-1}. The detection limit is found to be 0.12 mg l^{-1} with 120 s accumulation time. The method was applied to determine RDX in several soil samples. Online monitoring of trace TNT in marine environment is also attempted using a square wave voltammetric operation based electrochemical flow system [26]. The system showed the detection limit down to 25 ppb level. It responds rapidly to the sudden change in TNT concentration, i.e. 600 runs/h.

An amperometric method for the screening of "total" contents of nitroaromatic explosives or organophosphorus (OP) nerve agent compounds, as well as the detailed chromatographic separation and identification of such compounds is described in literature [27]. The method is based on the single-channel microchip platform. Potential interferences from electroactive interferences (that may give a false alarm in total assays) are expected to be negligible in this approach. Apart from this, an amperometric device based on capillary electrophoresis microsystem has also been developed [28] for the separation and determination of TNT and other common nitroaromatic explosives. The system is capable of analyzing explosive contents in soil extracts and groundwater. The results obtained with this system were validated by liquid chromatographic method recommended by U.S. Environmental Protection Agency. High sensitivity and reduced cost can be achieved with this system by coupling the microelectrode with CE chips. Marple and LaCourse [29] used photoassisted electrochemical detection in conjunction with ultra-violet absorbance detection system for determining explosives in environmental samples. The system utilizes an on-line solid-phase extraction technique for sample pretreatment. Limits of detection for explosives ranged from 0.0007 to 0.4 μg l^{-1}.

However, electrochemical sensors suffer from limited sensitivity and require mobile electrolyte. Also, electrodes can be easily fouled. Conducting polymer coatings can help in this regard; however, this also introduces more complexity to the sensor.

2.2. Mass sensors

These devices typically adsorb the chemicals of interest onto the surface and the device detects change in mass. The detection can be accomplished through changes in acoustic waves propagating along the surface (SAW devices) or by actual bending or a change in the shape of the device as mass is accumulated (micro-cantilever devices).

2.2.1. Surface acoustic wave sensors (SAW)

Surface acoustic wave sensors detect a chemical by measuring the disturbance it causes in sound waves across a tiny quartz crystal. An acoustic wave confined to the surface of a piezoelectric substrate material is generated and allowed to propagate. If a vapor is present on the same surface, then the wave and substances in the vapor will interact to alter the properties of the wave (e.g. amplitude, phase, harmonic content, etc.). The measurement of changes in the surface wave characteristics is a sensitive indicator of the properties of the vapor.

A good amount of evidence is available on the use of polymer films to fabricate surface acoustic wave sensors for the detection of explosive and explosive related compounds. Coating of Carbowax-1000 polymer has been used by Kannan et al. [30] for the fabrication of surface acoustic wave (SAW) based sensor for the detection of buried/hidden explosives. The results indicated that the carbowax-1000 had a very good chemical interface for the detection of low levels of explosive material. The carbowax polymer exhibits hydrogen-bonding acidic prop-

erties, that is, it readily and reversibly adsorbs nitro aromatic analytes. Response is observed in the range of 0.56–1.1 Hz/ppb for 2,4-DNT in laboratory conditions. Houser et al. [31] also attempted to use polymer coated surface acoustic wave devices for detecting various explosive vapors. DNT detection limits were determined in the range <100 ppt. However, their objective was to design and synthesize sorbent coatings for explosives. McGill et al. [32] used some chemo selective polymers as sorbent coatings on surface acoustic wave devices for studying their sorption and selective properties towards some nitroaromatic compounds. The most sensitive of the new polymers exhibits detection limit for nitrobenzene (NB) and DNT in low ppb and low ppt concentration ranges, respectively. A surface acoustic wave (SAW) device using self-assembly of polymethylhydrosiloxane (PMHS) polymer film onto functionalized silicon oxide surfaces is also fabricated [33]. These microsensors coated with polymer films show high sensitivity towards DNT and o-nitrotoluene, an explosive simulant. It is observed that the sensors coated with functionalized cyclodextrins were able to detect 2,4-DNT and TNT under ambient laboratory conditions.

2.2.2. Microcantilever sensors

Microcantilever technology is based on the response of quartz crystal microbalance (QCM) to the changes in surface properties and mass [34–36]. Changes in the Gibbs surface free energy induced by surface–analyte interactions on the microcantilever lead to large surface forces. If such interactions are restricted to one surface, then the resulting differential stress leads to the bending of the cantilever. Sensors based on microcantilever transducers feature superior mass sensitivity, smaller size, low cost and excellent compatibility with large multisensor arrays.

Microcantilever coated with a self-assembled monolayer has been used by Pinnaduwage et al. for the detection of plastic explosives [37]. In this device, a triangular microcantilever is coated with gold and 4-mercaptobenzoic acid on one side, which makes it capable of binding with pentaerythritol tetranitrate (PETN) and RDX, selectively. When either of those substances binds, the microcantilever bends and the deflection is measured with a laser-photodiode system. Detection limit is 10–30 ppt for PETN and RDX. Nanoporous coatings of tert-butylcalix[6]arene (TBC6A) have also been used to coat microcantilevers for the detection of TNT vapors and its analogue [38]. These microcantilevers produce large bending responses in presence of TNT vapors and its analogue. The noise limited TNT detection threshold was estimated to be 520 ppt.

Dip pen nanolithography (DPN^{TM}) has also been used to fabricate a "Nano-Nose" for the detection of explosives and volatile materials [39]. The sensors consist of an array of microcantilevers coated with sensing material that reacts to energetic materials in the ambient. The sensitive and specific detection of explosives and volatile materials is carried out by measuring the relative changes in surface stress induced by these materials. The sensor platform is amenable for remote monitoring, is capable of periodic replenishment of sensors, does not require any sample preparation and does not require trained personnel to operate.

3. Optical sensors

Owing to the number and reliability of optical methods, a vast number of optical transduction techniques can be used for (bio) sensor development [40,41]. These may employ linear optical phenomena, including absorption, fluorescence, phosphorescence, polarization, rotation, interference, etc., or non-linear phenomena, such as second harmonic generation. The choice of a particular optical method depends on the nature of the application and desired sensitivities. In practice, fiber optics can be coupled with all optical techniques, thus increasing their versatility.

3.1. Fiber optic sensors

Fiber optic sensors are a class of sensors that use optical fibers to detect chemicals. They rely on the changes in the frequency or intensity of electromagnetic radiation (e.g. visible, infrared) to detect and identify the presence of chemicals.

Artificial nose technology is deployed to develop a field-deployable instrument for the detection of DNT vapors in unknown humidified soil samples [42]. The system employs an array of sensory materials attached to the distal tips of an optical fiber bundle. Each sensor within the array responds differentially to vapor exposure so the array's fluorescence response patterns are unique for each analyte. Albert and Walt [43] prepared optical microsensors for high speed detection of low level explosives and explosive like vapors. Changes in fluorescence properties of Nile red dye, which has been used as fluorescent dye, during the nitroaromatic compound vapor exposure was monitored. Explosives-like NACs, such as DNT and DNB are detected at low part-per-billion levels in seconds. Conder et al. [44] deployed solid-phase microextraction (SPME) fibers to measure TNT and its nitroaromatic (NA) degradation products in laboratory sediment toxicity tests and field sediments in situ.

Application of a fiber-optic biosensor developed by NRL is further extended for the onsite detection of explosives in ground water and soil extracts [45]. The extract was mixed with the buffer containing a fluorescent explosive analogue and exposed to the antibody-coated optical probes. In the presence of either TNT or RDX, a decrease in the fluorescence signal, proportional to the explosive concentration, was observed. Detection limits of $0.5\,mg\,kg^{-1}$ $(0.1\,mg\,l^{-1})$ of TNT and RDX in soil acetone extracts were obtained.

3.2. Spectrophotometric

3.2.1. Absorption based detection

This is the simplest method among different spectrophotometric methods. Several kinds of color change chemical sensors have been developed for rapid onsite detection of explosives.

Detection of trace amounts of NO_2 explosives or explosive related compounds (ERC) has been carried out by employing specific color reaction between cyclopentadienylmanganesetricarbonyl (cymantrene) and ERC [46]. Detection reaction was performed within a thin film/gel of a designer polymer with embedded "sensing" chemical—cymantrene. The tech-

nique provides fast and simple detection of explosive fingerprint residues on various surfaces. The detection limit of the proposed technique is about 0.2 ng of DNT.

Oh et al. [47] used spectrophotometric assay for the detection of TNT in culture media. Solution coloration and TNT absorption at 447 nm depends on the pH, which can be attributed to the dissociation of the benzylic proton from TNT. From studies, it was concluded that three TNT nitro groups were essential for absorbance at 447 nm and the loss of one nitro group resulted in the loss of color in alkaline range. Thus, in highly alkaline solution, TNT (pK 511.99) exhibits significant absorbance at 447 nm, while major metabolites like 2-amino-4,6-dinitrotoluene (2-ADNT), 4-amino-2,6-dinitrotoluene (4-ADNT) and 2,6-diamino-4-nitrotoluene (2,6-DANT) which contains one less nitro group than TNT, display no absorbance at this wavelength. Enzymatic transformation of TNT was completely inhibited by Cu^{2+} (5 mM) and was partially inhibited by other divalent metallic cations.

3.2.2. Photoluminescence based detection

The detection of nitroaromatic molecules in air by quenching of the photoluminescence of porous silicon (porous Si) films has been explored by Content et al. [48]. Detection is achieved by monitoring the photoluminescence (PL) of a nanocrystalline porous Si film on exposure to the analyte in a flowing air stream. The photoluminescence is quenched on exposure to the nitroaromatic compounds (nitrobenzene, TNT, DNT), presumably by an electron-transfer mechanism. Specificity for detection is achieved by catalytic oxidation of the nitroaromatic compound.

Photoluminescent property of polysilole has been exploited by Sohn et al. [49] for measuring explosive analytes like picric acid, nitrobenzene, DNT and TNT in air or seawater to locate buried and unexploded underwater landmines. The detection method involves measuring the quenching of photoluminescence of the polysilole by these mentioned analytes. Detection limit of this sensor is 4 ppb for TNT vapor in air, 1.5 ppt in seawater and 6 ppb for picric acid. Some lanthanides are also used as photoluminescent material for detecting trace explosives in the presence of intense background color and/or background fluorescence by time-resolved imaging [50].

3.2.3. Fluorescence based detection

This technique utilizes the quenching of fluorescence when a target molecule is attached. An important feature of fluorescence-based detection methods is the ability to detect explosives or landmines at a distance. In this method, either fluorescent sensory material (like 4-*N,N*-dimethylamino-4 methylacryloylamino chalcone (DMC), pentiptycene polymer, Nile Red dye, liquid-crystalline (LC) polyfluorenes, etc.) is spread over the suspected area to get the image of an object or sometimes fluorescent light is directly flashed onto the object/area so that the suspected area gets illuminated and gives an indication for the presence of explosive compound or material.

Semiconducting polymers are excellent candidate for being used as fluorescent material due to their electron rich behavior. Nitroaromatic explosives being electron deficient bind to these electron rich semiconducting polymers and quench their fluores-

cence by an electron transfer mechanism. This mechanism has been ultilized by Rose et al. [51] to detect the nitroaromatic explosive compounds. The emission quenching is enhanced when the excitons rapidly diffuse throughout the SOPs, thereby increasing the probability of an encounter with the explosive compound. Indirect laser induced fluorescence coupled with electrokinetic chromatography is also used for the detection of explosives [52]. Detection was carried out on a microfabricated chip and concentrations of 1 ppm of TNB, TNT, DNB, tetryl and 2,4-DNT could be detected using this method. However, the two nitramines (HMX and RDX) could only be detected at much higher concentrations, likely due to the low fluorescence quenching efficiencies of these compounds. And for the first time, a method of quantitative trace analysis of peroxide based explosives, i.e. HMTD and triacetone trieproxide (TATP) has been developed by Ladbeck et al. using fluorescence spectroscopy [53]. The limit of detection was 2×10^{-6} mol l^{-1} for both TATP and HMTD, respectively. Very recently, a chemical sensor based on bifurcated optical fiber has been fabricated for continuous monitoring of 2,6-dinitrophenol (2,6-DNP) also [54]. The sensor is based on the reversible chemical reaction between a novel functional poly(vinyl chloride) (PVC), which contains fluorescent moiety as the sensing material and the analyte; 2,6-dinitrophenol (DNP). PVC containing fluorescent moiety reacts with 2,6-DNP to form a complex with low fluorescence efficiency through hydrogen bonding. Formation of the complex gives significant fluorescence quenching which is suitable for signaling the occurrence of the host–guest interaction. At pH 3.50, the sensor exhibits a dynamic detection range from 2.5×10^{-6} to 7.0×10^{-3} mol l^{-1} with a limit of detection of 1.0×10^{-6} mol l^{-1}.

The fluorescence quenching approach has been explored for the analysis of nitrated explosives also [55]. The method has the ability to detect a wider range of organic and inorganic nitrated compounds. This fluorescence quenching method uses pyrene as fluorophore and is applied for the detection of RDX, HMX, TNT, nitromethane and ammonium nitrate. The response is based on the interactions of nitroaromatic quenchers with excited state pyrene molecules, which stabilize the excited state and shift the vibronic bands to slightly lower wavelengths.

3.2.4. Laser induced breakdown spectroscopy (LIBS) based detection

In LIBS, a short laser pulse is focused on the sample. Laser energy heats, vaporizes, atomizes and ionizes the sample material, generating a small area of plasma. Fig. 1 represents the principle setup of a system based on LIBS for the detection of explosives. Detection is based on the analysis of composition of an object like landmine or its contents, e.g. explosives. Excited atoms and ions in the plasma emit a secondary light, which is collected and spectrally resolved by the spectrophotometer and analyzed by a light detector. Each chemical element has its unique spectral signature, which can be discriminated from the obtained spectra. As a result, the multi-elemental composition of the sample can be determined. However, this might not be enough for the detection of explosives as polymers are also composed from the same elements. The US Army Research
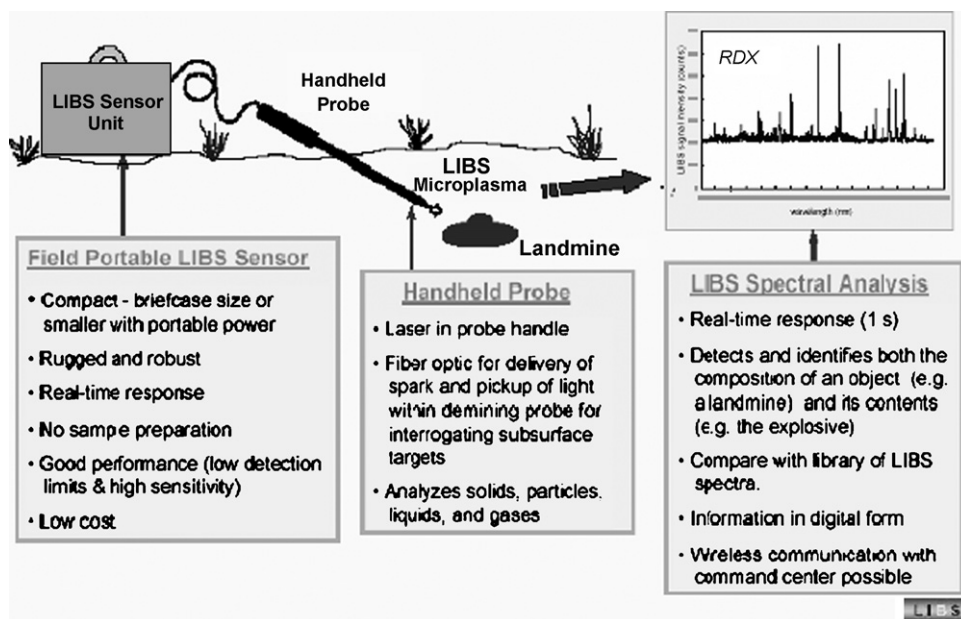
Fig. 1. Principle setup for the detection of landmine components using LIBS.

Laboratory (ARL) in collaboration with the University of Florida and spectrometer manufacturer Ocean Optics, Inc., is working on the development of a LIBS based portable instrument for detecting landmines [56]. After illuminating the sample with a laser, the emitted light will be taken from the probe by optical fibers to a spectrometer. This will analyze the light and compare its spectral characteristics with the stored database of spectra for explosives and mine casing materials. Dikmelik and Spicer [57] described the use of a high-power pulsed laser to form plasma on the material surface and the optical radiation from the plasma is spectrally analyzed to determine the material composition. This was studied for the detection of trace amounts of explosive-related compounds (ERCs), including the detection of TNT on brass and molybdenum substrates and RDX on molybdenum substrates. De Lucia et al. [58] studied black powder, TNT, PETN, HMX and RDX (in various forms), propellants, such as M-43 and JA2 and military explosives, such as C4 and LX-14 using LIBS. Each of these materials gives their unique spectrum. These nitrogen and oxygen-rich materials yield LIBS spectra in air that have correspondingly different O:N peak ratios compared with air. This difference helps in the detection and identification of such energetic materials. Moreno et al. [59] used LIBS for the detection and characterization of energetic materials like DNT and aluminium samples at distances up to 45 m. In this case, a field-portable open-path LIB spectrometer was used for carrying out testing of known and blind samples. Hydrogen, oxygen and nitrogen emission intensity ratios were the parameters studied to identify the analyte as an organic explosive, organic non-explosive and non-organic sample. Laser-based ionization technique combined with mass spectrometry is used for the rapid detection of nitro containing explosives and explosives-related compounds like nitrobenzene, *o*-nitrotoluene, DNB, DNT, TNT as well as the peroxide-based explosive TATP in the gas phase [60]. This technique does not require preconcentration and pretreatment of the analyte and the parent molecule is directly ionized using a vacuum ultraviolet (VUV) photon. The ions thus generated are detected using a time of flight (TOF) mass spectrometer. The limits of detection for NB and DNT was determined to be 17–24 and 40 ppb, respectively.

One major obstacle in the detection of explosives is their low vapor pressure at ambient temperature. To overcome this hurdle, Morgan et al. tried to use laser thermal desorption technique for the detection of explosives [61]. In this technique, the laser pulse of appropriate wavelength is focused onto the target spot. This increases the explosive vapor pressure in the headspace over the target and thus helps the detector to detect the explosive compounds.

3.2.5. Tetrahertz spectroscopy based detection

The THz explosive sensor is usually based on differential absorption. The given item/region is illuminated by THz radiation containing at least two distinct frequencies. The frequencies of radiation depend on the THz spectra of the targeted explosives and are chosen so as to maximize the contrast between the presence and absence of explosives. THz spectroscopy can be used to discriminate hazardous materials and it has been shown that not only can explosives be detected, but the specific type of explosive can be determined (i.e. TNT, HMX, RDX, Semtex H, etc.) [62], as the different explosives have unique tetrahertz spectral fingerprints. This technique is capable of detecting bombs and other explosive compounds through envelope, clothes, suitcases, soil, etc.

Liu et al. [63] employed THz time domain spectroscopy for the detection of RDX and RDX related explosives even if they are covered with opaque material. RDX strongly absorbs at 0.82 THz, which can easily be measured by diffuse reflection method. Short pulse generation based THz techniques have

been used by Choi et al. [64] to find the possibility of sensing non-metallic enclosures (including plastic explosives) to fight concealed threats. It was found that the pattern of reflection versus frequency is specific to the composition of target.

Cook et al. [65] studied quantitative THz spectroscopy of some explosive materials like PETN and RDX. The explosives are used in their powdered polycrystalline form and are dispersed in polyethylene, which is used as a binder, to record the spectra. Sengupta et al. [66] measured reflection spectra of C-4 explosive using THz time domain spectroscopy. C-4 explosive shows significant absorption around 0.8 THz. The spectral data is used for the simulation of interferometric detection in a stand-off THz imaging system. The feasibility of THz spectroscopy in the range 1–10 THz has been studied by Fitch et al. [67] to detect and identify explosives and related compounds (ERCs). The chemical modeling is used to obtain spectroscopic information on ERCs and environmental background. THz pulsed spectroscopy coupled with Fourier transform infrared spectroscopy has been deployed for measuring the absorption spectrum of RDX by Shen et al. [68] to use it for security screening of explosives.

4. Biosensors

A biosensor is an analytical device that integrates a biological element on a solid-state surface, enabling a reversible biospecific interaction with the analyte and a signal transducer. The biological element is a layer of molecules qualified for biorecognition, such as enzymes, receptors, peptides, single-stranded DNA, etc. The major advantage of biosensor is associated with high specificity of biomolecules for their target substrate.

Maltose binding protein (MBP) nitroreductase (NR) fusion (MBP-NR) has been immobilized onto an electrode modified with an electropolymerized film of *N*-(3-pyrrol-1-ylpropyl)-4,4′-bipyridine (PPB) for the preparation of an amperometric biosensor for TNT [69]. The kinetics of the catalytic reaction between the biosensor, TNT and DNT were characterized using rotated disk electrode and cyclic voltammetry techniques. Rate constant values were $1.4 \times 10 \, M^{-1} \, s^{-1}$ for TNT and $7.1 \times 10^4 \, M^{-1} \, s^{-1}$ for DNT. VanBergen et al. [70] worked on a fiber optic biosensor for onsite analysis of explosives in groundwater for site characterization and remediation. TNT and RDX could be detected at concentrations greater than or equal to $5 \, \mu g \, l^{-1}$ in less than 20 min with little sample preparation or waste generation. A microalgal biosensor has been developed for the detection of explosive TNT using a wild type strain (DcG1wt) of *Dictyosphaerium chlorelloides* (Chlorophyceae) as the sensitive organism and a TNT-resistant mutant, obtained from the DcG1wt strain [71]. The inhibition of chlorophyll *a* (photosynthesis-related chlorophyll *a* used as fluorescence induction) fluorescence of PSII by TNT was used as biological signal. Significant differences in fluorescence maxima of light-adapted algae (F'_m) between wild-type DcG1wt cells and TNT-resistant mutants were observed in all TNT concentrations tested (from 0.5 to 31.3 mg l^{-1}) after only 3 min of exposure.

Immunosensor is a class of biosensors and it involves the use of antibodies as biosensing element. Reaction takes place between a target analyte and a specific antibody [72].

These immunosensors are used for the detection of explosive compounds also. An electrochemiluminescence immunoassay system has been developed for TNT detection, in which enzyme labeled antibodies bound to paramagnetic beads are concentrated on an electrode magnetically [73]. The light emitting from the reaction between chemiluminescent substrate and enzyme labeled antibodies is triggered electrochemically. The time required for the detection was only 80 s and the detection limit for TNT was 31 ppb. Not only this, radial capillary array electrophoresis microdevices have also been used to develop a homogeneous immunoassay for TNT detection [74]. The sample consisted of equilibrium mixtures of anti-TNT antibody (Ab), fluorescein labeled TNT and various concentrations of unlabeled TNT. The equilibrium ratio formed by the competition between the labeled and unlabeled TNT for Ab binding was analyzed in a wide dynamic range from 1 to 300 ppb.

Goldman et al. [75] reported a rapid, simple and sensitive assay for the analysis of TNT. The basis of assay is the change in fluorescence emission intensity of a fluorescently labeled TNT analogue pre-bound to an anti-TNT antibody. The change in intensity occurred due to competitive displacement of labeled TNT by TNT. In other work, Goldman et al. [76] worked on the detection of TNT using recombinant antibodies. Antibody fragment binding to TNT in solution was demonstrated using competition ELISA and this helped to examine the cross-reactivity towards several TNT-related compounds and other explosives. Goldman et al. continued to work along with his coworkers on the detection of TNT in soil and water samples using homogeneous assay [77]. A continuous flow immunosensor has been tested for the field screening of environmental samples for the detection of explosives like TNT and RDX [78]. The system is based on displacement immunoassay in which monoclonal antibodies to TNT and RDX are immobilized on solid support and allowed to bind to the fluorescently labeled antigens and then exposed to explosives. Explosive compound displace proportional amount of fluorescent-labeled antigen. Although continuous flow methods can provide results in only few minutes, they suffer from significant sample throughput limitations that are inherent to the flow format.

It is possible to detect TNT and RDX at high femtomole using a compact membrane-based displacement immunoassay (Fig. 2) [79]. In this system, antibodies are immobilized onto the membrane and are saturated with labeled antigen. When unlabeled antigen (sample) is introduced through flow system, the proportionate amount of labeled antigen is displaced from the immobilized antibody binding sites and this displacement is subsequently detected downstream using fluorometer. The concentration of displaced labeled antigen detected is proportional to the concentration of the target analyte introduced into the system. A highly sensitive immunochemical method for immunoaffinity purification (IAP) and detection of trace amounts of TNT is also developed by immobilizing antibodies (Abs) in a ceramic matrix (sol–gel) [80]. The sol–gel-based immunoassay method is a one-step procedure that has high potential to serve as a suitable and convenient immunoassay device for extracting TNT from "real field" samples. Green et al. [81] worked for the development of an immunosensor based
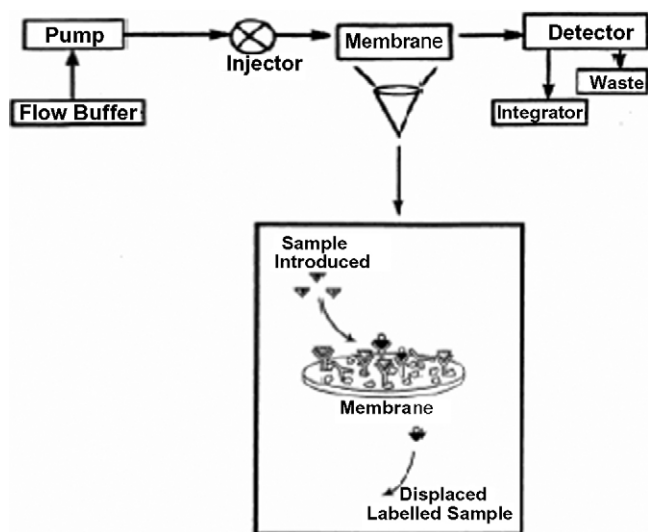
Fig. 2. Schematic diagram representing the membrane based displacement flow immunoassay. Immobilized antibody is saturated with labeled antigens [79].

on reverse displacement format for the detection of TNT in seawater. Limits of detection were 2.5 ppb for TNT in saline buffer and 25 ppb in seawater with an analysis time of 10 min. Charles et al. [82] worked on the detection of TNT with a reversed displacement immunosensor using chemically modified borosilicate glass microcapillary. The inner core of the glass microcapillary was modified with 3-aminopropyltriethoxysilane and functionalized with the TNT analog, trinitrobenzene sulfonic acid (TNBSA). When sample containing TNT comes in microcapillary, TNB-anti-TNT antibody complex is displaced and change in fluorescence is measured by fluorometer with analysis time less than 5 min.

A new surface plasmon resonance (SPR) immunosensor based on the principle of indirect competitive immunoreaction using trinitrophenol-bovine serum albumin (TNP-BSA) conjugate and anti-TNP antibody has been demonstrated by Shankaran et al. [83] for the determination of 2,4,6-trinitrophenol (TNP). TNP in solution competes with immobilized TNP-BSA conjugate for binding with anti-TNP antibody, which inhibit the immunoreaction between TNP-BSA conjugate and anti-TNP antibody. The dependence of inhibition on the concentration of TNP forms the basis of quantification of TNP. The sensor exhibited sensitivity from 10 ppt to 100 ppb for the detection of TNP. Shankaran et al. [84] also described the development and comparison of two immunoassays for the detection of TNT based on competitive inhibition. Two polyclonal antibodies; one prepared from 2,4,6-trinitrophenol-bovine serum albumin conjugate (anti-TNP-BSA Ab, goat IgG) and another from 2,4,6-trinitrophenyl-keyhole limpet hemocyanine conjugate (anti-TNPh-KLH Ab, rabbit IgG) were used in the immunoassay. Immobilized TNP-BSA conjugate interact with these antibodies and the resonance angle changes due to the biomolecular interactions were monitored by SPR. This change in the resonance angle was used for the quantification of TNT. Both antibodies showed a high degree of affinity for TNT. In the recent past, a biochip technology has been developed for the

detection of TNT [85]. The chip is designed to function as a platform for a competitive label-free immunoassay using SPR and quartz crystal microbalance (QCM) as transducers, which monitor the dissociation of on-line immobilized monoclonal antibodies produced against TNT. However, immunosensors based on surface plasmon resonance are not robust and lack sensitivity.

All above discussed immunosensors suffer with a setback that the antibodies of all explosive materials likely to be encountered are needed, i.e. specific antibody is required for each compound of interest. This adds to the cost of an immunosensor. Also, when multianalyte immunosensors are used, there is poor signal discrimination and as a result sensitivity is lost [86]. These methods were not yet precise and accurate to eliminate the requirement for further laboratory confirmation [87]. The primary problems involved matrix effects, non-specific interactions and heterogeneity.

5. Conclusion

Detection of traces of explosives either as contaminant in soil and water or as a hidden threat using various types of sensors is explored in this review. The aim of this review is to explore the vast diversity of sensors currently available for the detection and analysis of explosives in soil, water or as hidden material. Explosives can readily enter into the food chain and underground supplies from contaminated soil and pose severe health hazards. And one of the prime challenges to combat terrorist activities is to screen the public without being noticed. However, the most reliable and rapid means to detect explosives is through trained canines. Detailed research has shown that the dogs indeed detect the explosive vapors but they also suffer from some limits. It is therefore, high time to make efforts towards the development of portable, automated, low cost sensors which can mimic the olfaction of the dogs without having their drawbacks and which will overcome the limitations of various other methods of explosive detection. Sensors allow sensitive and selective estimations of the explosives or explosive related compounds.

Electrochemical methods have been examined in this review for the detection of explosives. An advantage of this approach is that the chemical properties of the signal, namely the potential at which an electron is injected or removed, provide some specificity. Sensors based on microcantilever transducers feature superior mass sensitivity, smaller size, low cost and excellent compatibility with large multisensor arrays. Functionalized optical fiber sensors have emerged as alternatives to other conventional methods of explosive detection. Optical sensors not only have the adaptability for multiplexing and miniaturization, but also may be used for remote monitoring. Fluorescent methods are generally regarded as providing the highest sensitivity in conventional sensors. Hence, there has been considerable interest in the detection of explosives by this technique. Sensors utilizing this principle have been developed using small molecule and polymeric fluorophores. Biosensor development and production are currently expanding due to their diverse applications including environmental monitoring. Immunosensors are affinity ligand-based biosensor solid-state devices in

Table 3
Comparative table showing summary of the performance of various sensors reported in this review

Transducer	Field of application	Explosive detected	Detection limit	Ref.
Electrochemical	Soil samples	RDX	0.12 ppm	[25]
Electrochemical	Marine water	TNT	25 ppb	[26]
Electrochemical	Forensic laboratory	DNB and TNT,	60 ppb for both	[27]
Electrochemical	Soil extract and ground water	RDX, TNT, 2,4-DNT, 2,3-DNT, 2,4-DNT	RDX 0.2 ppm, TNT 0.11 ppm, 2,4-DNT 0.15 ppm, 2,6-DNT 0.16 ppm, 2,3-DNT-0.15 ppm	[28]
SAW	Laboratory samples	2,4-DNT		[30]
SAW	Laboratory samples	DNT	92 ppt	[31]
SAW	Laboratory samples	2,4-DNT, TNT		[33]
Microcantilever	For detection of explosive vapors	PETN and RDX	A low femtogram (10^{-15} g)	[37]
Microcantilever		TNT	520 ppt	[38]
Optical	Field test (soil samples)	DNT	120 ppb	[42]
Optical (fiber optic based)	Ground water and soil extracts	TNT and RDX	0.1 ppm	[45]
Optical (photoluminescence based)	Air and sea water	TNT, Picric acid	4 ppb for TNT vapor in air, 1.5 ppt for TNT in sea water, 6 ppb for picric acid in sea water	[49]
Optical (fluorescence based)	Laboratory samples	TNB, TNT, DNB, tetryl, and 2,4-DNT	1 ppm for all these explosives	[52]
Optical (fluorescence based)		TATP and HMTD	2×10^{-6} mol L^{-1} for both TATP and HMTD	[53]
Optical (fluorescence based)	Water samples	DNP	1.0×10^{-6} mol L^{-1}	[54]
Optical (LIBS)		DNT, NB	40 ppb for DNT and 17–24 ppb for nitrobenzene	[60]
Optical fiber (biosensor)	Ground water	TNT and RDX	0.05 ppb for both RDX and TNT	[70]
Electrochemical (biosensor)	Laboratory samples	TNT	31 ppb	[73]
Optical (immunosensor)	Artificial sea water	TNT	0.05 ppb	[75]
Electrochemical (immunosensor)	Environmental samples and clinical assay	TNT	1 ppt	[76]
Optical (fluoroimmunoassay)	Soil and water samples	TNT		[77]
Optical (immunosensor)	Laboratory samples	TNT and RDX	450 fmol for TNT, 1 ppb for RDX	[79]
Optical (immunosensor)	Seawater	TNT	250 ppt	[80]
Electrochemical (immunosensor)	Seawater	TNT	2.5 ppb in saline buffer and 25 ppb in seawater	[81]
Optical (SPR based immunosensor)	On-site detection of landmines	TNP	10 ppt	[83]
Optical (SPR based Immunosensor)	Laboratory samples	TNT	6 ppt	[84]

which the immunochemical reaction is coupled to a transducer. The fundamental basis of all immunosensors is the specificity of the molecular recognition of antigens by antibodies to form a stable complex. However, the primary requirements of an immunoassay for the detection of explosives are specificity (to avoid false positive or false negative responses to interferents), low detection threshold (to identify targets at low concentration) and a rapid response time (to shorten analysis time and reduce costs). Immunosensors has been developed which meet all these requirements. Fluorescence immunosensor displacement assays based on antibodies are widely used in biological sensing and explosive detection systems. Although immunosensors are known for their selectivity but they cannot be applied for airport security screening application because they use antibodies as sensing element and these reacted antibodies are not reusable. The presence of these already reacted antibodies could also change the sensitivity of the sensor. So, this technique is usually employed for the analysis of explosive residues in soil and water in laboratory. These sensors have good potential due to the their reduced analysis time. Usually, these are operated under continuous flow conditions. Table 3 shows the summary of the results obtained with different types of sensing systems.

However, still there is not a single sensor that promises speed, selectivity and sensitivity all together. Although each of these methods reported here exhibit one or more inherent advantages and disadvantages, their common feature is a high degree of complexity that adversely affects their compatibility with miniature mass-deployable devices. Some of them were not applied to real samples or practical situations. The main challenge of continuous, real-time detection of nitroaromatic explosive compounds is related to their extremely low vapor pressures and, concentrations, respectively, in air at ambient temperatures. Many of the works referred, although describing optimization and, sometimes, showing preliminary results, present insufficient data concerning the analytical performance. At the same time, researchers are now turning their direction to new sensors using biomolecules, nanostructures and nanodevices. Single molecule detection is now at hand. It is expected that the future years will witness a variety of sensors based on new sensing principles, such as those used by insects. Efforts in

molecular electronics could make possible simultaneous recognition and signal transduction in single molecular complexes.

Acknowledgements

References

[1] K.G. Furton, L.J. Meyers, The scientific foundation and efficacy of the use of canines as chemical detectors for explosives, Talanta 54 (2001) 487.

[2] G.R. Asbury, J. Klasmeier, H.H. Hill Jr., Analysis of explosives using electrospray ionization/ion mobility spectrometry (ESI/IMS), Talanta 50 (2000) 1291.

[3] Environmental Protection Agency, Health Advisory for TNT, Criteria and Standard Division, Office of Drinking Water, Washington, DC, 1989.

[4] S.S. Talmage, D.M. Opresko, C.J. Maxwell, C.J.E. Welsh, F.M. Cretella, P.H. Reno, F.B. Daniel, Nitroaromatic munition compounds: environmental effects and screening values, Rev. Environ. Contam. Toxicol. 161 (1999) 1.

[5] W.J. McConnell, R.H. Flinn, Summary of twenty-two trinitrotoluene fatalities in World War II, J. Ind. Hyg. Tox. 28 (1946) 76.

[6] Army, A literature review—problem definition studies on selected toxic chemicals, Occupational health and safety aspects of 2,4,6-trinitrotoluene (TNT), vol. 3, Contract no. DAMD 17-77-C-7020, U.S. Army Medical Research and Development Command, Frederick, MD, Fort Detrick, Document no. AD A055683, 1978.

[7] J.A. Hathaway, Trinitrotoluene: a review of reported dose-related effects providing documentation for a workplace standard Minutes of the Seventeenth Explosives Safety Seminar, vol. I, Denver, Colorado, September 1976, p. 693.

[8] L. Djerassi, Hemolytic crisis in G6PD-deficient individuals in the occupational setting, Int. Arch. Occup. Environ. Health 71 (1998) 26.

[9] L.S. Djerassi, L. Vitany, Haemolytic episode in G6PD deficient workers exposed to TNT, Br. J. Ind. Med. 32 (1975) 54.

[10] E. Duque, A. Haidour, F. Godoy, J.L. Ramos, Construction of a Pseudomonas hybrid strain that mineralizes 2,4,6-trinitrotoluene, J. Bacteriol. 175 (1993) 2278.

[11] C.E. French, S. Nicklin, N.C. Bruce, Aerobic degradation of 2,4,6-trinitrotoluene by Enterobacter cloacae PB2 and by pentaerythritol tetranitrate reductase, Appl. Environ. Microbiol. 64 (1998) 2864.

[12] C. Vorbeck, H. Lenke, P. Fischer, H.J. Knackmuss, Identification of a hydride-Meisenheimer complex as a metabolite of 2,4,6-trinitrotoluene by a Mycobacterium strain, J. Bacteriol. 176 (1994) 932.

[13] P. Kolla, The application of analytical methods to the detection of hidden explosives and explosive devices, Angew. Chem. Int. Ed. Engl. 36 (1997) 800.

[14] W.R. Davidson, W.R. Stott, R. Sleeman, A.K. Akery, Synergy or dichotomy: vapor amd particle sampling in the detection of contrabands, Proc. SPIE 2092 (1994) 108.

[15] R.J. Harper, J.R. Almirall, K.G. Furton, Identification of dominant odor chemicals emanating from explosives for use in developing optimal training aid combinations and mimics for canine detection, Talanta 67 (2005) 313.

[16] L. Wu, J.R. Almirall, K.G. Furton, An improved interface for coupling solid-phase microextraction (SPME) to high performance liquid chromatography (HPLC) applied to the analysis of explosives, J. High Resolut. Chromatogr. 22 (1999) 279.

[17] R.J. Harper, J.R. Almirall, K.G. Furton, Improving the scientific reliability of biological detection of explosives by Canis familiaris through active odor signatures and their implications, in: Proceedings of the 8th International Symposium on the Analysis and Detection of Explosive (ISADE), Ottawa, Canada, 2004.

[18] C. Cummings, Detection of explosives vapors using the Nomadics FIDO sensor, in: Proceedings of the 1st Olfactory-Based Systems for Security Applications meeting (OBSSA), London, UK, 2004.

[19] M.E. Walsh, T.F. Jenkins, P.G. Thorne, Laboratory and field analytical methods for explosives residues in soil, J. Energetic Mater. 13 (1995) 357.

[20] Q. Lu, G.E. Collins, M. Smith, J. Wang, Sensitive capillary electrophoresis microchip determination of trinitroaromatic explosives in nonaqueous electrolyte following solid phase extraction, Anal. Chim. Acta 469 (2002) 253.

[21] C.D. Gwenin, M. Kalaji, P.A. Williams, R.M. Jones, The development of a novel amperometric biosensor for the detection of nitro explosives, International Society of Electrochemistry, 55th Annual Meeting, Thessaloniki, 19–24th September 2004.

[22] K. Masunaga, K. Hayama, T. Onodera, K. Hayashi, N. Miura, K. Matsumoto, K. Toko, Detection of aromatic nitro compounds with electrode polarization controlling sensor, Sens. Actuators B 108 (2005) 427.

[23] R. Pearson, Electrochemical techniques for detection of TNT and other explosives using disposable screen printed carbon electrodes, A thesis submitted in partial fulfillment of the requirements for the Master of Science Degree, Department of Environmental Studies, Greenspun College of Urban Affairs, 2001.

[24] K.B. Lee, M.B. Gu, S.H. Moon, Degradation of 2,4,6-trinitrotoluene by immobilized horseradish peroxidase and electrogenerated peroxide, Water Res. 37 (2003) 983.

[25] S.Y. Ly, D.H. Kim, M.H. Kim, Square-wave cathodic stripping voltammetric analysis of RDX using mercury-film plated glassy carbon electrode, Talanta 58 (2002) 919.

[26] J. Wang, S. Thongngamdee, On-line electrochemical monitoring of (TNT) 2,4,6-trinitrotoluene in natural waters, Anal. Chim. Acta 485 (2003) 139.

[27] J. Wang, M. Pumera, M.P. Chatrathi, A. Escarpa, M. Musameh, Single-channel microchip for fast screening and detailed identification of nitroaromatic explosives or organophosphate nerve agents, Anal. Chem. 74 (2002) 1187.

[28] A. Hilmi, J.H.T. Luong, Micromachined electrophoresis chips with electrochemical detectors for analysis of explosive compounds in soil and groundwater, Environ. Sci. Technol. 34 (2000) 3046.

[29] R.L. Marple, W.R. LaCourse, A platform for on-site environmental analysis of explosives using high performance liquid chromatography with UV absorbance and photo-assisted electrochemical detection, Talanta 66 (2005) 581.

[30] G.K. Kannan, A.T. Nimal, U. Mittal, R.D.S. Yadava, J.C. Kapoor, Adsorption studies of carbowax coated surface acoustic wave (SAW) sensor for 2,4-dinitrotoluene (DNT) vapour detection, Sens. Actuators B 101 (2004) 328.

[31] E.J. Houser, T.E. Mlsna, V.K. Nguyen, R. Chung, R.L. Mowery, R.A. McGill, Rational materials design of sorbent coatings for explosives: applications with chemical sensors, Talanta 54 (2001) 469.

[32] R.A. McGill, T.E.M. lsna, R. Chung, V.K. Nguyen, J. Stepnowski, The design of functionalized silicone polymers for chemical sensor detection of nitroaromatic compounds, Sens. Actuators B 65 (2000) 5.

[33] X. Yang, X.X. Du, J. Shi, B. Swanson, Molecular recognition and self-assembled polymer films for vapor phase detection of explosives, Talanta 54 (2001) 439.

[34] E.A. Wachter, T. Thundat, Micromechanical sensors for chemical and physical measurements, Rev. Sci. Instrum. 66 (1995) 3662.

[35] L.J. Kepley, R.M. Crooks, A.J. Ricco, A selective SAW based organophosphonate chemical senor employing a self assembled composite monolayer, a new paradigm for sensor design, Anal. Chem. 64 (1992) 3191.

[36] J.P. Cleveland, S. Manne, D. Bocek, P.D. Hansma, A nondestructive method for determining the spring constant of cantilevers for scanning force microscopy, Rev. Sci. Instrum. 64 (1993) 403.

[37] L.A. Pinnaduwage, V. Boiadjiev, J.E. Hawk, T. Thundat, Sensitive detection of plastic explosives with self-assembled monolayer-coated microcantilevers, Appl. Phys. Lett. 83 (2003) 1471.

[38] P.G. Datskos, N.V. Lavrik, M.J. Sepaniak, Detection of explosive compounds with the use of microcantilevers with nanoporous coatings, Sens. Letts. 1 (2003) 25.

[39] I.C. Nelson, D. Banerjee, W.J. Rogers, M.S. Mannan, Detection of explosives using heated microcantilever sensors micro (MEMS) and nanotechnologies for space applications, in: G. Thomas, C. Zhong-Yang (Eds.), Proceedings of the SPIE, vol. 6223, 2006, p. 62230O.

[40] V. Lopez-Avila, H.H. Hill, Field analytical chemistry, Anal. Chem. 69 (1997) 289R.

[41] J. Janata, M. Josowicz, P. Vanysek, D.M. DeVaney, Chemical sensors, Anal. Chem. 70 (1998) 179R.

[42] K.J. Albert, M.L. Myrick, S.B. Brown, D.L. James, F.P. Milanovich, D.R. Walt, Field- deployable sniffer for 2,4-dinitrotoluene detection, Environ. Sci. Technol. 35 (2001) 3193.

[43] K.J. Albert, D.R. Walt, High speed fluorescence detection of explosive like vapors, Anal. Chem. 72 (2000) 1947.

[44] J.M. Conder, T.W.P. La, G.R. Lotufo, J.A. Steevens, Nondestructive minimal disturbance direct burial solid phase microextraction fiber technique for measuring TNT in sediment, Environ. Sci. Technol. 37 (2003) 1625.

[45] L.C. Shriver-Lake, C.H. Patterson, S.K. van Bergen, New Horizons: explosive detection in soil extracts with a fiber-optic biosensor, Field Anal. Chem. Technol. 4 (2000) 239.

[46] L.M. Dorozhkin, V.A. Nefedov, A.G. Sabelnikov, V.G. Sevastjanov, Detection of trace amounts of explosives and/or explosive related compounds on various surfaces by a new sensing technique/material, Sens. Actuators B 99 (2004) 568.

[47] B.T. Oh, G. Sarath, P.J. Shea, R.A. Drijber, S.D. Comfort, Rapid spectrophotometric determination of 2,4,6-trinitrotoluene in a Pseudomonas enzyme assay, J. Microbiol. Methods 42 (2000) 149.

[48] S. Content, W.C. Trogler, M.J. Sailor, Detection of nitrobenzene, DNT and TNT vapors by quenching of porous silicon photoluminescence, Chemistry 16 (2000) 2205.

[49] H. Sohn, R.M. Calhoun, M.J. Sailor, W.C. Trogler, Detection of TNT and picric acid on surfaces and in seawater by using photoluminescent polysiloles, Angew. Chem. 13 (2001) 2162.

[50] E.R. Menzel, K.K. Bouldin, R.H. Murdock, Trace explosives detection by photoluminescence, Sci. World J. 4 (2004) 55.

[51] A. Rose, Z. Zhu, C.F. Madigan, T.M. Swager, V. Bulovic, Sensitivity gains in chemosensing by lasing action in organic polymers, Nature 434 (2005) 876.

[52] S.R. Wallenborg, C.G. Bailey, Separation and detection of explosives on a microchip using micellar electrokinetic chromatography and indirect laser-induced fluorescence, Anal. Chem. 72 (2000) 1872.

[53] R.S. Ladbeck, P. Kolla, U. Karst, Trace analysis of peroxide-based explosives, Anal. Chem. 75 (2003) 731.

[54] X. Wang, H. Zeng, L. Zhao, J.M. Lin, A selective optical chemical sensor for 2,6-dinitrophenol based on fluorescence quenching of a novel functional polymer, Talanta 70 (2006) 160.

[55] J.V. Goodpaster, V.L. McGuffin, Fluorescence quenching as an indirect detection method for nitrated explosives, Anal. Chem. 73 (2001) 2004.

[56] R.W. Bogue, Boom time for LIBS technology, Sensor Rev. 24 (2004) 353.

[57] Y. Dikmelik, J.B. Spicer, Femtosecond laser-induced breakdown spectroscopy of explosives and explosive-related compounds, detection and remediation technologies for mines and mine like targets X, in: R.S. Harmon, J.T. Broach, J.H. Holloway Jr. (Eds.), Proceedings of the SPIE, vol. 5794, 2005, pp. 757–761.

[58] F.C. De Lucia Jr., R.S. Harmon, K.L. McNesby, R.J. Winkel Jr., A.W. Miziolek, Laser-induced breakdown spectroscopy analysis of energetic materials, Appl. Opt. 42 (2003) 6148.

[59] C.L. Moreno, S. Palanco, J.J. Laserna, F. Delucia, W.A. Miziolek, J. Rose, A.R. Walters, A.I. Whitehouse, Test of a stand-off laser-induced breakdown spectroscopy sensor for the detection of explosive residues on solid surfaces, J. Anal. At. Spect. 21 (2006) 55.

[60] C. Mullen, A. Irwin, B.V. Pond, D.L. Huestis, M.J. Coggiola, H. Oser, Detection of explosives and explosives-related compounds by single photon laser ionization time-of-flight mass spectrometry, Anal. Chem. 78 (2006) 3807.

[61] J.S. Morgan, W.A. Bryden, J.A. Miragliotta, L.C. Aamodt, Improved detection of explosive residues by laser thermal desorption, Johns Hopkins Apl. Tech. Digest. 20 (1999) 389.

[62] The Promise of High-Average, High-Peak Power THz Sources: Standoff Detection of Chemical, Biological, Nuclear, Radiological and Explosive (CBNRE) and Inspection of Personnel and Cargo, RadiaBeam Technologies, January 2005.

[63] H.B. Liu, Y. Chen, G.J. Bastiaans, X.C. Zhang, Detection and identification of explosive RDX by THz diffuse reflection spectroscopy, Opt. Express 14 (2006) 415.

[64] M.K. Choi, A. Bettermann, D.W. van der Weide, Potential for detection of explosive and biological hazards with electronic terahertz systems, Philos. Trans. R. Soc. Lond. A 362 (2004) 337.

[65] D.J. Cook, B.K. Decker, M.G. Allen, Quantitative THz spectroscopy of Explosive Materials, presented at Optical Tetrahertz Science and Technology, Orlando, FL, 14–16 March, 2005.

[66] A. Sengupta, A. Bandyopadhyay, R.B. Barat, D.E. Gary, J.F. Federici, THz reflection spectroscopy of C-4 explosive and its detection through interferometric imaging, terahertz and gigahertz electronics and photonics V, in: R. Hwu, Jennifer, Linden, J. Kurt (Eds.), Proceedings of the SPIE, vol. 6120, 2006, p. 58.

[67] J.M. Fitch, D. Schauki, C.A. Kelly, R. Osiander, R.J. Hwu, THz Imaging and Spectroscopy for landmine detection, in: Proceedings of the SPIE, vol. 5354, 2004, p. 45.

[68] Y.C. Shen, T. Lo, P.F. Taday, B.E. Cole, W.R. Tribe, M.C. Kemp, Detection and identification of explosives using terahertz pulsed spectroscopic imaging, Appl. Phys. Lett. 86 (24) (2005), id. 241116 (3 pages).

[69] Z. Naal, J.H. Park, S. Bernhard, J.P. Shapleigh, C.A. Batt, H.D. Abrun, Amperometric TNT biosensor based on the oriented immobilization of a nitroreductase maltose binding protein fusion, Anal. Chem. 74 (2002) 140.

[70] S.K. VanBergen, I. Bakaltcheva, J.S. Lundgren, L. Shriver-Lake, On-site detection of explosives in groundwater with a fiber optic biosensor, Environ. Sci. Technol. 34 (2000) 704.

[71] M. Altamirano, L.G. Villada, M. Agrelo, L.S. Martn, L.M. Otero, A.F. Moya, M. Rico, V.L. Rodas, E. Costas, A novel approach to improve specificity of algal biosensors using wild-type and resistant mutants: an application to detect TNT, Biosens. Bioelectron. 19 (2004) 1319.

[72] J.M.V. Emon, V. Lopez-Avila, Immunochemical methods for environmental analysis, Anal. Chem. 64 (1992) 78A.

[73] R. Wilson, C. Clavering, A. Hutchinson, Paramagnetic bead based enzyme electrochemiluminescence immunoassay for TNT, J. Electroanal. Chem. 557 (2003) 1.

[74] A. Bromberg, R.A. Mathies, Multichannel homogeneous immunoassay for the detection of 2,4,6-trinitrotoluene (TNT) using a microfabricated capillary array electrophoresis chip, Electrophoresis 25 (2004) 1895.

[75] E.R. Goldman, G.P. Anderson, N. Lebedev, B.M. Lingerfelt, P.T. Winter, C.H. Patterson Jr., J.M. Mauro, Analysis of aqueous 2,4,6-trinitrotoluene (TNT) using a fluorescent displacement immunoassay, Anal. Bioanal. Chem. 375 (2003) 471.

[76] E.R. Goldman, A. Hayhurst, B.M. Lingerfelt, B.L. Iverson, G. Georgiou, G.P. Anderson, 2,4,6-Trinitrotoluene detection using recombinant antibodies, J. Environ. Monit. 3 (2003) 380.

[77] E. Goldman, T. Cohill, C.H. Patterson Jr., G. Anderson, A. Kusterbeck, J.M. Mauro, Detection of 2,4,6-trinitrotoluene in environmental samples using a homogeneous fluoroimmunoassay, Environ. Sci. Technol. 37 (2003) 4733.

[78] L.C. Shriver-Lake, P.T. Charles, A.W. Kusterbeck, Non-aerosol detection of explosives with a continuous flow immunosensor, Anal. Bioanal. Chem. 377 (2003) 550.

[79] S.Y. Rabbany, W.J. Lane, W.A. Marganski, A.W. Kusterbeck, F.S. Ligler, Trace detection of explosives using a membrane-based displacement immunoassay, J. Immunol. Methods 246 (2000) 69.

[80] M. Altstein, A. Bronshtein, B. Glattstein, A. Zeichner, T. Tamiri, J. Almong, Immunochemical approaches for purification and detection of TNT traces by antibodies entrapped in sol–gel matrix, Anal. Chem. 73 (2001) 2461.

[81] T.M. Green, P.T. Charles, G.P. Anderson, Detection of 2,4,6-trinitrotoluene in seawater using a reversed-displacement immunosensor, Anal. Biochem. 310 (2002) 36.

[82] P.T. Charles, J.G. Rangasammy, G.P. Anderson, T.C. Romanoski, A.W. Kusterbeck, Microcapillary reversed-displacement immunosensor for trace level detection of TNT in seawater, Anal. Chim. Acta 525 (2004) 199.

[83] D.R. Shankaran, K.V. Gobi, K. Matsumoto, T. Imato, K. Toko, N. Miura, Highly sensitive surface plasmon resonance immunosensor for parts-per-trillion level detection of 2,4,6-trinitrophenol, Sens. Actuators B 100 (2004) 450.

[84] D.R. Shankaran, K. Matsumoto, K. Toko, N. Miura, Development and comparison of two immunoassays for the detection of 2,4,6-trinitrotoluene (TNT) based on surface plasmon resonance, Sens. Actuators B 114 (2006) 71.

[85] A. Larsson, J. Angbrant, J. Ekeroth, P. Mansson, B. Liedberg, A novel biochip technology for detection of explosives—TNT: synthesis, characterization and application, Sens. Actuators B 113 (2006) 730.

[86] U. Narang, P.R. Gauger, A.W. Kusterbeck, F.S. Ligler, Multianalyte detection using a capillary-based flow immunosensor, Anal. Biochem. 255 (1988) 13.

[87] P.G. Thorne, K.F. Myers, Evaluation of Commercial Enzyme Immunoassays for the Field Screening of TNT and RDX in Water, Special Report 97-32, CRREL, Hannover, NH, 1997.