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Vapour sensing of explosive materials

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The ability to accurately and reliably detect the presence of explosives is critical in many civilian and military environments, and this is often achieved through the sensing of the vapour emitted by the explosive material. This review summarises established vapour detection techniques as well as outlining recent technological developments. It starts by defining different types of explosive materials and discussing the main challenges of explosives vapour detection. This is followed by a section on animal olfaction, which is one of the most sensitive methods, and then goes on to describe methods based on the separation and detection of ions or molecules, such as gas chromatography, mass spectrometry and ion mobility spectrometry. New sensing technologies involving polymers, nanomaterials and microcantilevers are then described, followed by a section outlining how an electronic nose approach can be used to increase selectivity to different types of explosives.

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1. Introduction

Reliable detection of explosive substances is of critical importance in a variety of settings. For example, in a civilian context fixed monitoring stations in airports are used to prevent explosives-based terrorist attacks.[1] For military applications explosives detection is required to locate landmines and improvised explosive devices (IEDs). Finding unexploded ordinance is also a critical element in humanitarian demining activities. Explosives detection systems need to be able to detect a large range of explosive materials, including both traditional high explosive materials, such as TNT, and chemicals used in IEDs, such as ammonium nitrate. The continued development and improvement of new techniques remains important in order to overcome existing challenges and meet challenges posed by new developments in the field of explosives.

The focus of this review is on explosives vapour sensing. Vapour sensing can be used directly to detect vapours emitted by bulk explosives, and indirectly to detect trace quantities of explosives residue that have been vaporised within a detector. Direct vapour sensing of explosives is especially important as it allows stand-off detection of concealed explosives. It is perhaps surprising that the gold standard for vapour detection is still the olfactory sense of a trained sniffer dog. However, through the improvement of existing techniques, and the development of novel sensors, it is likely that technology will at some stage

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overtake animal olfaction. This review outlines the various explosives vapour sensing methods, both established and recent, and starts by defining explosive materials and the challenges in detecting their vapour.

2. Explosives detection

2.1. Explosive materials

Explosive materials are defined as materials that can, after initiation, undergo a very fast and self-propagating decomposition. Upon decomposition more stable compounds are formed, and a pressure effect can take place and heat can be released.[2] For example, trinitrotoluene (TNT) whose formula is $C_7H_5N_3O_6$ decomposes into N_2, H_2, H_2O, CO and C. This is a very rapid and highly exothermic reaction, but it has a reasonably high activation energy and is therefore stable in an ambient environment. Explosives can be classified in various ways. Firstly one can make a distinction based on the speed of the explosion. Low explosives detonate relatively slowly, of the order of cm s^{-1}, and there is no associated shock wave. Black powder and pyrodex are examples of low explosives. High explosives detonate at speeds of the order of km s^{-1} and cause a shock wave.[2,3] Examples of high explosives include TNT, tetryl and picric acid as shown in Fig. 1.[4] Although many explosive materials are similar in that they often contain nitro groups they can have very different properties. Nitroglycerine, for example, is very sensitive to physical shock, making it much less stable than TNT. And cyclonite (RDX) is more powerful than TNT. High explosives can be further divided into primary explosives and secondary explosives. Primary explosives are more easily initiated than secondary explosives because they are more sensitive to impact, friction or heat.[3] Primary explosives are often used to initiate secondary explosives.[2] It is also possible to distinguish between molecular explosives such as TNT, where the fuel and oxidiser are contained in the same molecule, and binary explosives that are a mixture of a fuel and an oxidiser, for example a mixture of ammonium nitrate and fuel oil. Furthermore, explosives can be classified based on their chemistry. From a chemical point of view the following types of explosives can be identified: nitro compounds, nitric esters, nitramines, derivates of chloric and perchloric acids, azides, and various other compounds that can produce an explosion, such as fulminates, acetylides, and nitrogen rich compounds such as tetrazene, peroxides and ozonides.[5]

2.2. Challenges to explosives detection

A large range of explosives detection methods have been developed, and some of these methods have been in use for many years. A distinction is made between methods that are used for the detection of bulk explosives and methods for trace explosives detection, noting that direct vapour sensing detects trace quantities emitted from co-located bulk materials (unlike trace particle detection where trace residues may not correlate to the presence of bulk). In the case of bulk explosives detection, imaging or investigation of the nuclear properties of a material are used to detect macroscopic amounts of explosive compounds. Trace explosives detection is the detection of small amounts of explosives, often in the form of small quantities of

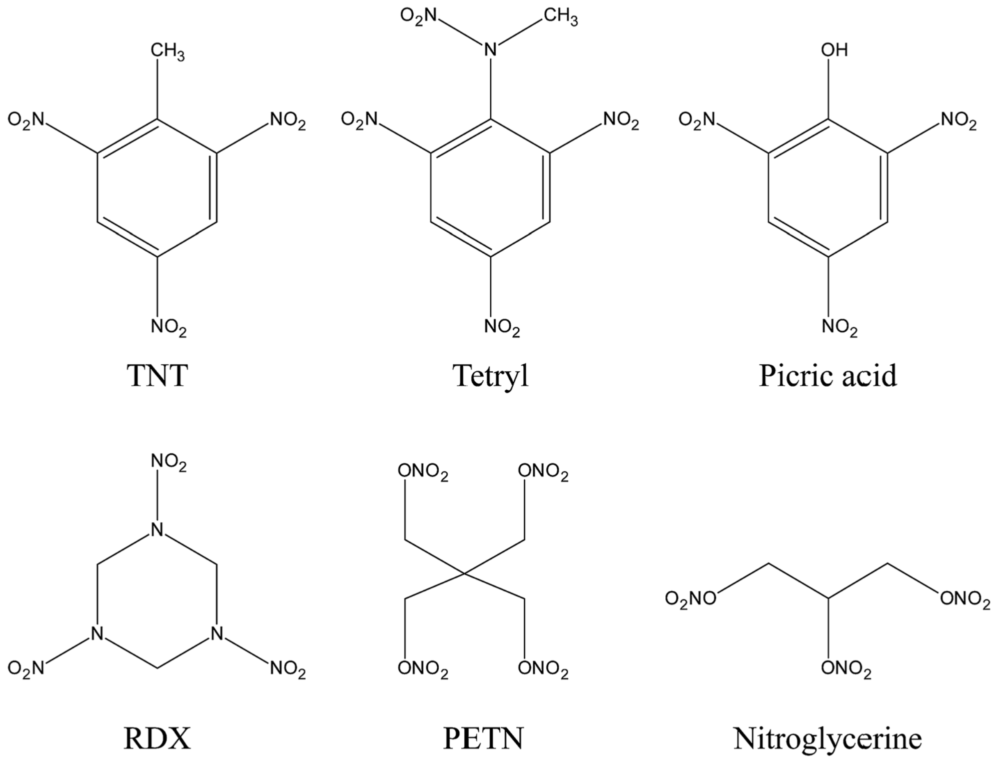

Fig. 1 Examples of explosive materials and their structural formula.

explosives that have been vaporised or particulates. A distinction can be drawn between direct vapour detection in the environment and the detection of particulates of explosive materials that have been collected and then vaporised within the analysis instrument. Many of the existing technologies can be used for both these types of detection. The difference between directly detecting vapours and the detection of vaporised materials is more closely related to the sample preparation method than to the detection method itself. After all, vaporising (a sample preparation step) turns the sample into a vapour that can be analysed in the same way as an authentic vapour. Animal olfaction directly senses vapours. However, most other techniques, for example ion mobility spectrometry, mass spectrometry, and fluorescent polymer based methods, can be used for both. They can be operated both by direct sampling of the air containing the authentic vapours as well as by vaporising a sample that was collected by swiping a surface contaminated with explosive particulates. A distinction can also be made between contact and standoff detection of explosive materials. Related to this are the different ways in which samples can be collected. Contact detection requires direct collection of the sample, for example by swiping a surface, whereas standoff detection must often make use of explosive vapours. However, the equipment for standoff detection must often still be within one metre from the item or area that is screened for explosives.[6]

Apart from simply being able to detect explosive materials, there are other things that should be taken into account when developing an explosives detection system. Some of these additional requirements are determined by the situation in which the device will be implemented. A device that is used as a safety measure at airports will have other requirements than one that will be used in the field during military missions. There are different requirements to the throughput and, because of elevated background levels in military environments, the dynamic range. Furthermore, during military missions portable devices are often required instead of fixed devices. Another consideration is the difference between detection and identification. In some instances a device will be used to sense whether an explosive is present, whereas in others it is also necessary to determine which explosive compound it is. Furthermore, it can be important to consider how many different compounds, or groups of compounds, one device must be able to detect or identify.

It is furthermore possible to distinguish between methods that allow for continuous sensing and methods that allow for the analysis of individual samples. It depends on the application which of these methods is preferred. Other considerations include the detection time, the size and weight of the device, the reset time needed before a next measurement can be conducted, and the power source, and its lifetime, needed for the explosives detection device. Furthermore, it is important that an explosives detection device is user friendly and does not require much user training.

There are several challenges to the detection of explosives vapours emitted by bulk explosives. One of the main challenges is that most explosive materials have very low vapour pressures. The equilibrium vapour pressure at 300 K of for example TNT is 13 ppb, that of pentaerythritol tetranitrate (PETN) is 0.026 ppb, and that of RDX 0.0084 ppb.[7] Other challenges in explosives vapour detection include the relatively small sample sizes, the variety of explosive compounds available, deliberate concealment of the explosives, and interference from other compounds that are present, including the influence of humidity and dust on the detection of explosives.[7]

Since the vapour pressures of explosive materials under ambient conditions are very low, sample preparation must be done in such a way that the analyte becomes detectable. This often requires pre-concentration of the sample, for example by using a material that adsorbs explosive molecules. An example of such a pre-concentration system, incorporated in explosives detection, is single sided membrane introduction mass spectroscopy (MIMS). In this method one side of an absorbant membrane is first exposed to the air and then to the mass spectrometer, which reduces the analyte losses compared to for example two sided MIMS.[3]

Instead of detecting the explosive compounds themselves, one could also aim to detect other materials that could indicate the presence of an explosive material. One could detect associated compounds, compounds that tend to be present when explosives are present, or even taggants, materials that have been added during the production of the explosive to facilitate detection. An advantage of this approach is that taggants and some associated compounds have a higher vapour pressure than the explosive compound itself, and are thus easier to detect. However, associated chemicals are also likely to be more prevalent in the environment than explosives themselves, and thus potentially cause higher false alarm rates.

In addition to the sensitivity, the selectivity of the detection system should also be considered. The selectivity of vapour sensing detectors may be increased by using them in an array. By using them in an array it is possible to obtain a signal similar to an artificial olfactory system. The responses of a number of sensors are combined to give a fingerprint-like signal. Pattern recognition methods can be used to analyse the signal, match it to known responses from a database, and thus identify the analyte.[8] This approach will be discussed in more detail in Section 8.

3. Animal olfaction

One of the most effective methods for explosives vapour sensing is to use trained animals. Trained sniffer dogs are frequently used in the detection of explosives because of their high odour sensitivity. Detection limits as low as 1.14 ppt have been reported for canine olfaction,[9] and for this reason the performance of other methods is often judged in comparison with dogs.[3] The vapour enters the canine olfactory system through the nose, where the vapour is dissolved in the mucus in the nasal cavity and interacts with receptors. This interaction causes a signal to travel through the olfactory nerve to the brain, where the signal is interpreted, leading to perception by the animal. Purging of the system must then take place to ensure that the system is reset and can be stimulated again.[10] Canine olfaction is a complicated system in which many different organs are involved. This includes the main olfactory system, where olfactory receptors, a type of G-protein-coupled receptors (GPCRs), are expressed. Olfactory receptors can be distinguished from other GPCRs by their specific amino acid patterns.[11] In addition to the main olfactory systems canine olfaction has an accessory olfaction system, consisting of the accessory olfactory bulb and the vomeronasal organ. The vomeronasal organ expresses vomeronasal receptors, binding pheromones, and formyl peptide receptors.[11] Other organs that play a role in expressing chemical receptors and may be involved in canine olfaction are Masera's organ, which expresses some olfactory receptors, and the Grueneberg ganglion, which has been shown to play a role in the expression of some vomeronasal receptors as well as the expression of trace amine-associated receptors.[10,11]

Apart from simply having a sensitive olfactory system animals have to be trained to react to certain smells to alert their handler to the presence of a vapour, for example by freezing or sitting or through another behavioural response. They have to be trained to recognise that specific smells are of interest to their handler. Dogs are trained by exposing them to samples with known compounds, often at known concentrations or vapour pressures, and rewarding specific behaviour by the dog upon smelling the compound. As well as a sample of analyte material, interferents or samples of other materials and background signals can be used to make detection more difficult. These situations might be more similar to real situations where interference from materials in the environment might also play a role. It is furthermore important to eliminate unintentional cuing of canine detection behaviour by ensuring tests are double blind where possible, *i.e.* the handler and any test monitors present are unaware of the presence or position of targets or interferents. The animals can be trained to react to a whole range of explosive materials, including traditional and improvised explosive materials, as well as associated chemicals such as taggants.[9] It has for example been shown in the case of sniffer dogs working in narcotics detection that they often use the smell of associated compounds to detect the analyte materials, rather than the smell of the analyte material itself.[10]

In an attempt to determine the limit of vapour sensing by dogs, dogs were first trained to indicate which of five locations contained a target odorant with a behavioural response. The concentration of the odorant were then systematically lowered until the response of the dogs became dependent on chance. It has been observed that dogs can reliably find the target odorant down to concentrations of 1–2 ppt.[9]

Apart from a high sensitivity, canine olfaction has several other advantages compared to instruments for vapour sensing of explosives. These advantages include good selectivity often resulting in a smaller number of false positives, generally faster detection, high mobility, very efficient sampling, and ease in identification of the source of the vapour. A disadvantage of using dogs for explosives detection is the amount of training needed for the dog and the handler, and the fact that dogs can get tired or bored, and need care. Therefore, possibilities of using other animals, that are more cost effective, have been investigated. This includes rats, which also have a sensitive olfactory system. Advantages of using rats for explosives detection include their small size, reduced cost of raising, training and care relative to dogs, and their less strong attachment to humans or specific handlers.[12]

More recently the use of honey bees for explosives sensing has also been researched. Bees can be used over relatively long distances, up to 100s of metres, while the handlers are able to stay at a safe distance from the explosives. Furthermore, there is no risk of the bees setting off a mine.[13] As part of their training the bees' food is injected with a small amount of the target material, which will encourage the bees to search for 'food' with the same smell. It has been observed that bees that have been trained in this way, tend to fly along the vapour plumes towards the source of the analyte material. They then pause above the source of the vapour before they continue their flight. For bees, vapour detection has been observed at a similar sensitivity to that of dogs, in the ppt range.[13] However, the use of free flying bees has significant challenges, such as the presence of other food sources and variations in climate. The response of trained moths to explosives vapour has also been investigated.[14] Like bees, moths are relatively easy to train, inexpensive to take care of, and cannot set off an explosive. Like dogs and rats, a behavioural response to specific vapours can be harnessed in moths.

Although there are several possible ways in which animal olfaction can be used for vapour sensing of explosive materials, and animal olfaction is very sensitive, it is not always the best option. In many cases it would be better if a sensitive and selective, equivalent technological solution could be used. Instruments have many advantages over animals, for example a theoretical 24 hour 'duty cycle', the possibility to not only detect but also identify different analyte materials, the small influence of the handler, and generally long life time of the instrument.[10]

4. Separation and ion detection techniques

A number of techniques used for detection of explosives rely on molecular separation processes, which involves separating different types of molecules in the vapour into their fractions. For some methods the molecules themselves are broken up into fragments or their constituent elements. The most popular techniques are gas chromatography, mass spectroscopy, and ion mobility spectrometry, as discussed individually in the following sections. These techniques can be used individually, however for greater efficacy they are often used in combination with each other.

4.1. Gas chromatography

Gas chromatography is used to separate and analyse a variety of compounds including explosives. The compounds are vaporised without decomposing them. A carrier gas carries the vapour through a column that is coated with a liquid or polymer, called the stationary phase. Due to different interactions with the stationary phase, different constituents of the vapour have different retention times in the column, which allows for

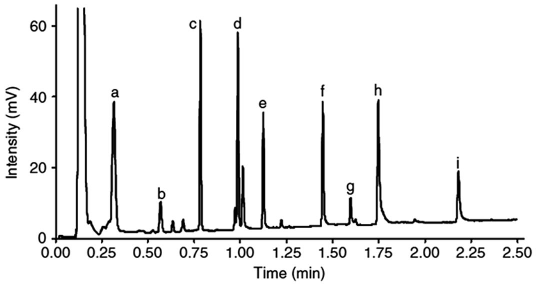

Fig. 2 An example of a gas chromatogram, where the peaks correspond to (a) ethylene glycol dinitrate, (b) 4-nitrotoluene, (c) nitroglycerine, (d) 2,6-dinitrotoluene, (e) 2,4-dinitrotoluene, (f) trinitrotoluene, (g) pentaerythritol tetranitrate, (h) cyclotrimethylenetrinitramine, and (i) 2,4,6-trinitrophenylmethylnitramine.[15] *Copyright 2006 by American Academy of Forensic Sciences*.

the separation of the materials present in the sample. There is a large range of detectors that can be used to detect the materials exiting the column, including electron capture detectors, thermal conductivity detectors and nitrogen-phosphorus detectors. It has, for example, been shown that gas chromatography with an electron capture detector can be used to analyse a mixture of nine explosive compounds in less than 140 seconds (Fig. 2).[15] Furthermore, gas chromatography is often combined with other detection methods, such as mass spectrometry. Explosives detection systems that combine gas chromatography and mass spectrometry are commercially available. For example, it has been shown that gas chromatography in combination with tandem mass spectrometry can be used to detect various explosives within a few minutes.[16] It is also possible to use a combination of gas chromatography columns with different separation conditions, allowing for the separation of materials that were not separated by the first column. Techniques in which two or more separation steps are used are called multidimensional separation techniques. In two-dimensional gas chromatography the sample is passed through two columns that use different separation conditions (Fig. 3).[17] It has, for example, been shown that fast two-dimensional gas chromatography can be used for the detection of RDX, PETN and TNT.[18] Gas chromatography can be a relatively fast detection method. When short columns are used in a highly efficient setup for gas chromatography detection takes only a few seconds.[3]

4.2. Mass spectrometry

There are several spectrometry methods, including mass spectrometry that can be used for explosives detection, and have been successfully implemented in commercially available devices. In mass spectrometry the analyte is split into charged fragments, that are then separated based on their mass-to-charge ratios using a magnetic and/or electric field. The sample is introduced into a sample chamber, either at atmospheric pressure or in vacuum. It is then ionised, for example using ion impact, electron impact, vacuum ultraviolet (VUV), or resonance enhanced multiphoton ionization. The ions are then accelerated into the tube where they are separated (Fig. 4).[19,20] The presence and relative abundance of the different molecular fragments can be used to analyse the analyte material. An advantage of this method is the relatively short analysis time of approximately 5 seconds. One impressive example is the sub-ppt detection of RDX, within 1 to 2 seconds, without sample pre-concentration, using selective atmospheric pressure ionisation using nitrate reactant ions.[21] Work on further improvement of mass spectrometry for explosives detection is aimed at reducing cost and size, and further improvement of the portability of the equipment.[3]

Apart from standard mass spectrometers used for explosives detection, such as an atmospheric pressure ionization tandem mass spectrometer, an atmospheric sampling glow discharge ion trap mass spectrometer and an atmospheric pressure ionisation time of flight mass spectrometer, systems have been developed that make use of some of the specific properties of many explosive materials. For example, many explosives have a large electron attachment cross section. Detection systems that make use of this property include a reversal electron attachment mass spectrometer and an electron capture negative ion mass spectrometer. This last system makes it possible to distinguish between various explosives containing NO_2 by measuring the energy at which the NO_2 ion is formed.[19]

4.3. Ion mobility spectrometry

Ion mobility spectrometry is used to separate ionised molecules based on their mobility in a drift gas. The flow time of the ions through an ion mobility spectrometry tube, with a gas flow and an electric field, depends on the mass, charge and dimensions of the ion, and thus allows for separation and identification of the ions. The ionisation takes place at atmospheric pressure.

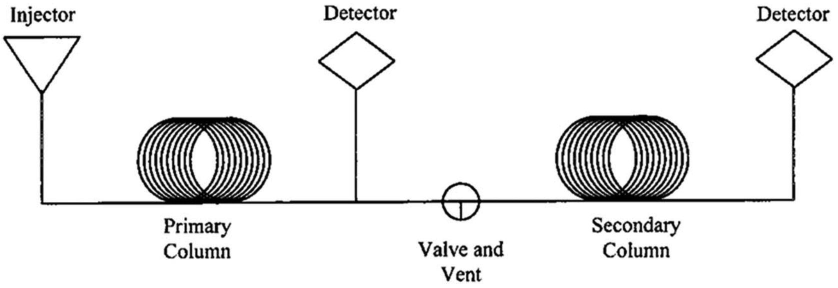

Fig. 3 Schematic representation of a two-dimensional gas chromatography system, where the vapour is passed through two columns with different separation conditions, such as the temperature or the coating of the columns.[17] *© WILEY-VCH Verlag GmbH, D-69451 Weinheim 1999*.

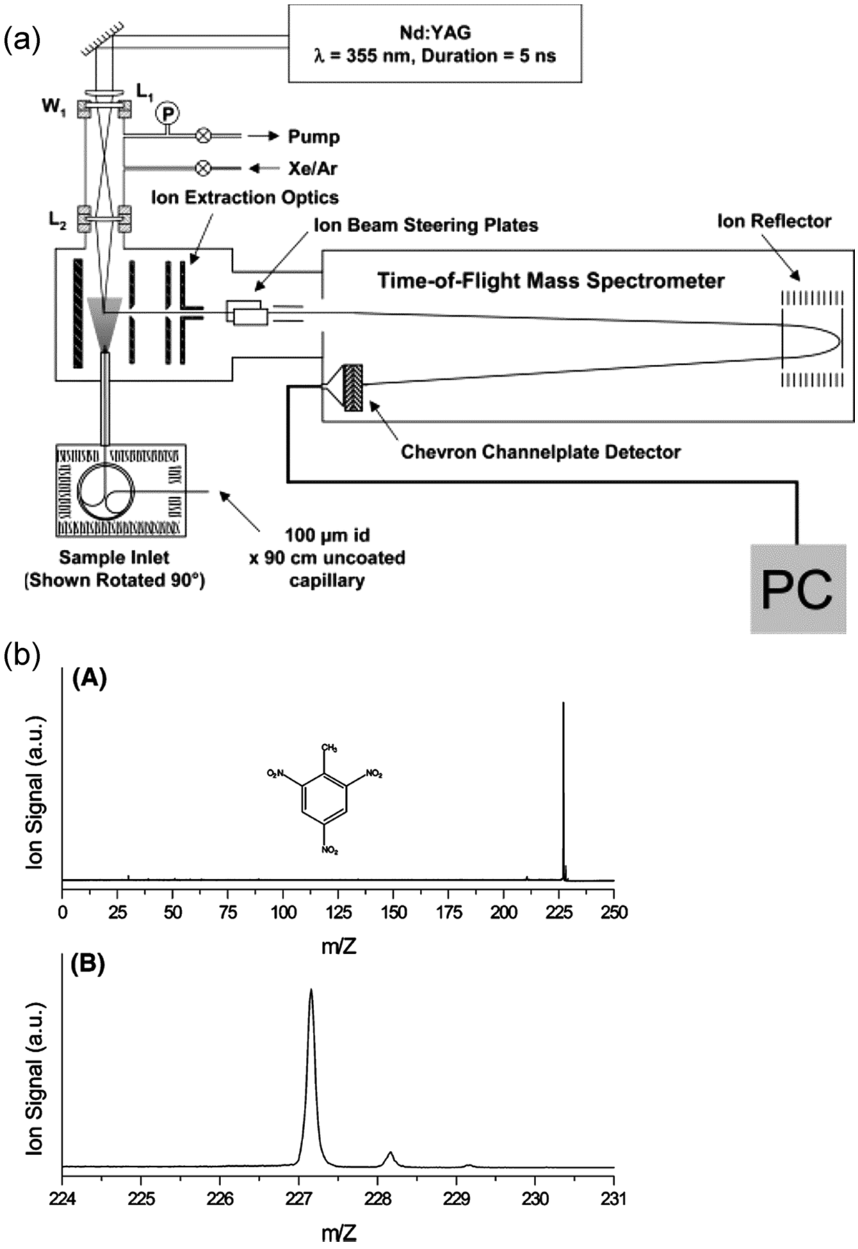

Fig. 4 (a) Schematic representation of a single photon laser ionisation time-of-flight mass spectrometer. (b) An example of a single photon ionisation mass spectrum of 2,4,6-trinitrotoluene (A) and an expanded view of the molecular ion region (B).[20] *Reprinted with permission from ref. 20, Copyright 2006 American Chemical Society.*

Usually the relative abundance of the ions is used for identification of the compound instead of absolute quantities because the ratios are less dependent on the conditions.[19] Ion mobility spectrometry is particularly suited to explosives detection because the ionisation step itself is highly selective for most explosives because of their high electron affinity. Ion mobility spectrometry is currently implemented in many commercial explosives detection systems. Much work has been done to improve the sensitivity and detection speed of such systems. This can be realised by improving several individual parts of the system. It is for example possible to change the sample collection method. Ion trap mobility spectrometry is a technique that allows for higher sensitivity, by eliminating losses that occur at the shutter in conventional ion mobility spectrometry, and is thus able to detect lower concentrations.[22] It is also possible to change the ionisation technique that is used. Radioactive materials such as ^{63}Ni can be used to ionise the sample. However nonradioactive ionisation sources such as secondary electrospray ionisation (Fig. 5) and corona discharge can also be used for the detection of explosives using ion mobility spectrometry.[23] An additional advantage of positive corona discharge ion mobility spectroscopy is that it allows for high sensitivities because a positive corona discharge results in a greater total ion current.[24]

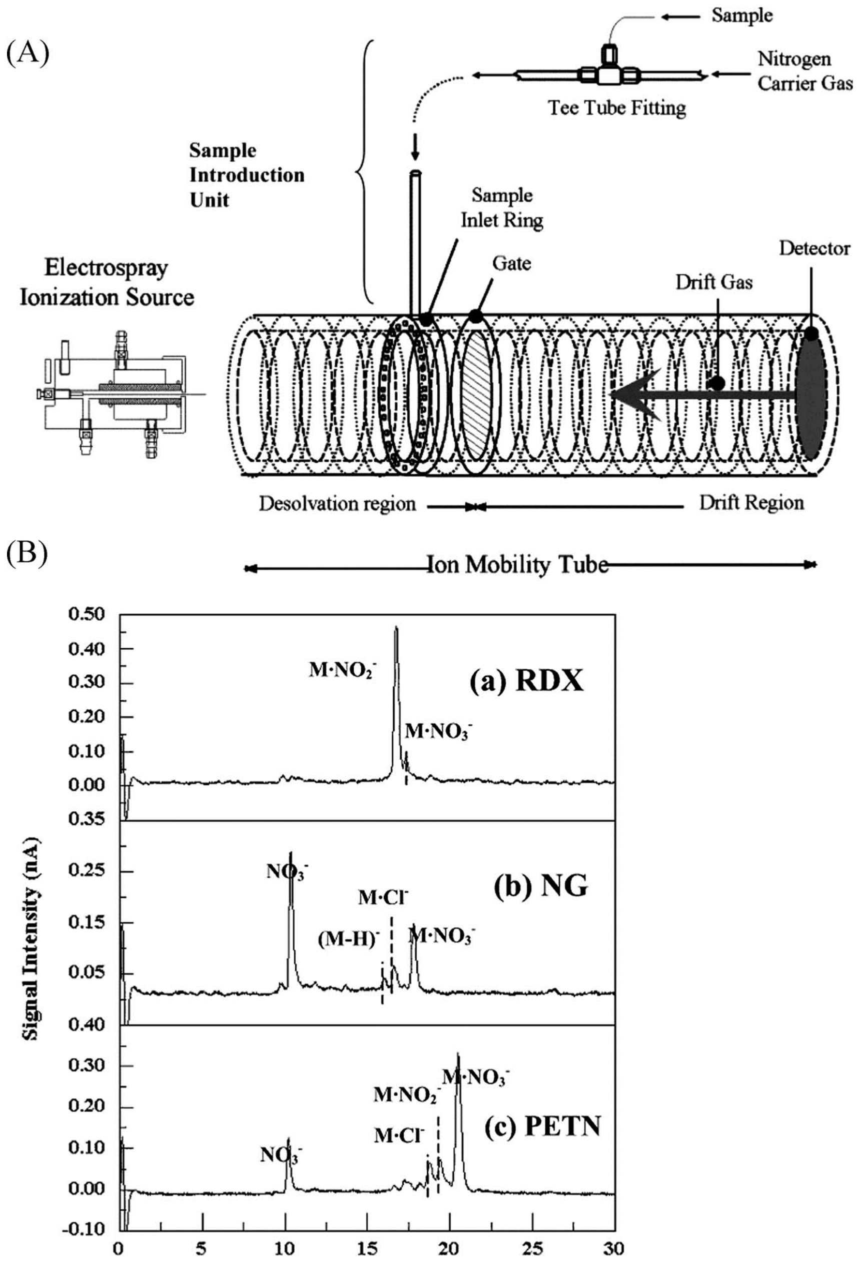

Fig. 5 (A) Schematic representation of a secondary electrospray ionisation ion mobility spectrometer. (B) Secondary electronspray ionisation ion mobility spectra of RDX, NG, and PETN.[23] *Reprinted with permission from ref. 23, Copyright 2004 American Chemical Society.*

5. Polymers

5.1. Conductive polymers

Polymers are a very versatile class of materials and can be used in a large range of applications. Initially polymers were mainly thought to be electrically insulating, however, research leading to the 2000 Nobel Prize in Chemistry demonstrated the existence and versatility of conductive polymers. Due to the combination of conductivity with other properties of polymers, such as ease of processing and functionalization, conductive polymers are of interest for a large range of applications. This includes electrochemical gas sensors and other electronic devices. Conductive polymers can be used to form transparent conductors, and semiconductors in which the Fermi level can be shifted and controlled over a relatively large range.[25] For conducting polymer-based sensors it has also been shown that the responses to the analyte materials tend to be reversible.[26] Examples of conducting polymers include polyacetylene, polythiophene, polypyrrole, and polyaniline[25,27] (Fig. 6).

The intrinsic conductivity of conjugated polymers is relatively low. However, the conductivity can be increased by doping, or introducing charge carriers into the system.[28] It has for example been shown that the conductivity of polyacetylene can be increased by a factor 10^7 through doping.[25] Although doping the polymers allows for a higher conductivity, intrinsically conductive polymers are also used for various applications.

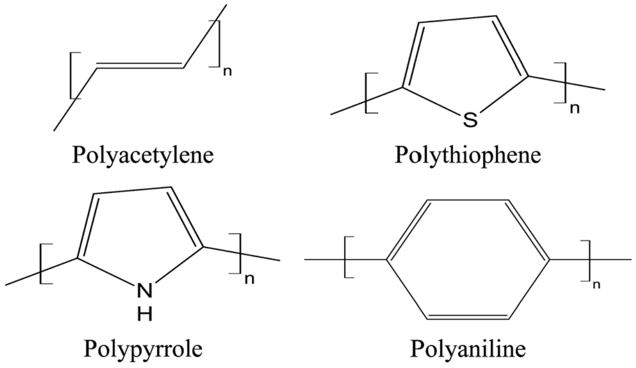

Fig. 6 Examples of conductive polymers and their structural formula.

Some polymers, such as polyaniline and polypyrrole, are unstable in their undoped state, others, such as polythiophene, are stable in the intrinsic or very lightly doped state.[29]

Two ways in which analyte gases can interact with conducting polymers can be distinguished. Gases can interact with a conductive polymer through a chemical reaction or by physically adsorbing onto the polymer, causing a change in the doping level or depletion region respectively.[27,30] In both cases a change in the electrical properties of the polymers can be measured.

There are several ways in which the polymers can be made sensitive to specific materials, or groups of materials. If the overall chemical or electrostatic properties of the conductive polymer do not allow for sensitivity to the analyte materials, this can be obtained by covalent or physical integration of synthetic or natural receptors or by imprinting.[31]

Conductive polymers can be incorporated into different device configurations such as chemiresistors, chemically sensitive field-effect transistors, diodes or capacitors. A further advantage is that due to the versatility with which they can be processed they can be incorporated into sensors in various forms.[28,29] It is possible to use polymer thin films, but also polymer based nanomaterials, which are interesting for sensing applications because they have a relatively large exposed surface area.[32]

There are several properties of conductive polymers that can be used for sensing, which means that several different detection methods can be used. These methods include for example optical methods and methods based on changes in the electrical properties of the polymer.[26] Examples of polymers used for sensing applications include phospholipids for the detection of volatile anaesthetics,[33] polypyrrole[34] and polyaniline[35] for the detection of ammonia, and polymer nanojunctions for the detection of TNT.[36]

5.2. Fluorescent polymers

Fluorescent polymers can be used for explosives vapour sensing (Fig. 7)[37] through a mechanism whereby the fluorescence of the polymer is switched on or off upon interaction with the analyte. In the case of a switch off system quenching of the fluorescence is observed upon interaction, whereas in the case of a switch on system an increase in fluorescence is observed. In most cases an on-switch system does not have an advantage with respect to an off-switch system, because both systems will suffer from background fluorescence. However the turn-on system does have a slight advantage in environments where there are many background vapours, as the turn-off, or quenching, system suffers from more false-positives due to interference from the environment.[38]

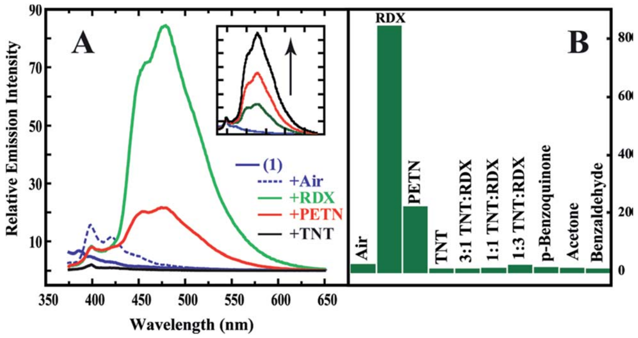

Fig. 7 (A) Emissions profiles of a chemical sensor in acetonitrile (1), in acetonitrile after 120 s irradiation at 313 nm (air), and with RDX, PETN, and TNT in acetonitrile after 30 s irradiation. The inset shows the peak at 480 nm with increasing irradiation times (10 s intervals). (B) Emission intensity at 480 nm for various analyte materials after irradiation for 30 s.[37] *Reprinted with permission from ref. 37, Copyright 2007 American Chemical Society.*

The term amplifying fluorescent polymers (AFPs) is often used because there can be a gain in signal when the polymer interacts with the analyte material.[38] Amplification occurs because fluorescent polymers are an efficient electrical transport medium, allowing a delocalised exciton to sample many binding sites along the polymer chain in the life-time of one exciton. Increasing the number of pathways available for diffusion of the exciton through the polymer strongly increases the amount of amplification of the signal.[38]

The use of fluorescent polymers for vapour sensing has the usual polymer advantages. Like other polymers, fluorescent polymers allow for relatively easy processing and the tailoring of the polymer to meet the requirements of a specific application. Additionally it is relatively easy to observe changes in fluorescence, either by visual inspection or through spectrometric methods.

An example of the application of fluorescent polymers for the vapour detection of explosive materials is the commercially available Fido device. In this system the real-time monitoring of the fluorescence of a conductive polymer thin film takes place while the system is exposed to analyte vapours. The sensitivity of this system to TNT and DNT vapours has been demonstrated to be comparable to that of sniffer dogs.[38]

5.3. Other

Other uses of polymers in vapour sensing have been demonstrated. For example using the swelling of nonconductive polymers as an analyte vapour is absorbed.[4] A change in colour of polymers upon interaction can also be used for vapour sensing, which has not only been done with polymers but also with other chemically reactive materials.[4,39] Furthermore, polymers can be used in combination with other techniques, some of which will be discussed in the next sections of this review, to make the systems used in those techniques more sensitive to specific analyte materials. Examples of polymers used in combination with another system include surface acoustic wave (SAW) devices, where polymers are added to cause interactions with specific molecules. In the case of a SAW device a sound wave is guided across a small quartz crystal. If molecules from a vapour have adsorbed onto the crystal this will change the propagation of the sound wave. The way in which the acoustic wave is affected provides information about the properties of the vapour molecules with which it has interacted.[2] Polymer coatings are used on the sensor surface to bind specific materials to the sensor surface. It has been shown that carbowax, or polyethylene glycol, can be used to coat SAW devices for DNT detection (Fig. 8).[40] Similar to polymers, the specific interactions of biomaterials can also be used to sensitise SAW sensor surfaces.[41]

6. Nanomaterials

There are many different types of nanomaterials, for example nanoparticles, nanowires, nanotubes, and composite materials. Many nanomaterials have properties that are changed by the adsorption of an analyte, making them suitable for sensing applications. Functionalization of the nanomaterials can also be used to allow tailoring for specific requirements, including explosives vapour sensing.[42] Successful explosives vapour sensing has been demonstrated in a laboratory environment for systems based on various types of nanomaterials. A particularly versatile nanomaterial used in sensing are carbon nanotubes (CNTs). The electrical properties of CNTs are especially sensitive to interactions with other molecules *via* chemical doping and charge transfer. CNTs are well-suited for sensing applications because of their large surface to volume ratio, the possibility to tailor the electrical properties by changing the size or composition, and because it is relatively easy to incorporate CNTs into small electronic devices.[43] It has been shown that single walled CNTs have different sensitivities to the adsorption of different classes of molecules. Furthermore, their selectivity can be increased by coating the nanotubes with chemically selective layers.[8]

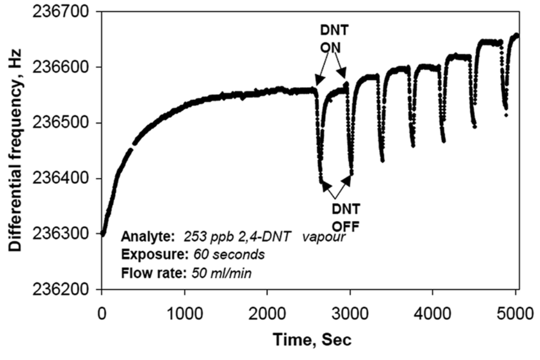

Fig. 8 Response of a carbowax coated SAW sensor to DNT.[40] *Reprinted from ref. 40, Copyright 2004, with permission from Elsevier.*

Chemically modified silicon nanowire arrays can be used for vapour sensing of explosives, without the need for pre-concentration. When the wires are functionalised with 3-aminopropyltriethoxy silane (APTES), the amine groups can interact with the aromatic ring of TNT, which leads to changes in the conductance of the sensor. It has been shown that such as device can reliably detect TNT concentrations between ppb and ppt, and that the system can be reset by washing the surface of the sensor with a water/DMSO solution (Fig. 9).[42]

Nanoparticles coated with an organic layer, forming a metal–insulator–metal system, have been used for vapour sensing. Because it is possible to tune the size, inter-particle distance, composition and functional groups of such systems, it is possible to use those properties to enhance the sensitivity, selectivity, and response time of systems in which they are used.[44]

It is also possible to make vapour sensors based on localised surface plasmon resonances (LSPR) of metal nanoparticles. Changes in the LSPR spectrum of silver particles were observed upon interaction with an analyte material. In this case the surface can also be modified to enhance the vapour selectivity. Detection limits in the 18–30 ppm range have been observed for this device, depending on the functionalization of the silver nanoparticles. Furthermore, it has been shown that the interaction between the sensor and the analyte molecules is reversible and the sensor reusable.[45]

7. Microcantilevers

Nanomechanical effects caused by molecular adsorption can also be used for explosives detection. Vapour sensing of explosives using microcantilevers has been demonstrated in laboratory settings. Microcantilevers used for sensing are usually

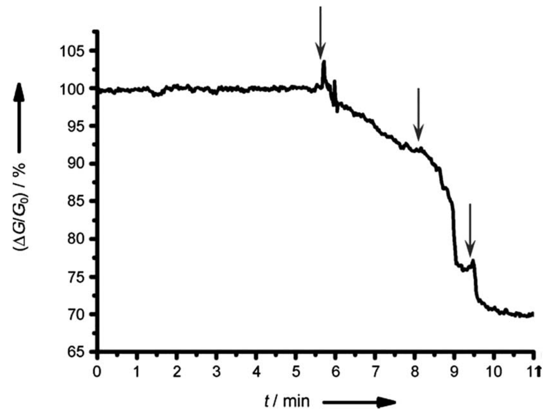

Fig. 9 Relative conductance of a silicon nanowire based FET sensor after TNT was introduced at approximately 1 ppt in a carrier gas. The pulses (indicated by arrows) were 5 s in duration. A decrease in conductivity after each pulse is measured.[42] *Copyright © 2000 by John Wiley & Sons, Inc.*

based on those used in atomic force microscopy (AFM), and are typically 100 μm long, 50 μm wide and 0.5 μm thick.

Several different sensing principles can be used (Fig. 10). First of all it is possible to use the change in mass due to the adsorption of analyte molecules on the cantilever. Since cantilevers with high resonance frequencies have a high sensitivity to mass absorption, the increase in mass changes the resonance frequency of the cantilever, which can be detected.[46] The second sensing principle makes use of changes in the surface stress. In this case one side of the cantilever is sensitised whereas the other side is passivated. When the adsorption is restricted to one side of the cantilever the cantilever undergoes bending. The bending does not depend on the mass of the adsorbed molecule but on its binding energy.[8] The change in surface stress that occurs between the sensitised and passivated sides of the cantilever upon interaction is measured.[47] In the third sensing principle changes in the bulk stress of the cantilever material are used, using cantilevers consisting of two different materials.[46]

There are several ways in which the changes in bending or resonance frequency of the cantilever can be measured. Because very small deflections have to be measured the system has to be very sensitive. One of the simplest and most well-known read-out methods is optical leverage, known from AFM, where a laser is focussed on the back of the cantilever and the reflected laser light is detected by a position sensitive photodetector. However, this method is more difficult to apply to arrays of cantilevers, is not suitable for very small, for example nanometer sized, cantilevers, and can suffer from optical artefacts such as in the case of changes in refractive index.[46] There are many other read-out methods, for example capacitive methods which can be used for nanometre-sized cantilevers, piezoelectric methods which can be used for both read-out and actuation, piezoresistive and integrated optical methods, such as wave guides, which can be used for large arrays.[46]

When cantilevers are used for explosives vapour sensing, the sensing relies on either the surface of the cantilever being sensitised for specific interaction with analyte molecules, or properties of the explosive materials such as phase transitions. Sensitivities to PETN and RDX in the 10–30 ppt range have been reported for functionalised cantilevers.[48] The selectivity of such systems have been shown to be dependent on the coating used to functionalise the cantilever (Fig. 11).[49] Local differential thermal analysis can also be used to obtain thermal fingerprints of the analyte material. Cantilevers are ideal substrates for this because of their low thermal mass, allowing for fast response times. Finally, the cantilevers can be used for photothermal deflection spectroscopy because the cantilevers are very sensitive to changes in temperature. In this method information about the absorption spectrum of a material can be obtained by measuring the heat produced upon absorption of light of specific wavelengths.[46]

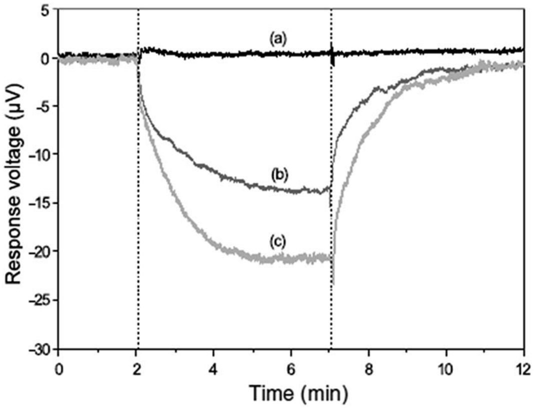

Fig. 11 Response of a cantilever to TNT at about 7.6 ppb without self-assembled monolayer (SAM) (a), modified with a 4-mercaptobenzoic acid SAM (b), and modified with a 6-mercaptonicotinic acid SAM (c).[49]

8. Electronic nose approach

Adding functionalised groups to polymers used in polymer based sensing, or coating nanomaterials or cantilevers used for sensing allows for selectivity, to one compound, or more likely to one group of materials that all have similar properties or a similar chemical group. However, this is often not sufficient to be able to distinguish between similar compounds, and to be able to detect different types of analyte materials with one device. Furthermore, it is important to be able to distinguish not only between different analyte materials, but also between analyte materials and harmless background signals, such as variations in humidity, air pressure, and temperature.

To allow for the required selectivity an array of sensors with different functionalization, and thus different responses to different materials, can be used. An array of sensors is able to detect different materials using a fingerprinting or electronic nose method. This is an approach similar to the olfactory system of mammals, where a number of receptors is used, that on their own are not highly selective, but the pattern of all the responses of the separate receptors combined is interpreted by the brain as a specific odour.[50,51]

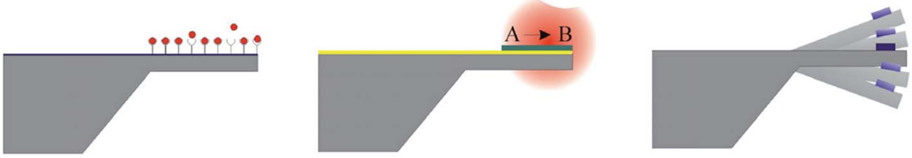

Fig. 10 Schematic representations of the operation modes of microcantilever based sensors: surface stress changes (left), bulk stress changes (centre), and mass changes (right).[46] © *IOP Publishing. Reproduced with permission. All rights reserved.*

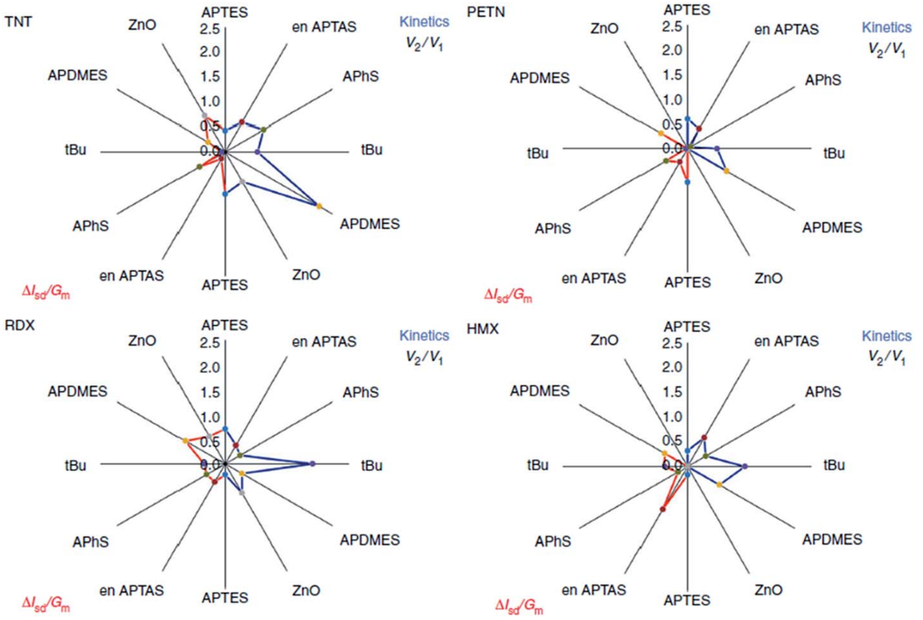

Fig. 12 Fingerprinting results derived from a combination of thermodynamic (red) and kinetic (blue) responses of a silicon nanowire based electronic nose type sensor upon exposure to TNT, RDX, PETN and HMX.[50] *Adapted with permission from Macmillan Publishers Ltd, copyright 2014.*

The sensors used in an array for an electronic nose approach can be based on many different types of sensing methods. These sensors can for example be based on polymers or nanomaterials. The detection can take place through changes in the electronic, florescent, or optical properties of the materials, which means that this is a method that can be used in combination with many of the recently developed techniques. This approach is especially interesting in combination with small scale sensors.

Detection of and discrimination between various explosives vapours has been demonstrated in a laboratory environment. It has for example been shown that an array of nanowire based field-effect transistors can be used to detect and discriminate between different explosive materials. In this case surface modification was used to create eight chemically different regions on a chip (Fig. 12).[50]

9. Summary

Explosives detection has many applications in both military and civilian situations. One of the main challenges are the low vapour pressures of many explosive materials, but there are many methods, both established and more recently developed, that can be used for explosives vapour detection.

Established methods play an important role in explosives vapour sensing. Animal olfaction, for example, is important because of the very high sensitivity, where dogs, as well as other animals such as rats and bees, can be used. However, the use of live animals is not always practical and many other techniques have been developed. Other traditional methods include separation methods that identify molecules or ions, such as gas chromatography, ion mobility spectrometry, and mass spectrometry.

Newer methods often use materials that allow for the creation of small electrochemical devices. Polymers, for example, are an interesting group of materials because they are easy to process and can be tailored to meet specific requirements. In polymer-based sensors changes in, for example, fluorescence or conductivity can be used to indicate the presence of an analyte material. Furthermore, polymers can be used as a coating to sensitise other types of devices, such as those based on nanomaterials or microcantilevers. Nanomaterials themselves can also be used for explosives vapour sensing and are especially interesting because their properties can be tailored and because they have a large surface area. Mechanical properties of cantilevers are used for vapour sensing using various mechanisms. Selectivity to different types of explosive can be improved by using an electronic nose approach. By using an array of sensors with different functionalization, a fingerprint-like signal can be recorded and interpreted to identify the analyte vapour.

A large range of techniques has been investigated, however only a few have successfully transitioned to field use. Ion mobility spectrometry is still the most common detection technology. Mass spectrometry is only just transitioning effectively to fieldable systems for trace detection. In the broader chemical sensor category only fluorescent polymer systems, such as the FLIR Fido systems, are being successfully implemented in the field. Many other systems that performed well in laboratory environments have not been successfully developed into fieldable systems. This is possibly due to issues with for example the sensitivity, specificity, cost, or practicality of the system. Understanding why newer methods have not transitioned effectively to commercial systems will be key to ensuring that new techniques can be exploited effectively.

Most current and future work is focussed on either improving traditional sensing methods to increase sensitivity and decrease detection times, or on developing new methods. Small scale devices and materials that are easy to functionalise and process, in combination with an electronic nose approach are especially promising.

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