# Explosives Detection – A Technology Inventory

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# 1 Utökad sammanfattning (Executive abstract in Swedish)

Under senare år har terrorism blivit ett allt mer uttalat hot mot vårt fredstida samhälle. Explosivämnen som utnyttjas för terroriständamål orsakar stora förluster av såväl människoliv som materiella värden, rent faktiskt är dessa förluster gigantiska i jämförelse med förluster som orsakats av kemiska, biologiska eller radioaktiva stridsmedel. Även länder inom Europa är idag utsatta för terroristattacker. Bland de mer uppmärksammade händelserna är de tre explosioner som inträffade ombord på Madrids pendeltåg i mars 2004 och attentatet i Londons tunnelbana i juli 2005. Ur ett militärt perspektiv utgör dolda explosiva laddningar i form av IEDer (Improvised Explosive Devices) ett svårt problem.

På grund av detta uttalade hot behöver medel för att skydda infrastrukturen utvecklas och införas. En viktig del av detta skydd är känsliga och noggranna explosivämnesdetektorer som kan upptäcka och varna för förekomsten av explosivämnen och IEDer. Uppgiften är inte lätt, eftersom olika scenarier ställer olika krav på detektionsutrustningen. Möjliga scenarier innefattar skydd av allmänna kommunikationsmedel, skydd av transport, skydd mot ”roadside bombs”, check in-kontroller vid flygplatser, kontroll av containertrafik, skydd av infrastruktur såsom kraftförsörjning, vattenförsörjning och kommunikationssystem och bemötande av bombhot.

Idag finns inga detektionsmetoder som kan svara mot samtliga krav som ställs för dessa scenarier. Kraven som ställs är nämligen mycket höga, speciellt med avseende på känslighet och noggrannhet. Dagens system klarar inte mer än ett fåtal explosivämnen, och falsklarm eller missade identifieringar utgör ett stort problem. Antalet explosivämnen som borde kunna detekteras är högt, inte minst med tanke på de många olika ”hemkokade” explosivämnen som blivit allt vanligare. Samtidigt som metoderna behöver utvecklas för att klara mindre mängder med större säkerhet ställs också krav på att de skall vara billiga, robusta, snabba och lättskötta. Allra helst skall de dessutom kunna användas från ett säkert avstånd – så kallad ”stand off detection”. Inom detta senare område läggs stora resurser på forskning och utveckling i delar av världen, men problemet är mycket svårt, och det finns ingen självskriven lösning.

Detektionsmetoder för explosivämnen kan delas in i två olika grupper – bulkdetektion och spårmängdsdetektion. Vid bulkdetektion behövs en större mängd explosivämne för att en identifiering skall kunna genomföras - dessa metoder är ofta avbildande, och idag ofta förekommande t ex vid bagagekontroller vid flygplatser. Spårmängdsdetektion utgår istället från den mängd av explosivämne som finns närvarande i gasfas eller i form av partiklar som fastnat på händer, kläder eller förpackningar.

Denna rapport utgör en inventering både av detektionsmetoder som finns utvecklade idag men också av metoder som fortfarande är på forskningsstadiet. Både bulk- och spårmängdsmetoder tas

upp, men huvudfokus ligger på spårmängdsdetektion. Även metoder som utvecklas för ”Stand off detection” har fått ett kapitel. En del av dessa har sitt ursprung i bulkdetektion, andra är spårmängdsmetoder, men på längre avstånd är det svårt att se hur dessa metoder kan fungera på annat än en större mängd explosivämnen.

Slutligen finns också ett kapitel om analysmetoder, som idag framförallt har sin användning i labbmiljö. Med utvecklingen av mikroteknologi (MEMS, Micro-Electro-Mechanical System) följer också möjligheten att flytta ut labbet till fältet. Användandet av t ex gaskromatografi (GC) eller masspektrometri (MS) – båda vanliga tekniker inom labbanalys - är också vanligt i kombination med spårmängdsdetektion för att få större noggrannhet genom extra separation av provet eller en ytterligare ämnesspecifik parameter.

Bulkdetektion inriktar sig ofta på att kvantifiera andelen av specifika atomer, såsom väte, kol, kväve och syre. Genom att bestämma kvoten av kol/syre eller kväve/syre kan man särskilja många explosivämnen (t ex TNT, RDX, HMX) från andra ämnen. Genom att använda flera detektorer kan man skapa bilder som presenteras för en operatör. Misstänkta substanser kan t ex färgläggas för att märkas bland övriga objekt på bilden, och färgkodning i kombination med föremålets geometri utgör tillsammans underlag för operatörens bedömning. Metoderna baserar sig ofta på kärnfysikaliska tekniker som röntgenstrålning, neutronstrålning och gammastrålning, vilket gör att de inte används för personscreening.

Andra avbildande bulkmetoder är ”Millimeter Wave Imaging” och ”THz Imaging”, som båda har egenskapen att material såsom tyg blir närmast genomskinliga, medan tätare material, därmed t ex gömda vapen, syns tydligt vid en avbildning. THz-spektroskopi kan också ge mer specifik kemisk information.

Spårmängdsdetektion är beroende av att hitta och identifiera extremt små mängder av explosivämne. Därför blir tekniker för att samla in prov, i gasfas men kanske framför allt i partikelform, oerhört viktiga för dessa typer av detektionsinstrument. Idag är det vanligt att man tar ett strykprov med en liten trasa som sedan matas in i detektorn. I andra fall finns en portal som samlar in småpartiklar som frigörs med en riktad luftström när någon passerar. I båda fall finns stort behov av effektivare metoder.

Antalet spårmängdsdetektionsmetoder är oerhört omfattande. Även om avsikten med metodinventeringen var att ge en så heltäckande sammanfattning som möjligt är det helt säkert så att några metoder saknas. Nedan finns en översiktlig beskrivning av ett litet urval av metoder som ingår i inventeringen

Ett område där mycket utvecklingsarbete pågår är ”electronic noses” – eller elektroniska näsor. Idén här är att instrumentet är sammansatt av en hel samling av elektronisk/kemiska sensorer som delvis skiljer sig från varandra vad gäller kemisk känslighet. Rent idealt ger varje specifikt ämne

ett unikt responsmönster från sensorerna, ett mönster som sammanställs och analyseras med hjälp av databehandling. Ibland används t ex neurala nätverk, som också i någon mån kan tränas till att ge det eftersökta utslaget. Olika typer av sensorer och material som används till explosivämnesdetektion med elektroniska näsor inkluderar SAW-sensorer (Surface Acoustic Wave), halvledande polymerer, fluorescerande polymerer, fiberoptiska sensorer, elektrokemiska celler och ”microcantilevers”.

Ett annat stort område är olika typer av immunosensorer, sensorer som baseras på reaktioner mellan analyter och deras specifika antikroppar. Denna typ av reaktion har ofta mycket hög känslighet och selektivitet, men kräver olika antikroppar för olika typer av explosivämnen. Detektionen sker ofta med kolorimetriska eller optiska metoder, då man studerar förändringar i färg eller i fluorescens- eller reflektions-intensitet hos den aktuella sensorn.

En i dag ofta använd spårmängdsdetektor är IMS (Ion Mobility Spectrometry), den finns t ex på många flygplatser runt om i världen. En IMS är liten, den kan ofta bäras, den är lätt att använda och billig. Den separerar explosivämnen genom att mäta drifttiden för laddade explosivämnesmolekyler då de färdas ”i motvind” genom en kammare med ett elektriskt fält. En IMS klarar att detektera ett ytterst begränsat antal olika analyter och signalen kan dränkas av interfererande substanser. IMS är ett typexempel på en detektor som med fördel kan kopplas till GC eller MS för förbättrad separation och identifikation.

Bl a för IMS men även för MS används ibland en laser för joniseringen av explosivämnet. Med vissa laserjoniseringstekniker är det möjligt att få en mycket molekylspecifik jonisering, något som ökar detektionsmetodens selektivitet avsevärt. Molekylspecifik information kan även fås med spektroskopiska metoder, t ex SERS (Surface Enhanced Raman Spectroscopy).

Avståndsdetektion, eller ”stand off detection”, omfattar såväl aktiva som passiva detektionsmetoder. Definitionsmässigt skall operatörer och de viktigare delarna av detektionsutrustningen vara på sådant avstånd från den explosiva laddningen att dessa inte skadas allvarligt vid en eventuell detonation. Typiskt kan avståndet variera mellan 10 och 100 meter beroende på vad som kontrolleras – person eller fordon. Idealt vore att detektionen också kunde göras i realtid och då hotet närmar sig med hög hastighet (såsom är fallet med ”roadside bombs”).

De metoder som idag bedöms ha störst potential för avståndsdetektion har gemensamt att de är optiska, laserbaserade metoder. Fördelen med att använda en laser är att det är möjligt att förflytta elektromagnetisk energi över långa avstånd utan någon betydande förlust. Bland metoderna finns flera spektroskopiska, men även ickelinjära metoder och reflekterande metoder finns föreslagna.

Sammanfattningsvis finns det flera viktiga slutsatser som kan dras utifrån denna översikt:

- Sensorer behöver vara specifika och snabba och de skall klara att detektera många olika ämnen.
- Idag finns det ingen sensor som kan möta alla scenariospecifika krav som ställs på en explosivämnesdetektor.
- Sensorer måste väljas utifrån det scenario i vilket de skall användas.
- För att lösa komplexa problem krävs flera olika typer av sensorer.
- Bulkdetektionsmetoder behöver utvecklas för att kunna ge mer ämnesspecifik information, så att även explosivämnen med låg densitet eller utan kväveatomer kan detekteras.
- Insamling av explosivämnen, både i gasfas och i partikelform, behöver utvecklas.
- Behovet av avståndsdetektionsmetoder är mycket stort, men den tekniska utvecklingen har långt kvar. Inom detta område behövs stora forsknings- och utvecklingsinsatser.
- Forskning och utveckling behövs således inom spårmängdsdetektion och insamling, bulkdetektion och avståndsdetektion.
- Det är önskvärt att det både finns gemensamma standarder för certifiering av explosivämnesdetektionsutrustning och oberoende aktörer vilka kan genomföra testning och certifiering.
- Explosivämnesdetektion är ett utmanande men också mycket angeläget problem att lösa, både ur civilt och militärt perspektiv. Det är ett teknologiskt område som borde ligga steget före utvecklingen av nya hot, men istället har området halkat flera steg bakom samtidigt som behovet av tillförlitliga detektionsmetoder är ständigt ökande. Det kommer att krävas omfattande forsknings- och utvecklingsinsatser inom detta område under en lång tid framöver.

# 2 Introduction

## 2.1 Background

During the last couple of years, terrorism has emerged as a prominent threat to society in times of peace. The by far most common form of terrorism uses only conventional explosives (Figure 1) and has cost the lives of far more people than the more commonly noticed biological, chemical and radioactive threat substances. Also, for the latter, explosives are often used to distribute the harmful radioactive material.

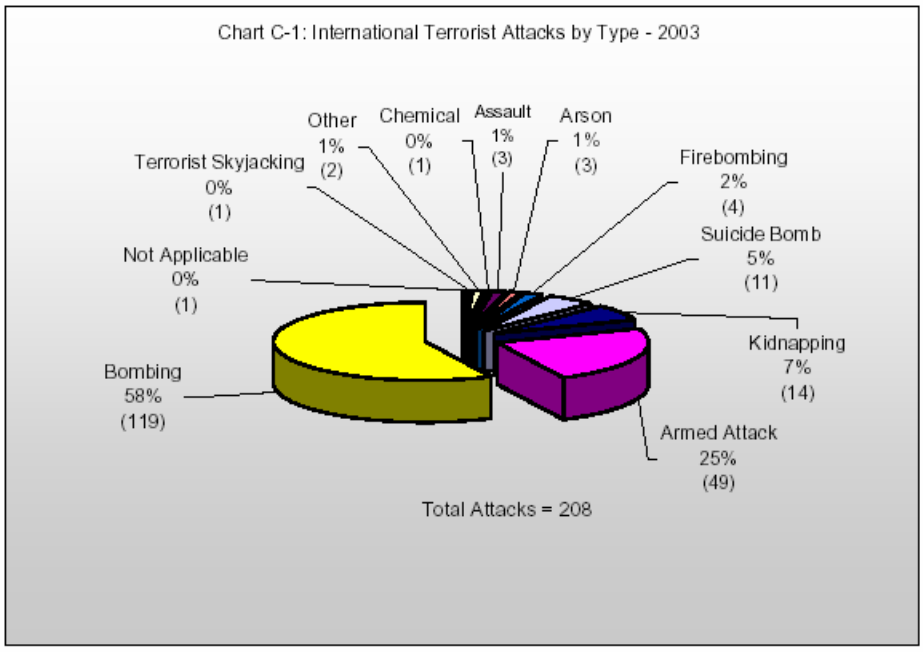


*Figure 1 About 20 people have lost their lives in terrorist attacks with chemical, biological and radiological warfare agents. This should be compared to attacks with explosives, which have killed tens of thousands of people. (From US Department of State[1]).*

The consequences of attacks with explosives are often extensive damage to property as well as people. Examples of well known attacks are the explosion on board Pan Am flight 103 over Lockerbie on December 21 1988 (270 dead) and the blasts on three commuter trains in Madrid on March 11 2004 (190 dead and 1500 wounded).

There are many places in a community where people and goods pass and where it is important to make sure that explosives do not. People are used to having their luggage checked and being screened themselves for weapons and explosives at airports, but other places are also of interest. Such places can be train stations, entrance to sports arenas, important buildings such as the parliament or a nuclear power plant or temporary check-points for vehicles or people.

Another important problem is harbour security. Enormous amounts of cargo are transported around the world on large container ships and there is very little time to check each container before it is transported from a harbour and into the country of arrival. These containers should be checked for explosives to avoid large scale terrorist attacks.

A common threat for international military operations today is Improvised Explosive Devices (IED). These are many times very difficult to reveal in time as they may be placed as roadside bombs that go off when a vehicle passes. IED's and roadside bombs constitute a daily problem in troubled spots around the world. Finding roadside bombs before they cause harm is a very tough problem with high demands for long range detection at high speed. A tragic example of roadside bombs connected to the Swedish Armed Forces is the bomb that recently killed two and wounded three Swedish soldiers in Afghanistan.

IED's can also be in the form of bombs hidden for example inside an empty building in which case the detection situation from a scientific point of view is easier to handle. Other possibilities are to find the explosives as they are being transported to where they will be used. Then detection equipment is needed to check people and vehicles at stationary or temporary check-points.

The need for good detection equipment has become of even more immediate interest in Europe as a result of the explosions in London (July 2005) and Madrid (March 2004).

## 2.2 Threat scenarios

It is important to keep in mind that different threats require different technical solutions and that a solution that is appropriate for one environment and type of situation is not necessary good for another situation. Such environments and situations can be:

- Protection of public transportation such as subways, commuter trains and buses
- Protection of rail transportation
- Protection against roadside bombs
- Airport check-points
- Monitoring of contents in container transportation
- Protection of infrastructure (power, water, communication systems)
- Response to bomb threats

Standoff detection poses requirements very different from a check-point type of scenario such as an airport check-point. Standoff detection has been given its own chapter (Chapter 5).

## 2.3 Properties of detection systems

An important weapon against IED's and other explosive devices is reliable detection methods. Some ideas involve looking for other parts than the explosive in the explosive device but in this report we will restrict ourselves to methods to detect the explosive. This is the dangerous and vital part of an explosive device and therefore what in the end needs to be detected.

*Figure 2 Left: A shoe packed with 100 g PETN. Right: Shoe inspection at an airport check-point.*

### 2.3.1 Detection principles

Detection methods can be divided into two groups, bulk detection methods and trace detection methods. Bulk detection methods look for the explosive itself in the explosive device and require presence of large amounts of explosives to find it. Trace detection methods work from trace amounts of explosives in gas phase or in the form of explosives particles. These traces are present around an object, on the packing material or on the person or persons handling the object. Methods for both bulk- and trace-detection with their respective advantages and disadvantages will be treated in this report. However, there is more focus on trace detection methods. The existence of spot tests for identification of unknown substances by colour change are mentioned in the trace detection chapter, but they are not extensively treated and no direct survey of available spot tests has been made.

The methods available today are generally able to detect a few explosives and markers* (substances with high vapour pressures that are easier to detect and which are mixed into explosives at manufacture to facilitate detection) and are too slow to allow for screening of all passengers at an airport for example. An overview of the available methods will also be given in

* Compare with for example EGIS: EGDN, NG, DNT, TNT, PETN, RDX, ANFO (optional), and markers (DNMB, o-MNT, p-MNT)

this report. It is focused on existing and emerging technologies for trace detection (including stand-off detection) but a short chapter on bulk detection is also included.

Due to time constraints during the preparation of this report, information about which techniques are used in commercially available equipment has not been clearly stated. However, a continuation of this work will be made for EDA in the project "Detection of Improvised Explosive Devices with CBRN Payload", contract 05-CAP-008. In the final report of that project, the boundaries between existing and emerging technology will be clarified. The most commonly used techniques are however based on X-ray for bulk detection and IMS for trace detection. Exact information about how a commercial instrument works is not always easily accessible, neither is an independent and reliable evaluation of performance (see chapter 2.3.3). More information about commercially available detection equipment can be found in several other reports eg. from Sandia NL[2,3] and ExploStudy[4] from École Polytechnique Fédérale de Lausanne.

### 2.3.2 Desirable development

One of the methods available for trace detection and most commonly used today is Ion Mobility Spectrometry (IMS). In a recent report[5], "*Opportunities to improve airport passenger screening with mass spectrometry*" one of the findings was that "*The relatively low chemical specificity of IMS means that the instrument alarm threshold must be set high to avoid excessive false alarms; yet, lower alarm levels are desirable to account for inefficient manual and portal sampling techniques and, possibly "cleaner" perpetrators*". It was also found that "*currently deployed IMS systems are designed to detect only a specific list of explosives and cannot easily be reconfigured to detect an expanded list of explosive, chemical and biological threat substances*".

This describes the needs for improvement very well. It can be concluded that it is desirable to find a better detection method with lower false alarm rate, higher selectivity and sensitivity and with an increased range of detectable threat substances. A complete list of desired specifications may not be easily realizable, since different applications specify different needs. However, certain criteria can be specified as universally desirable, such as;

***High selectivity:*** The selectivity of the method is of great importance since poor selectivity is detrimental to the failure-to-detect frequency as well as the false-alarm frequency.

***The limit of detection (LOD):*** A trace detection method per definition needs to be able to find very small amounts of explosives. Therefore, it is desirable to have a very low limit of detection, i.e. very high sensitivity. The exact amount detected is of less importance, but a measure of "much", "little" or "more" may provide useful information when attempting to determine the origin of a positive response.

***High detection probability / Low false alarm rate:*** For a detection method to be reliable, it must prove to have a very high probability for detecting explosives if they are present, and a very low risk of false alarms. Too many false alarms will make personnel handling the instrument less apt to take alarms seriously.

***Throughput:*** The speed by which the sample is being analyzed is of importance since it determines whether the technology can be used in real-time or not. In most situations it is necessary to check a lot of people, vehicles and luggage in a very limited amount of time. At an airport, the throughput goal is 6 passengers per minute or more[6].

***Ability to detect many / most / all substances:*** Today's explosives detection systems can only detect a few substances. The number of explosives available, especially home made explosives, is very high. The capability of a detection system to easily adapt to new threats is therefore very important.

***Harmless to humans when people are involved:*** Some bulk detection methods based on various types of radiation are not suitable for inspection of human subjects.

Other important factors are cost, size and mobility. The importance of these factors, as well as some of the above mentioned, varies with application. Below, a few other factors are listed. These relate to some of the factors considered for each detection method mentioned:

*The applicability* defined in this study as the principal applicability of a certain method not only to detect one specific explosive, but rather the lot.
*The cost* involved in utilizing the method. Within the concept of costs, also maintenance costs should be considered.
*The sample type* is also of importance. If two detection methods can be considered as equally good with respect to the other criteria, the method applicable to samples of all aggregation states (*solid*, *liquid* and *vapour*) will stand out as superior. The sample type applicable for a detection method will also be of guidance as to the complexity of the sample work-up procedures required prior to detection.
*The skill level* required of the operator handling the instrument will also influence the applicability. Most analytical systems require a quite large degree of knowledge on the principles of the methodology in order to work optimally. Also the interpretation of the signal response of the method should preferably be straightforward.
*The fieldability* is merely a factor discriminating certain methods from field use due to size, lack of robustness etc.

*The size* of the instrument (see above) could also be an important consideration. The rapid development of Micro-Electro-Mechanical System (MEMS) technology may render it possible to miniaturize some techniques without severely compromising their performance.

Depending on the scenario, not all properties of a detection system may be required at the same time. Each detection system must be appropriate for the use it is intended for. Therefore, the intended scenario must be taken into account when judging performance of a particular detection method or system.

An information list (LoD, speed, selectivity, applicability, cost, sample type, skill, fieldability and size) can be found in the end of the description of most trace detection methods. Information to complete this list is not always available. Sometimes the source is the manufacturer of a commercial instrument, sometimes it is a scientific paper. The available information, especially concerning selectivity, applicability, skill, fieldability and size has sometimes been subjectively estimated from crude knowledge about the technology needed and the information that can be extracted. This is especially true for emerging technologies where much of this information is lacking and future technical advances may change these estimations. When no information is available or it is not even possible to estimate n/a is given.

### 2.3.3 Certification of detector capability

Some countries, e.g. Great Britain and the United States, do their own testing of explosives detection equipment to determine their performance. However, there are no common standards that detection equipments are tested against and no common certification system. This means that most buyers of detection equipment are left with the data that the manufacturer provides, data that may not always be reliable.

The performance assessments of different methods given in this report are not based on any independent testing. Mostly they come from manufacturer’s data, scientific papers on the method or a subjective assessment of future potential.

It is also important to know the difference between performance and capability of a system in the lab and in a real environment. A lab environment often provides the best of circumstances, good “weather conditions” and no or little problems with interferents. The real environment on the other hand provides a wide variety in temperature, air humidity and weather conditions (at least in an outdoors environment) and is full of interfering substances, both in vapour phase and in particle form. In the lab, many tests at least begin with pure substances, while explosives used in real life are usually formulated with plastics or wax.

# 3 Bulk Detection Methods

Bulk detection of explosives is mostly based on the detection of atomic elements or density, often coupled with imaging. Most explosives (TNT, RDX, HMX) contain the elements hydrogen, carbon, nitrogen, and oxygen. Even though these elements are found in all materials, the element ratios and concentrations are material specific and lead to the possibility of identification. C/O and N/O ratios are used to differentiate explosives and innocuous materials[7] (Figure 3). Thus, the problem of identifying explosives is reduced to elemental identification. However, this information is not very selective. It can however indicate the presence of a possible threat. By accumulation of the signal for a specific element, the amount of that element inside the object can be deduced. The more different elements a system can detect and analyze the more sensitive it is and the fewer false alarms occur. A set of detectors allows taking an image of the investigated object for visual analysis. Some detection techniques also give information about material density and average atomic number (Figure 4).

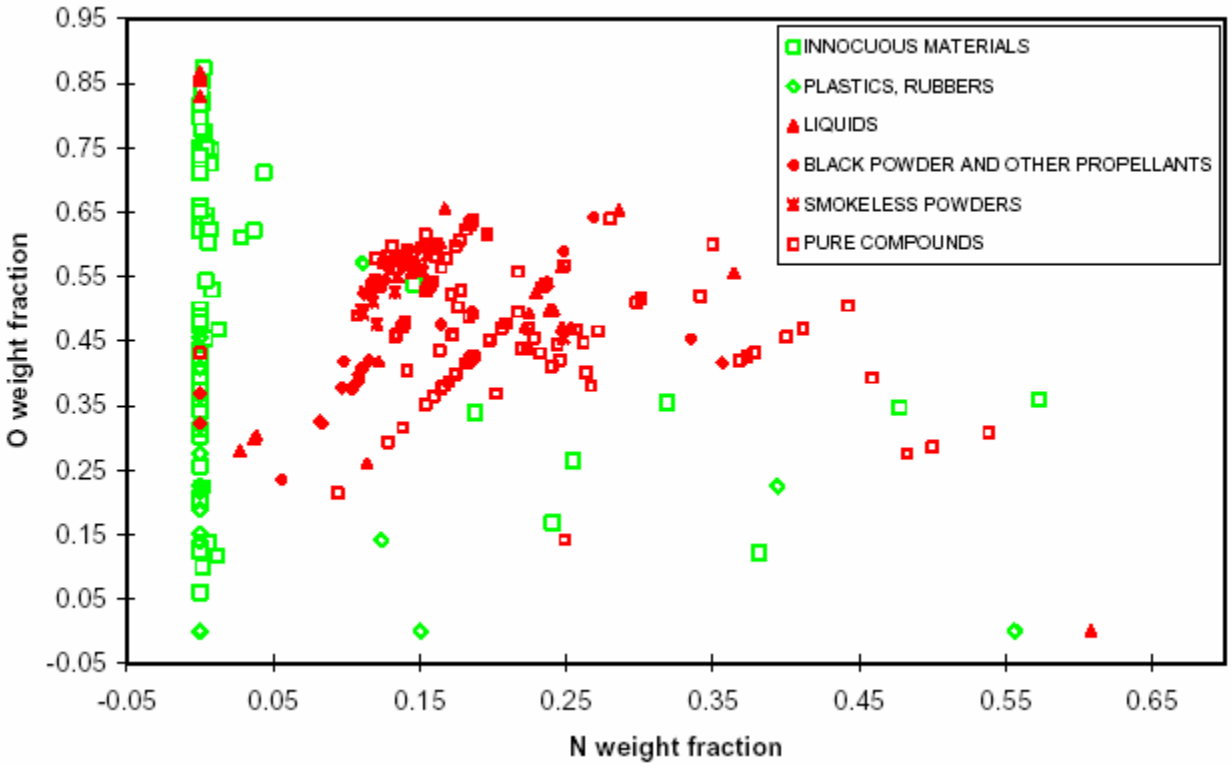


*Figure 3 Oxygen weight fraction plotted against nitrogen weight fraction for different types of explosives and innocuous materials. From Hallowell[8].*

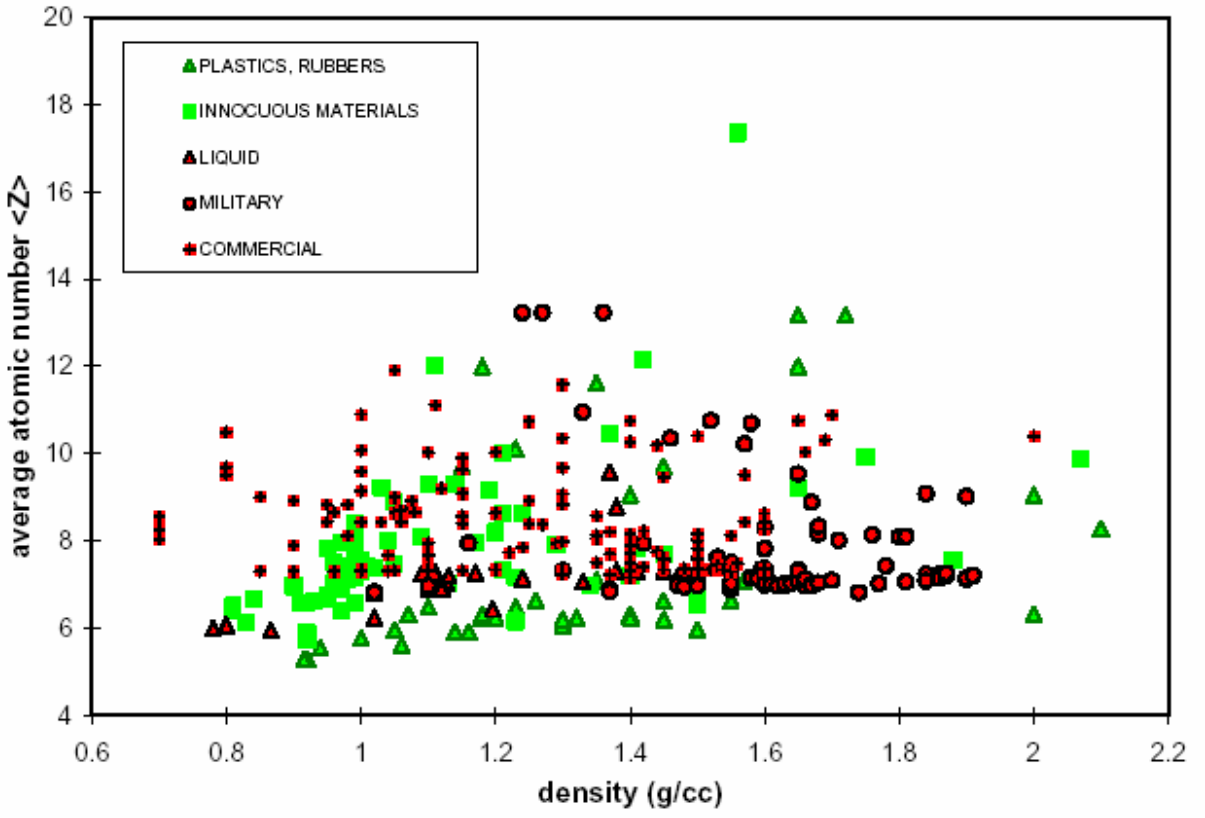


*Figure 4 Average atomic number plotted against Density for various explosives and innocuous materials. From Hallowell*[8].

Most bulk detection methods rely on nuclear techniques which result in fast, sensitive, non-intrusive and non-destructive elemental characterization[9].

## 3.1 X-Ray Scatter

X-rays emerge when fast electrons hit a barrier and are slowed down very quickly. In today's x-ray sources the electrons are produced by a heated cathode and accelerated with a voltage of around 200 V. The barrier is an anode made out of a high Z* material (Mo, Cu, or W). There, the electrons release their energy and transform it into continuous radiation and heat.

X-rays penetrate most materials deeply and are therefore ideal for investigating the contents in containers, packets, and suitcases. The radiation is harmful to health but modern, sensitive detectors allow the use of very small doses of x-rays so that it is even possible to search humans under certain circumstances[10].

Investigating objects by means of x-ray scattering is usually combined with imaging. A person has to inspect the photos of the contents of every investigated item on a monitor and decide whether they are dangerous or not. X-ray scanning can be done in transmission, where source and

* Z denotes the atomic number of the elements

detector are located opposite to each other with the object under investigation in between. More recent x-ray imaging uses backscattering where both detector and source are on the same side of the object. Figure 5 shows pictures of the same suitcase taken in both modes.

*Figure 5 Two ictures on left: The Z Backscatter image of a laptop in a briefcase clearly shows 3 concealed organic -- IEDs hidden in a laptop. The dual-energy transmission image is able to see fine details of the laptop, but it does not detect the organic material hidden in the dense electronics of the laptop. Note: Dual-energy X-rays color organic materials as orange, mixed materials as green, and metallics as blue. Two pictures on right: Gemini's Z Backscatter reveals $4,000 worth of illegal drugs concealed in a PDA and 10 feet of detonator cord wrapped around a laptop power cord - both of which the dual-energy image missed. Courtesy of American Science and Engineering, Inc. ©2006*

### 3.1.1 Compton-Scattering

The inelastic scattering of x-rays on weak bound electrons of a target is called Compton scattering. The impinging radiation looses energy and changes direction. The energy loss depends on the scattered angle while the total scatter intensity depends on the local electron density, a fundamental property of the target. Studying Compton scattering allows determination of this density which is proportional to the physical density for all low Z elements except hydrogen[11].

### 3.1.2 Coherent scattering

Coherent x-ray scattering occurs when photons are scattered elastically on the electrons in a target. Photons with constant energy are scattered on a specific target by a specific angle (angular dispersion). In the same manner, placing the detector at a fixed angle and using continuous x-ray radiation, information about the target (energy dispersion) is obtained. Thus, it is possible to measure the molecular structure of the target by either varying the angle of scatter at a constant energy, by varying the energy at a constant angle of scatter, or by varying both parameters. The scattered intensity and the atomic number of the scattering target are inversely proportional, therefore allowing the elemental composition of the target to be determined[11]. The relevant data sets of angles, photon energy, and relative signal intensities, for all the elements are found in literature.

### 3.1.3 X-Ray fluorescence (XRF)

XRF results from removing an electron from one of the inner shells of a target molecule due to incident x-rays. The absorption of a photon with an energy $E_0$, higher than the appropriate absorption edge leads to the removal of an electron, mostly of the K-shell, which is bound with the energy $E_K$. The energy balance requires that the removed electron carries the energy $E_0$- $E_K$. The resulting hole is filled up by electrons from outer shells. At the same time, the difference in bonding energy of those electrons will be emitted in form of photons with characteristic energies. Those peak energies in the emitted spectrum and the relative heights of the signals can be compared with the literature and lead to the identification of the high Z constituents of the sample. Thus, this method is useful to detect detonators of bombs which are frequently composed of high Z materials[11].

## 3.2 Neutron and γ -based techniques

Neutrons and γ-rays are able to penetrate the item under inspection through various materials to large depths. Thus, they are able to interrogate volumes ranging from suitcases to Sea-Land containers[7]. In the airline industry, it has been proposed to inspect every checked luggage for explosives by means of neutrons for the identification of the nitrogen content within. Both neutrons and γ-rays pose health hazards which make this technique applicable only for cargo situations. Furthermore, neutron-based techniques do not have a good potential for standoff detection

Neutron based techniques achieve explosive detection mainly through the production of characteristic gamma rays by nuclear reactions[12]. Irradiation of an object with neutrons can initiate one of several nuclear reactions with the chemical elements (Figure 6). In most cases a result of these reactions is the emission of γ-rays with characteristic and distinct energies.

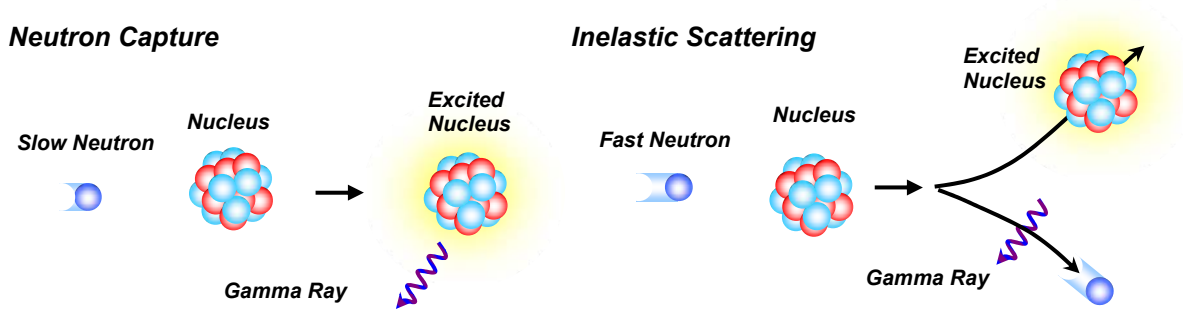


*Figure 6 Nuclear reactions initiated by thermal neutrons (capture reactions, left) and fast neutrons (inelastic scattering, right).*

Slow neutrons impinging on atoms in the item under investigation lead to the capture of a neutron and the emission of characteristic γ-rays (left). In contrast, when fast, a high energetic neutron is absorbed by the nucleolus it emits not only γ-rays but also another neutron or a proton. In that case, both emitted particles can be analyzed (right).

Depending on the chemical elements that should be measured, neutrons of several energies have to be used. The excitation of lot of elements like H, C, S, Cl, Fe etc. is possible through neutron capture reactions. However, other elements like C and O can be excited only by fast neutrons. Therefore, the required neutron source will be varying for different investigations. The outgoing signals are detected by appropriate detectors (usually bismuth germinate (BGO) scintillators) outside the object.

### 3.2.1 Thermal neutron analysis

Fast neutrons from a $^{252}$Cf-source ($10^7$ neutrons/s) are slowed down in a moderator and sent to the inspected area where they are eventually captured by the elements characterizing the investigated volume. The characteristic gamma radiation originating from the neutron induced reactions in several elements is detected and analyzed. This technique is deployed to search for an anomalous concentration of for instance nitrogen. Thus, it is implemented in a system to detect landmines for humanitarian demining. In this system, the lead-shielded neutron source is inserted in a spherical polyethylene cylinder. The geometry of the moderator is selected so that the neutron flux at the typical depth (20 cm) where landmines are buried is optimal[13].

### 3.2.2 Associated particle technique

In this technique, neutrons are produced by the reaction deuterium + tritium (d+t) that yields one neutron of 14 MeV and one alpha-particle at 3.5 MeV emitted back-to-back in the center of mass of the compound system. The possibility of detecting the α particle with high efficiency allows to determine the direction and the time of production of the associated neutron. In this way, the beam of tagged neutrons can be directed on the area which should be investigated. Like for the thermal neutron analysis, the characteristic gamma rays are measured but with reduced environmental background[13].

### 3.2.3 Pulsed Fast/Thermal Neutron Analysis (PFTNA)

The PFTNA principle combines irradiation of an item with fast and slow neutrons to make detection of many different elements possible. This can be accomplished by the use of a pulsed neutron generator.

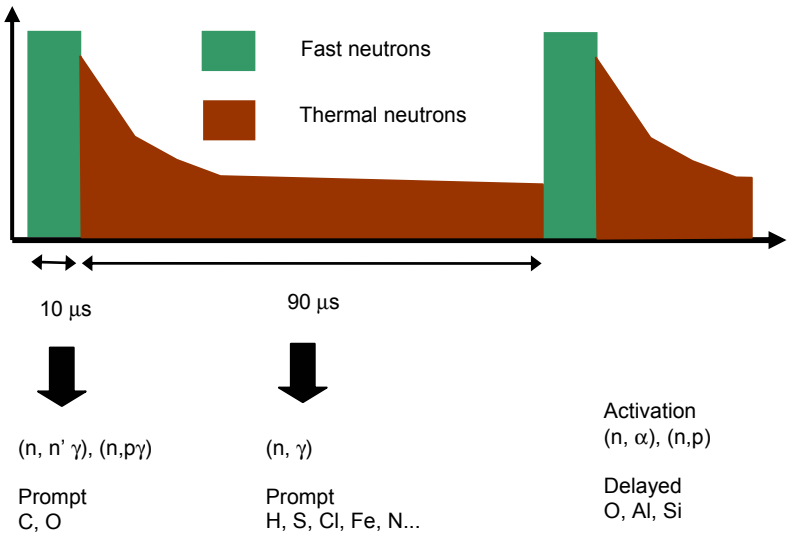


*Figure 7 Pulsed neutron generator time sequence (after Vourvopoulos[7]).*

The pulsed neutron generator utilizes the d+t reaction providing 14 MeV neutrons which initiate several types of nuclear reactions on the object of investigation. During the neutron pulse the γ-ray spectrum consists mainly of the γ-rays from the reactions between fast neutrons and elements like C and O. Between pulses, some of the fast neutrons which are still in the target loose energy through collisions with light elements composing the object. When these neutrons have energy lower than 1 eV, they can be captured by such elements as H, S, Cl, Fe, and N. The spectral data of both sets of reactions are detected by the same detector but stored in different memories of the data acquisition system. This procedure is repeated with a frequency of around 10 kHz. After a predetermined number of pulses, a longer pause allows detecting γ-rays emitted from elements such as Si, Al, and P that have been activated[7]. Therefore, by utilizing fast neutron reactions, neutron capture reactions and activation analysis, a large number of elements contained in an object can be identified in a continuous mode.

### 3.2.4 Neutron backscattering

Fast neutrons from a radioactive source like $^{252}$Cf are sent directly on the investigated target. In contrast to x-rays, neutrons are scattered on the atomic nucleus. The probability of emission of backscattered neutrons is several orders higher compared to that of the emission of specific γ-rays. This leads to the possibility of having a large counting rate even by using low activity neutron sources[14]. The flux of thermal or epithermal neutrons scattered backward is proportional to the inverse atomic number of the elements in the inspected volume. Thus, this method is ideal to detect anomalous concentrations of the lightest element, hydrogen. Neutron backscattering is

therefore used for land mine detection, since hydrogen concentrations are high both in the actual explosives in landmines and in their plastic cases[13,15].

## 3.3 Magnetic techniques

Magnetic resonance techniques rely on exciting either the nuclear magnetic resonance (NMR) of nuclei in explosive molecules in a magnet field or on the nuclear quadruple resonance (NQR) unique to the electric field gradients in explosive molecules.

### 3.3.1 Nuclear Magnetic Resonance

NMR is able to distinguish between different chemical species which makes this technique an obvious candidate for material detection applications. NMR works on nuclei that have a spin $I \neq 0$ , like $^{1}H$, $^{13}C$ or $^{14}N$, but the most important probe for NMR is $^{1}H$. These spins are orientated in the external magnetic field and changed later on by an element-specific excitation with radio frequency. The changing of the spin orientation is detected.

With today's technology, it is straightforward to observe magnetic resonance signals for a large number of explosives in a laboratory setting, but the desired application to identify these materials in the field is impossible[16]. There are severe practical difficulties associated with the use of a large magnetic field needed for such measurements. The difficulty of supplying a sufficiently large homogenous magnetic field is an obvious problem. Furthermore, benign material devices like magnetic recording media in packages or suitcases would be erased by the external magnetic field.

### 3.3.2 Nuclear Quadrupole Resonance

A method for observing magnetic resonance without a magnetic field is NQR. To use NQR, a nucleolus with a quadruple moment must be available, which is true for all nuclei with spin $I>1/2$, f.i. $^{14}N$, $^{35}Cl$, $^{37}Cl$, $^{39}K$. The quadruple moment results from a non-spherical charge distribution in the nucleus. This moment interacts with the electrical field gradient of the electrons around the nucleus and the chemical surrounding[16]. As a result of this interaction different spin orientations with energy levels occur. Like for NMR, transitions between those levels can be generated and detected.

The basic instrumentation and techniques required for those measurements are the same as those for traditional NMR though without the magnet. With NQR it is possible to detect buried metal-free mines[17].

## 3.4 Millimeter-Wave Imaging and THz Spectroscopy

A novel technology to detect explosives and other illicit substances sealed in non-metallic containers is Terahertz Spectroscopy[18]. Clothes and many other materials become nearly transparent for electromagnetic waves with a wavelength longer than 300 microns (~1THz). Imaging in this region allows the detection of explosives hidden under clothing without the danger of ionizing radiation. The method relies on the excitation of vibrational modes which may also provide spectroscopic and structural information.

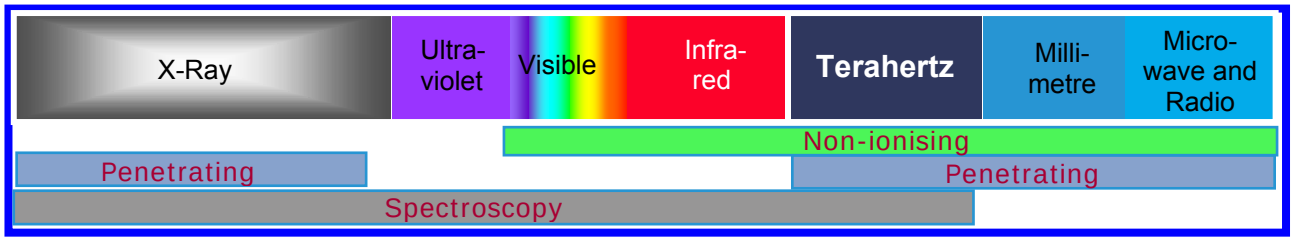


*Figure 8 Illustration of the electromegnetic spectrum showing the THz-region. (From Kemp[19].)*

### 3.4.1 Millimeter-Wave Imaging

Millimeter wave technology is an imaging technique to look through materials. Special sensors detect naturally emitted or from objects reflected waves with a wavelength of approximately 3 mm (equivalent to a frequency of 100 GHz). Clothing is transparent for this wavelength but dense objects reflect a clear profile by blocking the body's natural radiation[20]**.** Each type of material has its own frequency response, a feature which may be useful for material identification in the future.

In addition to the above-mentioned passive mode, the system can be operated in an active mode[21]. This technique is identical to the principle of a bat's orientation in the darkness. High frequency radiation (100 GHz) will be emitted from a source, followed by detection of the reflected waves. The radiation is completely harmless to people which makes the technique applicable for screening humans[20].

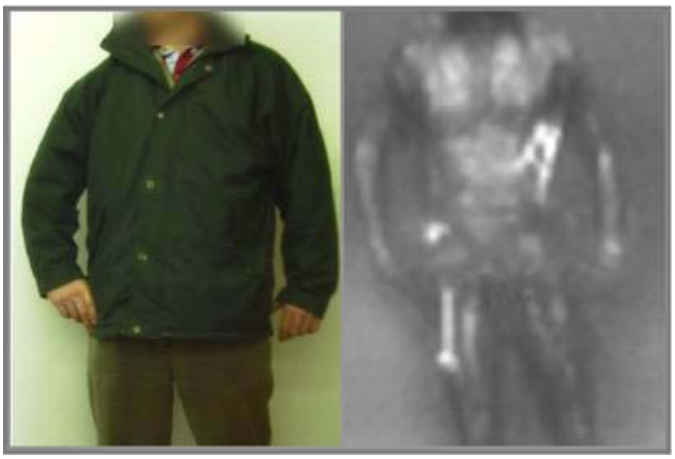

*Figure 9 Visualization of threat objects hidden under clothing by means of mm-wave technology. (Courtesy of Smiths Detection).*

### 3.4.2 Terahertz Spectroscopy

Irradiation of the object under investigation with electromagnetic radiation in the terahertz range results in vibrations, eg. the torsion of $NO_2$[22]. The absorption and reemission of the radiation which passed through a substance is individual to the substance and can be used to its identification. However, the sharp spectral lines associated with those vibrations in the gas phase are broadened in the liquid or solid phase which complicates unique identification[10]. Nevertheless, the characteristic transmission or reflection frequency can be used for spatial interferometric imaging. Since the penetration of terahertz waves in textiles, plastic, wood and sand is reasonable, objects hidden behind those materials can be visualized[23]. Health hazards do not appear with the use of terahertz radiation, so this technique can be used to screen people for hidden objects[10].

Kemp[24] has investigated the teraherz spectra of TNT, HMX, PETN, RDX, PE-4 and Semtex and found that they all show characteristic features in the range 0.5 to 3 THz. Tribe[25] investigated possible interferents and concluded that no significant confusion was found between explosives and harmless materials.

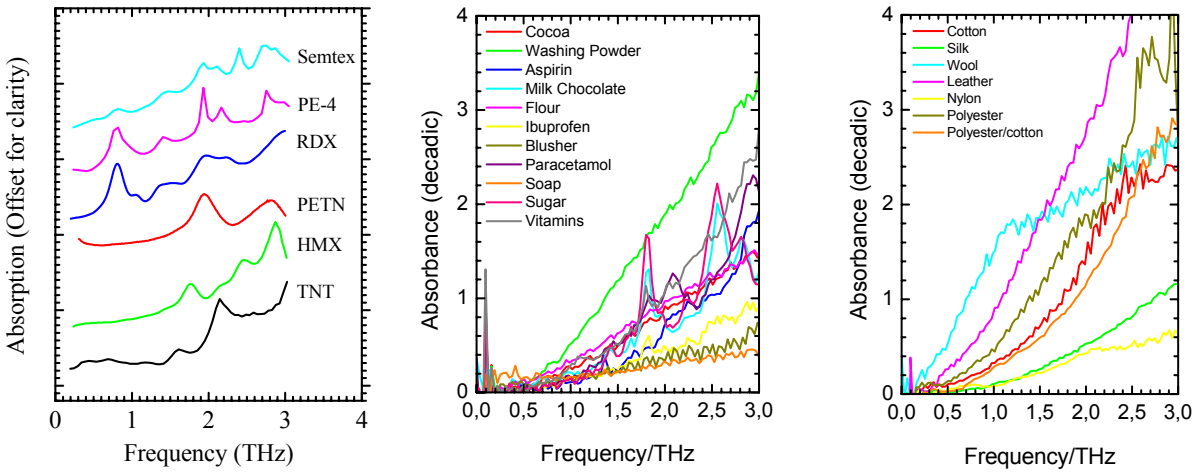


*Figure 10 Investigation of spectroscopic properties of some explosives and possible interferents in the THz region (From Kemp[19])*

# 4 Trace detection methods

Trace detection methods utilises the trace amounts of explosives present in gas phase or as explosives particles around an object, on the packing material or on the person or persons handling the object. Such traces are very difficult to avoid when handling explosives. To be able to take advantage of trace detection methods, sampling of vapours and particles is essential. Sampling of particles is mentioned in chapter 4.1, however, particle sampling has not been the scope of this study, so it is only a very brief description to make the reader aware of its importance for trace detection. No matter how good a trace detection method is, it is not useful at all without good sampling methods.

When available, information about limit of detection, speed of detection, selectivity, applicability, cost, sample type, skill needed for operation, fieldability, and size is given (see also chapter 2.3.2). However, this information is not always available, in which case n/a is given.

## 4.1 Collection/Sampling

Since many explosives have very low vapour pressure, there is not always enough explosives vapour available for gas phase sampling. In these cases it is necessary to collect explosives particles. Even when very thoroughly trying to avoid it, the handling of explosives leaves residues on hands and clothes. Explosives residues will be present on suitcases, passports and boarding passes. With 10 % collection efficiency a tenth generation fingerprint contains enough material to be detected by current trace detection technology[4].

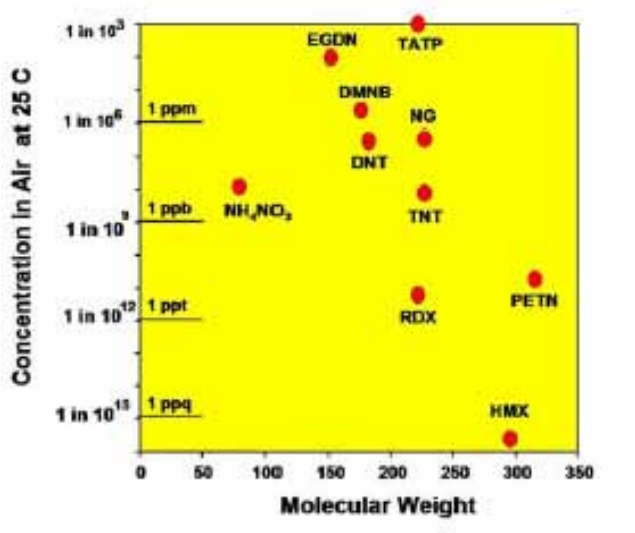


*Figure 11 Vapor concentration of high explosives in saturated air at 25°C. From Thiesen[3].*

Collection or sampling of explosives differs greatly depending on what type of environment is of interest. Detection in airports, with a large stream of passengers, requires very fast collection and detection, whereas detection of explosives in a building is less demanding. This literature review will not cover all types of collection/sampling systems for explosives, but a few examples will be given.

Most trace detection systems today have particle sampling by swipes (Figure 12). This is a time consuming procedure in which a swab is used on a piece of luggage and the swab is then analyzed for traces of explosives.

*Figure 12 Swiping a bag for particles for detection with Smiths Detection IonScan 400B (Courtesy of Smiths Detection.)*

It is desirable to make the collection of particles faster and without touching the inspected object or person. A system designed for sampling in e.g. an airport has been presented in a patent[26]. It is a walk-in inspection apparatus for production of air samples containing vapours of explosives, drugs or other substances carried by a person. In the collection of an air sample a blower outside the booth sucks a large volume of air around the person and horizontally through the funnels in the end wall and through ducts into a collection manifold for subsequent analysis. The dislodging of substances is facilitated by puffs of air blowing at the person.


*Figure 13 Left: Air-sampling walk-in apparatus for use in e.g. airports (From patent by Arney[26]). Right: The Sentinel II from Smiths detection, puffs air on occupants to dislodge particles for chemical analysis. (Courtesy of Smiths Detection.)*

## 4.2 Multiple parameter detection

The advantage with multiple detection methods or of one method measuring multiple parameters is well described by the following quote from "*Existing and Potential Standoff Explosives Detection Techniques*" [27]:

> *"Two or more explosives technologies are considered completely orthogonal if the detection methods detect independent characteristics of the explosives device. Three potential significant advantages of a system of orthogonal detection technologies are:*
>
> *1. A higher probability of detecting explosives over a range of potential threats,*
>
> *2. Increased difficulty in defeating the detection system, and*
>
> *3. Greater effectiveness in detecting explosives than any single technology."*

This is very important for the ability of a detection system to selectively identify multiple threats among all harmless substances also present in the detection environment.

In order to enhance selectivity and thus the detection limit of an explosives detection system, most systems use a separation step before the actual detection step. Separation can be achieved in several ways, but gas or liquid chromatography seems to be the most favoured methods. Especially gas chromatography is used in combination with a wide variety of detection methods (see Chapter 6).

Another example of how to achieve multiple information from a detection method is Laser Ionization Mass Spectrometry where a selective ionization step is followed by a mass spectrometer (see Chapter 0).

## 4.3 Detection methods

### 4.3.1 Chemiluminescence

Chemiluminescence (CL) can be defined as the characteristic emission of radiation from a molecule, atom or effective fluorophore, in an excited state, produced in an exothermic chemical reaction. It can take place in gas, liquid and solid state. In recent years, CL has become a powerful analytical tool for selective and sensitive detection of chemical species. CL applications in analytical chemistry have numerous advantages such as high sensitivity, a wide linear range, simple and inexpensive instrumentation, and considerable reduction of the background noise. On the other hand, the lack of selectivity (one of the most important disadvantages) can be improved by coupling CL with different separation methods[28].

Many explosives contain nitro ($NO_2$) or nitrate ($NO_3$) groups and these compounds can be detected by CL-based detectors. In order to improve the selectivity, most CL detectors are also coupled to a gas chromatograph. In order to obtain structural information, a second system, such as CL-MS is preferable. CL has been proved useful in detection of explosives such as hexogen (RDX), nitrotoluenes, dinitrotoluenes, trinitrotoluene (TNT), nitroglycerine, pentaerytritol tetranitrate (PETN) and ethylene glycol dinitrate (EGDN)[28].

An important CL-based system for the detection of trace levels of explosives is the thermal energy analyzer (TEA)[29]. Briefly, the fundamental operating principle is based on the chemiluminescent reaction between nitric oxide and ozone. Nitrogen containing components are pyrolysed at high temperature and nitrogen monoxide formed can be determined using the chemiluminescent reaction between this and ozone, which results in light emission, detected by using a photomultiplier tube. This reaction can be summarised as follows:

$$NO + O_3 \rightarrow NO_2^* + O_2 \qquad NO_2^* \rightarrow NO_2 + light$$

Gas chromatography with selective chemiluminescence detection, TEA, has been used by the Forensic Explosives Laboratory (Kent, UK) as its principle technique for explosive trace analysis since 1989. The sampling process usually used was a cotton wool swab. The identification of an explosive trace by GC-TEA is based on a comparison of relative retention times with those of explosives in a standard solution analysed both before and after the sample. A mixture of two retention reference markers is co-injected with every sample and standard solution, and retention

times are measured relative to these. TEA has been used both in public places and in soil in order to determine the presence of explosives. This detection technique has been suggested in a patent concerning how to collect air-samples from passengers at e.g. airports[26].

Limit of detection: nanogram
Speed: 20-45 s total analysis time
Selectivity: increased by GC or other types of separation techniques
Applicability: nitro- and nitroso compounds
Cost: low

Sample type: liquid, solid and gaseous samples
Skill: none
Fieldability: good
Size: small

### 4.3.2 Desorption electrospray ionization (DESI)

Desorption electrospray ionization (DESI) is carried out by directing electrosprayed charged droplets and ions of solvent onto the surface to be analyzed. The impact of the charged particles on the surface produces gaseous ions of material originally present on the surface. The resulting mass spectra are similar to normal ESI mass spectra in that they show mainly singly or multiply charged molecular ions of the analytes[30,31].

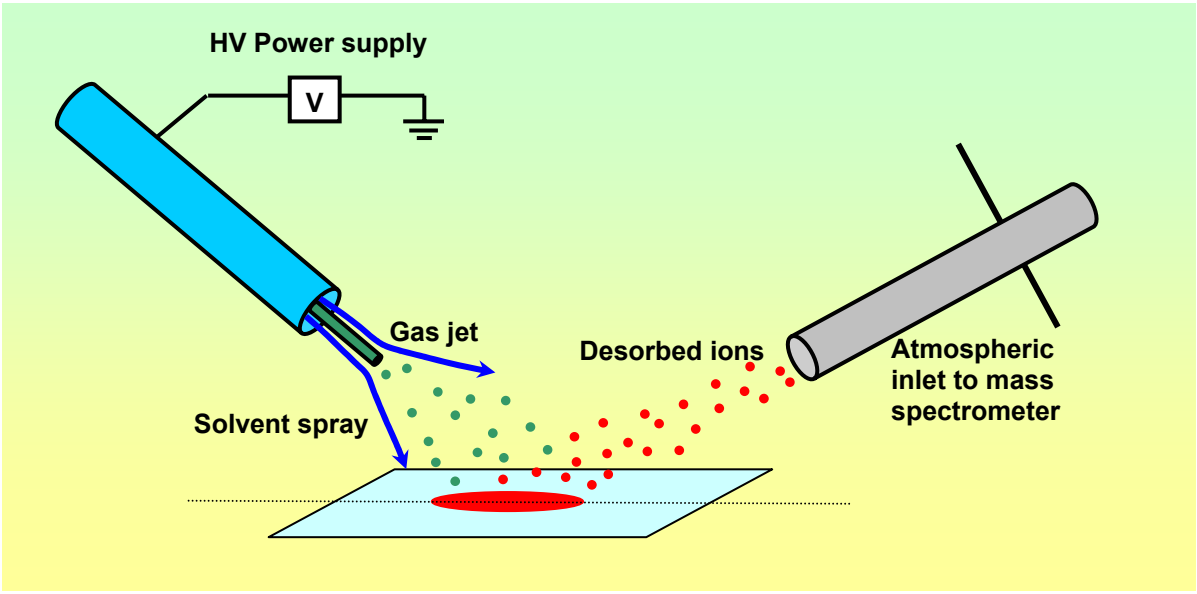


*Figure 14 The principle of DESI.*

In its simplest form, desorption electrospray experiment (Figure 14) uses an aqueous spray directed at an insulating sample or an analyte deposited on an insulating surface such as polytetrafluoroethylene (PTFE) (other materials such as metal and paper are also useable). The desorbed ions are sampled with a commercial ion trap mass spectrometer equipped with an

atmospheric interface connected via an extended and preferably flexible ion transfer line made either of metal or an insulator.

DESI has been used in trace detection of RDX, HMX, TNT, PETN and their corresponding compositions Composition C4, Semtex-H, Detasheet [32]. The analysis is performed under ambient conditions and in short time (< 5 s). Increased selectivity is obtained by using MS/MS detection or by adding additives in the spray solvent. In the analysis of RDX, HMX and TNT, additives were used but the plastic explosives were analysed without sample preparation. The limit of detection of the neat explosives was subnanogram in all cases and subpicogram in the case of TNT. DESI also allowed for detection of explosives in complex matrices, including lubricants, household cleaners, vinegar and diesel fuel[32].

Recently, also detection of TATP on paper, metal and brick as well as in methanol, vinegar and diesel, has been reported[33].

Limit of detection: subnanogram (RDX, HMX, PETN, TNT, Comp C4, Semtex-H, Detasheet), subpicogram (TNT)
Speed: < 5 s total analysis time
Selectivity: enhanced by using MS/MS and/or reactive desorption (ion/molecule reactions)

Applicability: all types of compounds
Cost: n/a
Sample type: liquid and solid samples
Skill: n/a
Fieldability: c.f. size
Size: likely to be small due recent advances in miniature mass spectrometers.

### 4.3.3 Matrix-assisted laser desorption/ionisation mass spectrometry

Matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) is a soft ionisation method followed by mass detection. It is widely used for analysis of both organic and biological polymers. In a typical implementation, the analysed sample is co-crystallised with a matrix, which is a compound that can absorb energy from the laser pulse. This energy then enables a phase transition of both matrix and sample from solid to the gas phase, whereby the sample is ionised and its mass-to-charge (*m/z*) ratio is determined. One of the disadvantages with conventional MALDI is that the matrices used are almost always acidic. This prevents the use of MALDI to analyse compounds that decompose in the presence of acid. Another problem when analysing low molecular weight samples is that the matrix ions interferes with the sample ions in the mass spectrum leading to lower sensitivity. To overcome these problems several solutions have been proposed including the use of high-molecular weight matrices[34]. Other less time consuming methods do not used a matrix at all. Matrices such as porous silicon surface (DIOS), non-porous

membranes[35], aerogels[36], liquid[37] and porous polymer monolithic matrices[38] have also been used to improve the analysis of low-molecular compounds.

The trace detection of explosives using MALDI-MS has been proposed in a patent[38], but no experimental evidence has been found.

Limit of detection: n/a
Speed: n/a
Selectivity: good
Applicability: all type of compounds
Cost: n/a

Sample type: solid and liquid samples
Skill: n/a
Fieldability: n/a
Size: n/a

### 4.3.4 Electronic noses

An electronic nose is defined as an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours[39]. The electronic nose is usually composed of a chemical-sensing system and a pattern-recognition system, such as an artificial neural network. Ideally, every vapour presented to the electronic nose sensor array causes some or all of the sensor elements to respond differentially, producing unique response patterns that encode each vapour. Computational analysis of these patterns generates a classifier that correlates response patterns with specific vapours. The use of such response patterns provides a combinatorial advantage that allows the discrimination of more odours than there are types of sensors[40].

The sensing system could either consist of a single sensor or an array of sensors. Sensor arrays offer several advantages over single sensors - selectivity to a wider range of analytes, better selectivity, multicomponent analysis, and analyte recognition - rather than mere detection. Sensor arrays are also more analogous to the olfaction system (dog's nose), which contains multiple receptors [41].

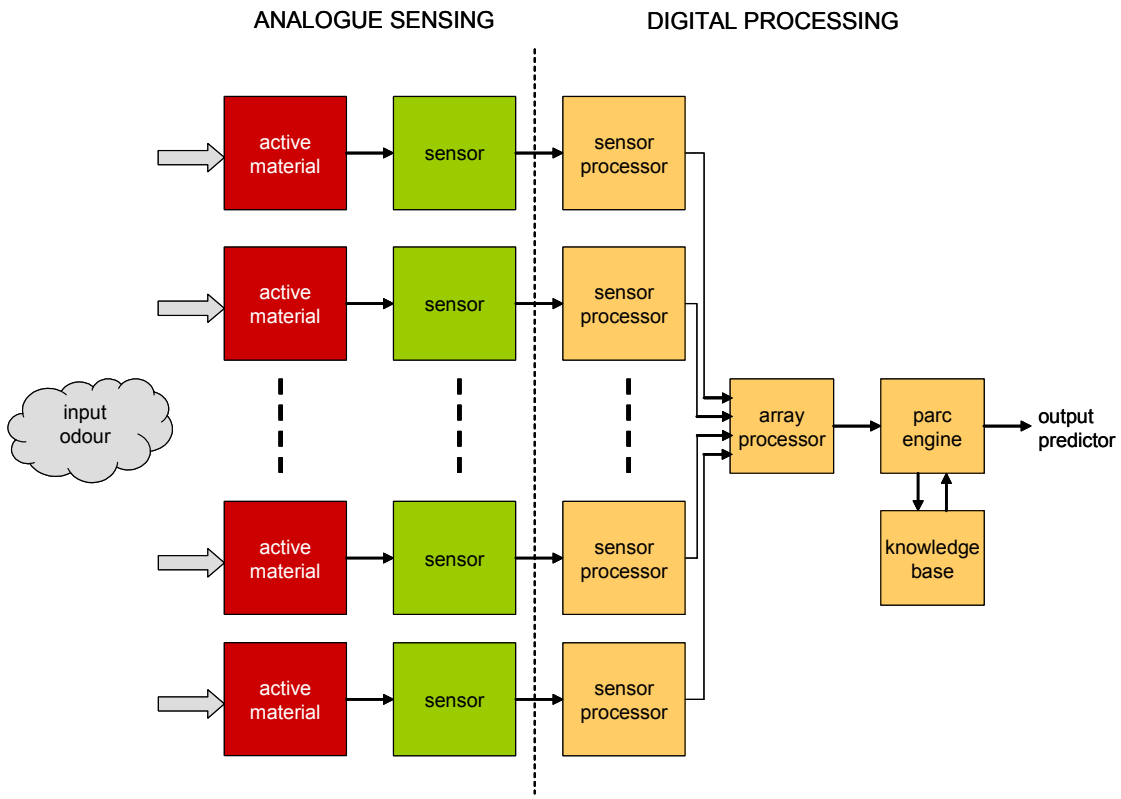


*Figure 15 Generic structure of an electronic nose (After Gardner[39]).*

There are several important considerations when evaluating gas or vapour sensors for electronic noses[42]:

- selectivity (individual sensors should respond to a broad range of compounds, but at the same time the response shown by different sensors within the array to a particular compound should not be highly correlated)
- response time
- saturation
- reproducibility in response over time (drift)
- reproducibility in response between sensors of the same type (e.g. different batches)
- poisoning (irreversible binding of an analyte to the sensor material)
- sensitivity to changes in temperature, humidity, and flow rate.
- size
- cost

There are several chemical sensor materials available; (a) inorganic crystalline or polycrystalline materials (semiconductors, metal oxides, zeolite absorbent materials, metallic catalysts). In general, these materials are robust and are often operated at elevated temperatures where they function as catalytic materials in irreversible, or chemically reactive, sensors; (b)

organic materials and polymers. These materials are more flexible in design and more readily modified chemically to develop arrays of materials with different properties - a feature which lends itself well to their application in electronic noses. In general, these materials are used at, or close to, room temperature and operate as reversible sensor materials; (c) biological derived materials (proteins, enzymes, antibodies). These materials offer considerably selectivity and have been much investigated as components of biosensors and immunoassays (see Chapter 4.3.5)[42]. Materials used for explosives detection includes surface acoustic wave devices, conducting polymers, fluorescent polymers/microspheres, fiber-optics, electrochemical cells, and microcantilevers. These will be described in more detail below.

#### *4.3.4.1 Surface acoustic wave sensors (SAW-sensors)*

The principle of surface acoustic wave sensors is that an acoustic wave confined to the surface of a piezoelectric substrate material is generated and allowed to propagate. If a vapour is present on the same surface, then the wave and any substances in the vapour 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 vapour[41]. The polymer film, in which the wave propagates, can also contribute to mass increase, swelling, and changes in the viscoelastic properties (plasticization or stiffening). Normally, these effects affect the velocity of the SAW, which can be readily monitored as a shift in the resonance frequency of the SAW sensor[43].

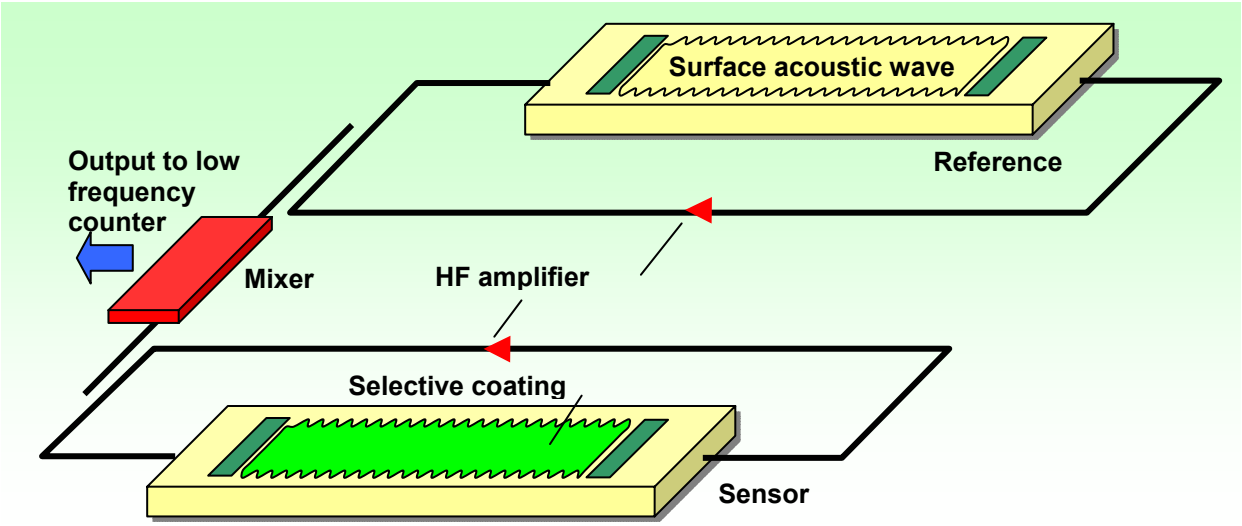


*Figure 16 Schematic drawing of a SAW sensor.*

SAW devices coated with a thin layer of chemo selective polymer can provide highly sensitive transducers for the detection of vapours or gases and have been evaluated as a detector for

explosives such as TNT and DNT[43]. Houser showed that the detection limit of 2,4-DNT by a hexafluoroisopropanol functionalized aromatic silicone polymer surface coated SAW was 92 ppt[43]. SAW sensors coated with functionalized cyclodextrin polymer films are also capable of detecting DNT vapour at ppb levels, and the authors suggest that in order to detect explosives at ppt concentrations, a delivery system with a pre-concentration tube may be necessary [44]. A SAW sensor coated with carbowax-1000 have been tested for different concentrations of 2,4-DNT at 50 ml/min of analyte and desorbing gas. The sensor was found to be sensitive (values of 117 ppb of DNT were reported) and gives linear response in the ppb range[45].

#### *4.3.4.2 Sensors based on conducting polymers*

Conducting polymers have attracted much interest as sensor materials for use in electronic noses for several reasons: a wide range of material can be synthesised; they respond to a broad range of organic vapours; they operate at room temperature. There are a large number of electrical conducting polymers. The common feature of each is the presence of a conjugated π-electron system which extends over the whole polymer backbone. The most commonly applied polymers for gas sensing applications have been those based on pyrrole, aniline, or thiophene monomers[42].

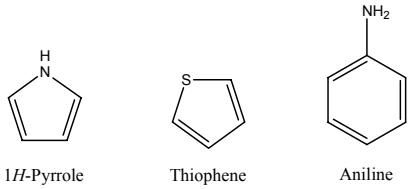


*Figure 17 The most commonly applied polymers for gas sensing applications have been those based on pyrrole, aniline, or thiophene monomers*

After exposure to a vapour of volatile substances, the changes in conductivity of conducting polymers are observed. The variation of the individual conductivity of conducting polymers can be treated as a significant ‘‘signature’’ of the volatile compound for an electronic nose[46,47].

Ultra-thin films of conducting polymers, such as polyaniline, have been used in gas sensors for $NO_2$ detection. This sensor had good sensitivity to $NO_2$ and the response time to 20 ppm of $NO_2$ was about 10 seconds[48]. Variations in $NO_2$ have also been monitored using composite materials based on gold particles dispersed in a highly plasticised polyvinyl chloride matrix. The response time is, however, for the moment too slow (4 hours) for the sensor to be useful for detection of explosives[49].

#### *4.3.4.3 Sensors based on fluorescent polymers/microspheres*

Several electronic noses use fluorescent polymers/microspheres as sensors[50,51]. They react to volatile chemicals such as nitrogen-based compounds from explosives. They have been successfully employed in the detection of TNT and one of the manufacturers claim that it has the same sensitivity as a canine. The function behind this type of sensor is described in another section of this review (see Chapter 4.3.7).

#### *4.3.4.4 Fibre-optic based sensors*

Another type of electronic nose uses a complex sensor array of fibre-optic cables[41]. A fiber optic-based sensor array has been employed to determine the presence or absence of nitroaromatic vapours in variable backgrounds of volatile organic vapour. The system is based on cross-reactive array technology and employs a sensor array attached to the distal tips of an optical fibre bundle. Four different sensors, with 50 replicates of each type, were used to train the system to detect and recognize the presence of 1,3-DNB, 2,4-DNT and 4-NT[52]. Fibre-optics has also been employed in biosensors and immunoassays. These have been used in detection of mainly TNT and RDX and are described in Chapter 4.3.5.

#### *4.3.4.5 Amperometric gas sensors*

In amperometric gas sensors, measurements are made by recording the current in the electrochemical cell between working (or sensing) and counter (or auxiliary) electrodes at a certain potential. Gas sensors are not sensitive enough to measure TNT vapour directly but if TNT is decomposed, the pyrolysis products (NO) can be detected. An amperometric sensor with gold electrodes was used to detect NO, $NO_2$ and $N_2O$ (it does not detect CO or $CO_2$)[53].

#### *4.3.4.6 Microcantilever sensors*

A suggested artificial nose is based on microfabricated nanomechanical cantilever sensors. A cantilever is a beam supported at only one end, like a diving board. They can e.g. be made of silicon and may measure a few hundred micrometers in length and a thickness of 1 μm. Each cantilever in an array is coated with a different sensor layer. When the sensor is exposed to an analyte, the analyte molecule adsorb on the cantilever's surface, which leads to interfacial stress between the sensor and adsorbing layer that bends the cantilever. Each cantilever bends in a characteristic way typical for each analyte. From the magnitude of the cantilever's bending

response as a function of time, a fingerprint pattern for each analyte can be obtained[41]. It has been demonstrated that a Si-based microcantilever is highly sensitive with the possibility of detecting adsorbed mass of the level of pg, and is fast enough to allow real-time monitoring of the adsorption and desorption of TNT vapour[54]. Another paper describes a piezoresistive microcantilever where the minimum amount of TNT detected on the cantilever depends on the cantilever dimensions and was approximately 50 pg for the batch of cantilevers used[55]. Pinnaduwage et al. have also monitored desorption of vapours of TNT, PETN, and RDX from silicon microcantilever surfaces. This study demonstrates that the three explosive vapours stay on the cantilever long enough to be probed by a voltage pulse. No information about the limit of detection was, however, presented[56].

#### *4.3.4.7 Quasi-electronic noses*

Various types of mass spectrometers, gas chromatographs, and ion mobility spectrometers have been miniaturised into mobile handheld explosive "sniffers". They are considered electronic noses because they are capable of detecting and identifying very low concentrations of vapours, thus imitating a canine's capabilities. One "quasi-electronic nose" is the "Chemical Sensor 4400" from Agilent Technologies. This instrument is simply a direct-injection quadrupole mass spectrometer. It is a conventional analytical instrument, but with reconfigured software to make the output look like an electronic nose system. The performance of this type of nose was attractive because the technology is mature, the limit of detection is down to the ppb level and there is practically no interference from ambient conditions, e.g. humidity, and airborne pollutants such as CO. Companies such as Alpha MOS and SMartNose also employ mass spectrometers for the recognition of odours[57]. Yet another example of a quasi-electronic nose is the use of a reconfigured GC column. One commercial example is the z-Nose which is a portable instrument based on a short, 1 meter long GC column with an uncoated surface acoustic wave detector. The instrument is calibrated using compounds similar to the target analyte and shows promise in detecting explosives[57].

Limit of detection: see individual sensors for information
Speed: 10 s (sensor based on a conducting polymer)
Selectivity: probably good
Applicability: demonstrated for 2,4-DNT,1,3-DNB, 4-NT, TNT, RDX

Cost: large analytical e-nose instrument range in price from € 40 000 to € 120 000
Sample type: mainly vapour
Skill: today - advanced, tomorrow - less/none
Fieldability: probably good
Size: ranging from small to large

### 4.3.5 Immunoassays or immunosensors

Immunoassays are immunochemical detection methods based on a reaction between a target analyte and a specific antibody. The antibody has a high degree of sensitivity to the target compound and the antibody's high specificity is coupled within a sensitive colorimetric reaction that provides a visual result. Quantisation is achieved by monitoring a colour change or by measuring radioactivity or fluorescence[41,58].

Immunoassays and colorimetric methods have been widely used in on-site analysis of explosives in soil. Immunoassays are in general more compound specific than colorimetric methods, where broad classes of compounds are detected[59].

*Colorimetric methods* measure coloured reaction products formed when nitroaromatic and nitramine compounds are reacted with alkali or acidic solutions. The operator can visually determine the presence of various compounds by the colour development of the extract. The absorbance at a specified wavelength is measured and correlated to the compound concentration. The CRREL-EnSys methods are examples of colorimetric methods[60].

*Immunoassay and biosensor methods* utilize the ability of antibodies to selectively bind to a primary target analyte present in low concentrations in a complex matrix. For immunoassay methods, the sample, an enzyme conjugate of the explosive, and particles with antibodies specific to the explosive attached are mixed. The enzyme conjugate, and any explosive in the sample, compete for antibody binding sites on the particles. The presence of the primary target analyte (explosive of main interest, e.g. TNT or RDX) is detected by adding an enzyme substrate and a chromogen. The enzyme conjugate bound to the target compound antibody catalyzes the conversion of the enzyme substrate/chromogen mixture to a coloured product. Since the enzyme conjugate was in competition with the primary target analyte in the sample for the antibody sites, the colour developed is inversely proportional to the concentration of the target compound in the sample. DTECH and Ohmicron are examples of immunoassay methods. Biosensor methods also utilize the ability of antibodies to selectively bind to a primary target analyte present in a water sample. Biosensors consist of a biological recognition element (i.e. labelled antibodies) in contact with a physical transducer, such as a fluorimeter or a photodiode. The NRL Continuous Flow Immunosensor (CFI) and Fiber Optic Biosensor (FOB) are biosensor methods[60]. There are also fibre-optic biosensors and these are based on a competitive fluoroimmunoassay performed on the surface of an optical fiber probe. When antibodies, immobilized on the fiber surface, bind the fluorescently labeled explosive analog, laser light in the evanescent wave excites the fluorophore, generating a signal. Explosives present in the sample, prevents such binding, thereby decreasing the signal[60].

There are several immunoassay-based methods developed for detection of TNT and RDX. These were originally developed for land mine detection and clearance of UXO at military bases. They differ a lot in simplicity, from easy strips for TNT detection to more complicated methods. Among the "simpler" methods, Environmental Protection Agency has two methods based on immunoassay technology for detection of TNT and RDX in soil and water. The method is performed using a diluted water sample or an extract of a soil sample. The detection limit of these assays is 5 µg/L in water and 0.5 mg/kg in soil[61,62]. Another simple test, a test strip to quantify trinitrotoluene (TNT) in water, has been developed using a homogenous apoenzyme reactivation immunoassay system (ARIS). In comparison with other test kits for the detection of TNT, the novel test strip is very easy to use. The test strip has only to be dipped into the aqueous sample. A blue colour develops on the reagent strips proportional to the TNT concentration. The concentration of TNT is determined either by visual comparison with a colour card, or more precisely using a reflectometer. A measuring range of about 1–10000 mg/l TNT in water have been demonstrated[63].

Among the more complicated methods Larson et al.[64] have presented a biochip based on ω-substituted alkyl thiols carrying TNT-analogues (Figure 18). Using this approach, TNT can be detected at trace levels in real-time with surface plasmon resonance and quartz crystal microbalance detectors. The detection limit of TNT was in the region of 1–10 pg/µl, depending on the relative composition of TNT-analogues on the biochip surface, as well as on the detector used.

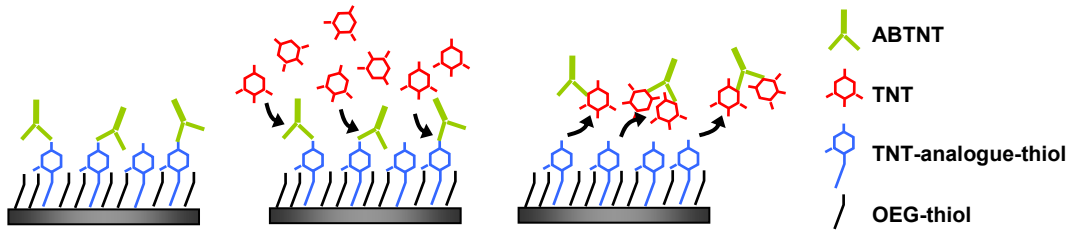


*Figure 18 Schematic illustration of the competitive immunoassay for TNT detection.*

There are several other examples of immunoassay methods developed for TNT and RDX. Schriver-Lake et al.[65,66] has developed a continuous flow immunosensor for the detection of TNT and RDX in soil, groundwater, and seawater. Detection of TNT and RDX in naturally contaminated samples at low ppb and even pptr levels has been demonstrated. Charles et al.[67] has demonstrated detection limits of 10 pptr (ng/l) of RDX by their microcapillary immunosensor. A compact membrane-based displacement immunoassay has been designed by Rabbany et al.[68]. for rapid detection of TNT and RDX at detection levels of approximately 450 fmol for TNT and RDX (100 ml of 1 ng/ml solution) in laboratory samples. Analysis of TNT in acetone extracts of soil has

also been demonstrated by Goldman et al.[69]. Quantisation of TNT in soil samples was demonstrated and the amount of TNT varied between 8-62 mg/l and the amounts were validated using HPLC.

Among the fibre-optic biosensors, Bakaltcheva et al.[70] have presented a biosensor developed for simultaneous detection of TNT and RDX. It uses competitive immunoassay in which antibodies against RDX or TNT are immobilized on the fibre surface. A fluorophore analog competes with the antigen for binding sites on the surface[71]. The detection limit of the multi-analyte assay was 6 ng/ml of TNT and RDX. The individual TNT fibre optic sensor was able to detect 20 µg/L of TNT in contaminated groundwater[72].

A field demonstration has been conducted to assess the performance of eight commercially-available and emerging colorimetric, immunoassay, and biosensor on-site analytical methods for explosives TNT and RDX in ground water and leachate at the Umatilla Army Depot Activity, Hermiston, Oregon and U.S. Naval Submarine Base, Bangor, Washington, Superfund sites. Over the range of conditions tested, the colorimetric methods for TNT and RDX showed the highest accuracy of the commercially-available methods, and the NRL Continuous Flow Immunosensor (CFI) showed the highest accuracy of the emerging methods for TNT and RDX. The detection limits of these methods were in the range of 0.07 - 20 µg/l for TNT and 3.8 - 20 µg/l for RDX[60].

Fieldability is an important consideration in developing detection methods for explosives and among the immunoassay based methods, a sensor platform with the physical characteristics needed for a portable field instrument, i.e. small, light-weight, and rugged, for RDX detection has been developed by Holt et al[73]. These capillary-based sensors exhibited sensitivity to low µg/l RDX concentrations and peak-to-peak signal variations that were generally less than 10% for multiple injections at a single RDX concentration. Another example of an small, fieldable sensor is the miniaturized portable surface plasmon resonance immunosensor applicable for on-site detection of low-molecular-weight analytes[74]. It has so far only been used to detect 2-hydroxybiphenyl, and has not been used for detection of explosives.

It has been proposed that immunoassay or colorimetric detection methods cannot discriminate between the biodegradation products of e.g. TNT (2-amino-4,6-dinotrotoluene, etc.) and that the assays have difficulties in detection of explosives at high levels of interferences from other explosive compounds [63,75]. The response of methods to secondary target analytes differs between colorimetric and immunoassay-based methods. For *colorimetric methods*, interference is defined as the positive response of the method to secondary target analytes chemically similar to the primary target analyte. Colorimetric methods have 100% interference for compounds within the same compound class (i.e., nitroaromatics or nitramines) and remain constant throughout the concentration range of the method. For the colorimetric TNT method, the primary target analyte is

TNT and the secondary target analytes are other nitroaromatics such as TNB, 1,3-dintrobenzene (DNB), dinitrotoluenes (DNTs), methyl-2,4,6-trinitrophenylnitramine (tetryl), etc. For the RDX colorimetric method, the primary target analyte is RDX and the secondary target analytes are other nitramines such as HMX and nitrate esters such as pentaerythritol tetranitrate (PETN)[60]. For *immunoassay-based methods*, cross-reactivity is defined as the positive response of the method to secondary target analytes chemically similar to the primary target analyte. Cross-reactivity occurs when the antibody recognizes compounds that are similar in structure to the primary target analyte. Cross-reactivity for immunoassay and biosensor methods is not 100% for compounds within the same compound class (i.e. nitroaromatics or nitramines) and is not constant throughout the concentration range of the methods. In addition, the cross-reactivities for all immunoassay-based methods are not the same and are based on the antibodies used to develop the specific method[60]. Cross-reactivity is a very important drawback in the field of immunoassays but recent results show that it is possible to develop immunoassays that show low cross-reactivity to structurally related nitroaromatic derivatives, such as 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 2-amino-4,6-dinitrotoluene (2A-4,6-DNT) and 4-amino-2,6-dinitrotoluene (4A-2,6-DNT)[76].

Limit of detection: 20 nanogram (nitroaromatics: TNT, tetryl, TNB, DNT, picric acid and its salts; nitrate esters and nitramines: Dynamite, NG, RDX, PETN, Semtex, NC, tetryl; inorganic nitrates: AN and related explosives)[77] 10-100 ppm (soil); 0.5-10 ppm (water)[58]. 1-10 pg/µl TNT [64]. 41ng/ml TNT [78]. 0.09 ng/ml [76]. 0.006 ng/ml (6ppt) of TNT [79]. 10 pg/ml [80]. 0.25 ng/mL (or 250 pptr) TNT [81].

Speed: < 1 minute (the fastest)
Selectivity: moderate (e.g. cannot differentiate between nitrates and nitrites)
Applicability: nitroaromatics, nitrate esters, nitramines and nitrates
Cost: low
Sample type:
Skill: no special training necessary
Fieldability: good
Size: small

### 4.3.6 Canine detection

Since World War II, dog-handler teams have been used extensively by the military to locate explosives. The civilian use of dogs began with tracking individuals and locating drugs and bombs. Civilian use has expanded to include the detection of e.g. guns, pipeline leaks, gold ore and in line-up for forensic evidence. In the last decade, dogs trained to detect flammable and ignitable liquid residues, called accelerant detector dogs, have become widely utilized and their alert has proven to be admissible as evidence. A number of studies have been performed on

detection dog-handler teams, but in many cases the results are confidential and therefore not easily available. A review was published in 2001 which summarises much of the information and presents an evaluation of the state of knowledge of explosive detection dog-handler teams[82]. This chapter is mainly based on this review.

The scientific evidence that the smell is the major sense used by dogs in detection tasks consists of studies demonstrating low thresholds for detection of odours, studies of the anatomy of the olfactory system of the dog and observations that dogs with measured or perceived problems with the sense of smell do not perform well in detection tasks. It has been discussed whether a dog can detect explosives vapour only or particulates as well and most researchers believe that they can utilise both for detection.

A general comparison between instrumental explosive detection devices and a trained detector dog has been done[82]. The overall conclusion from that comparison is that detector dogs still represent the fastest, most versatile, reliable real-time explosive detection device available. Instrumental methods, while they continue to improve, generally suffer from lack of efficient sampling systems, selectivity problems in the presence of interfering odour chemicals and limited mobility/tracking ability.

Limit of detection: The only verified value of a dogs detection limit is ppb levels or just below[83]. However, this is in vapour phase and it is believed that dogs can also detect particles so in real life they are presumed to be much more sensitive.
Speed: fast
Selectivity: excellent
Applicability: Training on target explosives necessary but no restrictions to what type of explosive exist. However, the number of targets it is possible to train each dog for is limited.
Cost: medium
Sample type: all types
Skill: training of dog-handler team necessary
Fieldability: good
Size: small

### 4.3.7 Photoluminescence and SOP (Semi Conducting Organic Polymers)

Photoluminescence detection can be used to provide sensitive, selective detection of one or a few target chemicals at the time. This can be done using semi conducting organic polymers (SOPs). SOPs are materials with highly non-linear characteristics due to their excited state transport, and are sometimes referred to as amplifying materials [84-86]. These electron rich polymers

bind well with molecules that have electronegative sites. This is favourable for the detection of some explosives, i. e. nitro aromatic compounds.

The basic function is to use a SOP that fluoresces when illuminated by ultraviolet light. When exposed to a certain (electro negative) target vapour, the vapour molecules binds to the surface of the SOP, which results in a decrease in fluorescence intensity. The fluorescence intensity is monitored, and a detected decrease alerts for the presence of a certain molecule [87].

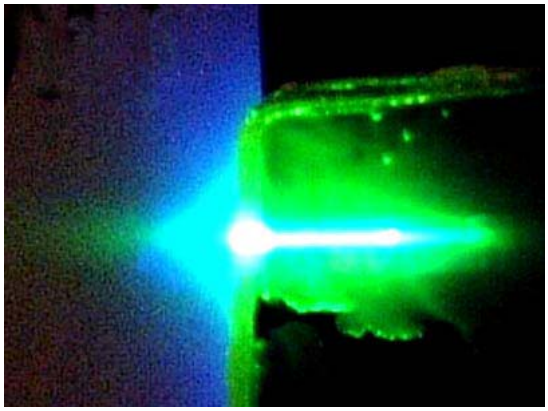

*Figure 19 A film of semiconducting organic polymer undergoes lasing process when exposed to UV-light[88]. When TNT is present, it binds to the polymer and quenches the beam. Courtesy of Massachusetts Institute of Technology.*

A recent publication[89] reports on a SOP that undergoes stimulated emission (laser activity) when illuminated by UV-radiation above a specific threshold. The vapour of TNT (2,4,6-trinitrotoluene) and DNT (2,4-dinitrotoluene) introduces non-radiative deactivation pathways, thus quenching the lasing.

The sensitivity for TNT/DNT-vapours of lasing SOPs is more than 30 times higher than for spontaneous emission SOPs. An article in Scientific American [90] gives the detection levels for the lasing SOP as 5 ppb for TNT and 100 ppb for DNT and the detection time 1 second. The simultaneous response for both TNT and DNT (and other nitro aromatic compounds) can be an advantage in buried landmine detection, since the concentration of DNT and other degradation products are present to a larger extent than the pure TNT. It is also very common that landmines contain TNT to full or some extent.

The method has been productified by Nomadics Inc. as a handheld detector prototype for buried landmines[91]. Nomadics reports fg detection limits of TNT in air. A blind field test performed at one of DARPAs (Defence Advanced Research Projects Agency) test sites showed equal or better performance than the two canine landmine detection teams that were also included in the test for comparison.

Limit of detection: fg

Speed: High

Selectivity: Poor, good for detection of TNT based explosives

Applicability: TNT/DNT

Cost:

Sample type: Vapor

Skill: Low

Fieldability: Good, handheld device available

Size: Small

### 4.3.8 Surface Plasmon Resonance – SPR

Surface Plasmon Resonance is based on optical refraction. When light passes through a material of higher refractive index (such as glass) into one of lower refractive index (e. g. water), some light is reflected from the interface. Above a certain incidence angle, the light is totally reflected. However, if the glass surface is coated with a thin layer of a noble metal, usually Au, the reflection is not total. Instead, some light is absorbed into the metal. There exists an angle where this light absorption is maximal – the surface plasmon resonance angle. This angle is a consequence of the resonant oscillation of mobile electrons (plasma) at the surface of the metal film. The oscillating plasma waves (surface plasmons) are influenced by the medium closest to the metal – the plasma wave reaches about 300 nm beyond the metal film. If there is a liquid phase in contact with the metal film, and a molecule binds to the metal surface, there is a shift in refractive index and thereby a shift in plasmon resonance angle.

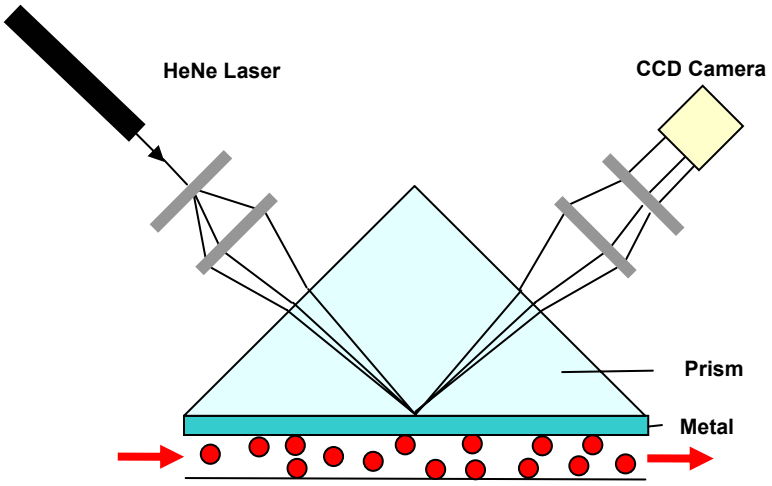


*Figure 20 The Kretschmann configuration. The CCD registers the dip in refracted light that is due to adsorption of a specific heavy molecule to the gold surface. This is a common configuration.*

The method is preferably applied on heavier molecules in order to get a good response in surface plasmon resonance angle. It is commonly used for determining properties of proteins, sugars and DNA. To detect explosives, which are relatively small molecules, a binding antibody can be used. The antibody has considerably larger molecular mass, and thus gives a good SPR response[92,93].

In [92],2,4,6-trinitrophenol-bovine serum albumina (TNP-BSA) was adsorbed on the Au surface. The binding of an anti TNP antibody to TNP-BSA was influenced by TNT, thereby giving a shift in resonance angle. In a timespan of 22 minutes, determination of TNT concentrations was possible in the range from 60 ppt to 1000 ppb.

Strong [93] uses an active biosurface made out of bovine serum albumine decorated with trinitrobenzene groups (TNB-BSA). Testing of their sensor platform demonstrated a sensitivity of 1 ppm TNT in a variety of soils. No false negatives were registred under the DARPA (Defence Advanced Research Programs Agency) supervised tests.

Published work on explosives detection with SPR has been focused on TNT detection, mainly for the purpose of fast and reliable detection of TNT contaminated soil (detection of buried land mines). However, at least one study focuses on the direct gold nano particle response to nitro compounds in general [94]. It is reported that the detection sensitivity is improved 35 times by using Au nanoparticels compared to conventional SPR. The effect seams generally applicable to $NO_2$-containing species. The detection limits reported are 1.2 nmol/l (29 ppb) for $NO_2$, 7.6 nmol/l (184 ppb) for $C_6H_5NO_2$ and 0.17 nmol/l (4.1 ppb) for DNT. The detection limits were concluded using Cavity Ringdown Spectroscopy (CRDS).

Limit of detection: 60 ppt to 1000 ppb detection range reported [92]
Speed: Slow – minutes. The method is still under development
Selectivity: Good if suiting binding antibody can be found
Applicability: Tested fot TNT and DNT
Cost: n. a.

Sample type: To date intended for soil samples
Skill: n. a.
Fieldability: Probably good
Size: Potentially small

## 4.4 Cavity Ringdown Spectroscopy (CRDS)

Cavity Ringdown Spectroscopy is a very sensitive, quantifying optical technique that can be used for analysing vapours. Light from a tuneable laser is coupled into a ring down cavity with highly reflective end mirrors. The light bounces back and forth in the cavity for several hundred roundtrips (typical pathlength is ~ 6km). Only a small fraction of light escapes through the mirrors, and this light is monitored using a detector. The intensity of the light decays exponentially.

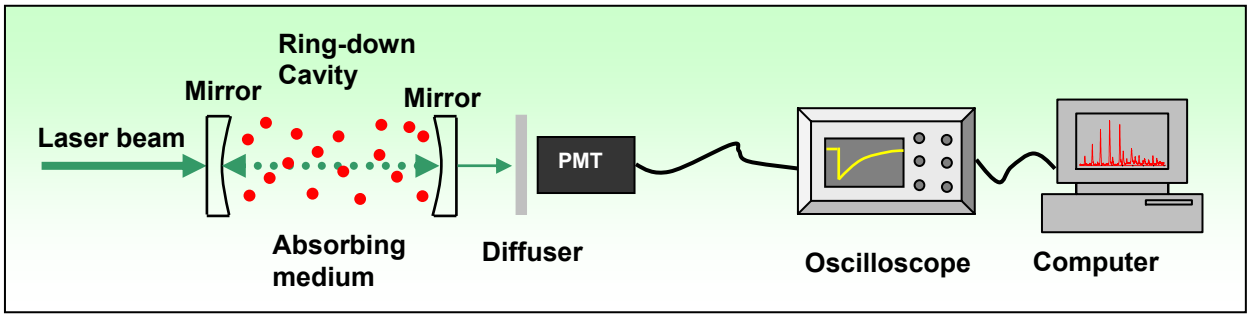


*Figure 21 Principle of Cavity Ring Down Spectroscopy.*

For wavelengths where there exists molecular specific absorption, the decay rate will be influenced by the absolute concentration of this molecule. By using tuneable lasers with good spectral resolution, it is possible to distinguish between different explosives and their interferences. A system developed for explosives detection [95] reports detection limits of 380 pg for RDX and 650 pg for TNT.

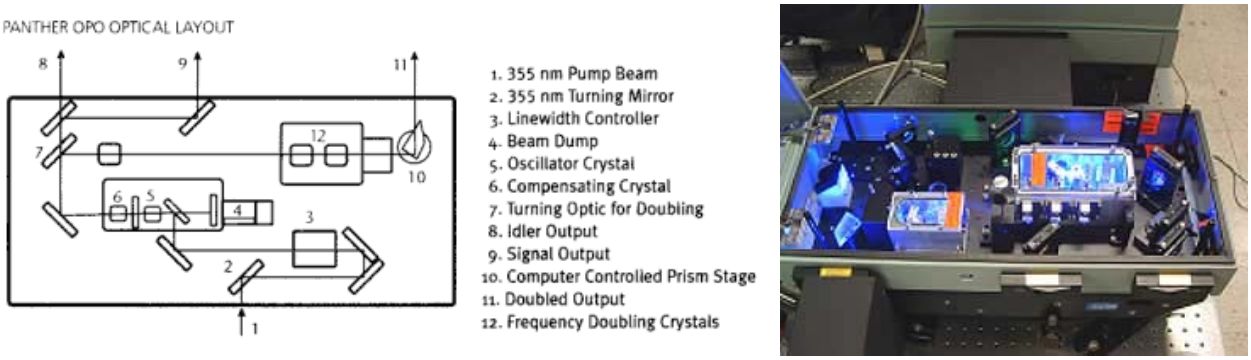


*Figure 22 Setup for Cavity Ring Down Spectroscopy (Courtesy of Paul J. Dagdigian and Christopher Ramos, Johns Hopkins University[96]).*

Another reference [97]reports mid IR CRDS spectra for TNT, TATP, RDX, PETN and Tetryl). Parts per billion (ppb) concentration levels of all mentioned could be detected without sample pre concentration. By introducing a membrane separator, the authors expect it possible to detect at TNT levels of 75 ppt.

Limit of detection: ppb measured today[95], possibility of increased sensitivity (low ppt) [97]

Speed: Probably high

Selectivity: Good

Applicability: Reported for TNT, TATP, RDX, PETN

Cost: n a

Sample type: Vapor

Skill: Could be low for fully developed instrument

Fieldability: Probably better for clean environments

Size: Probably mobile but not handheld.

### 4.4.1 Ion Mobility Spectrometry – IMS

Ion Mobility Spectrometry (IMS) is a detection technology that is commonly used for explosives screening of both people and carry-on luggage at airports. Typically, an IMS is comprised of four sub-components; an ion source region, an ion gate, a drift region and a detector.

The ion source is often made out of the radioactive $^{63}$Ni isotope. This radioactive source is used to produce ionized reactants, which in turn ionizes the sample molecules by APCI (Atmospheric Pressure Chemical Ionization). Other forms of ionization can also be used, such as corona discharge, laser ionization and ESI (Electro Spray Ionization).

The ion gate releases the ions in a discrete packet into the drift region. This gives a starting time for the drift time measurement of the collected ions. In the drift region, there is weak, constant electric field of typically 200 V/cm that accelerates the ions towards the detector. A drift gas, typically air or nitrogen, is used to decelerate the ions. The ions are influenced by the electric field to different extent depending on geometry, electronic configuration and molecular weight. The ion identification is made by the arrival time at the detector.

IMS is not a quantitative detection method. The response is affected by parameters like vapour concentration, memory and humidity. Therefore, the measured coefficient of mobility, K ($cm^2V^{-1}s^{-1}$) is normalized for pressure and temperature to the reduced mobility, $K_0$. In this way, $K_0$ for different analytes can be communicated internationally.

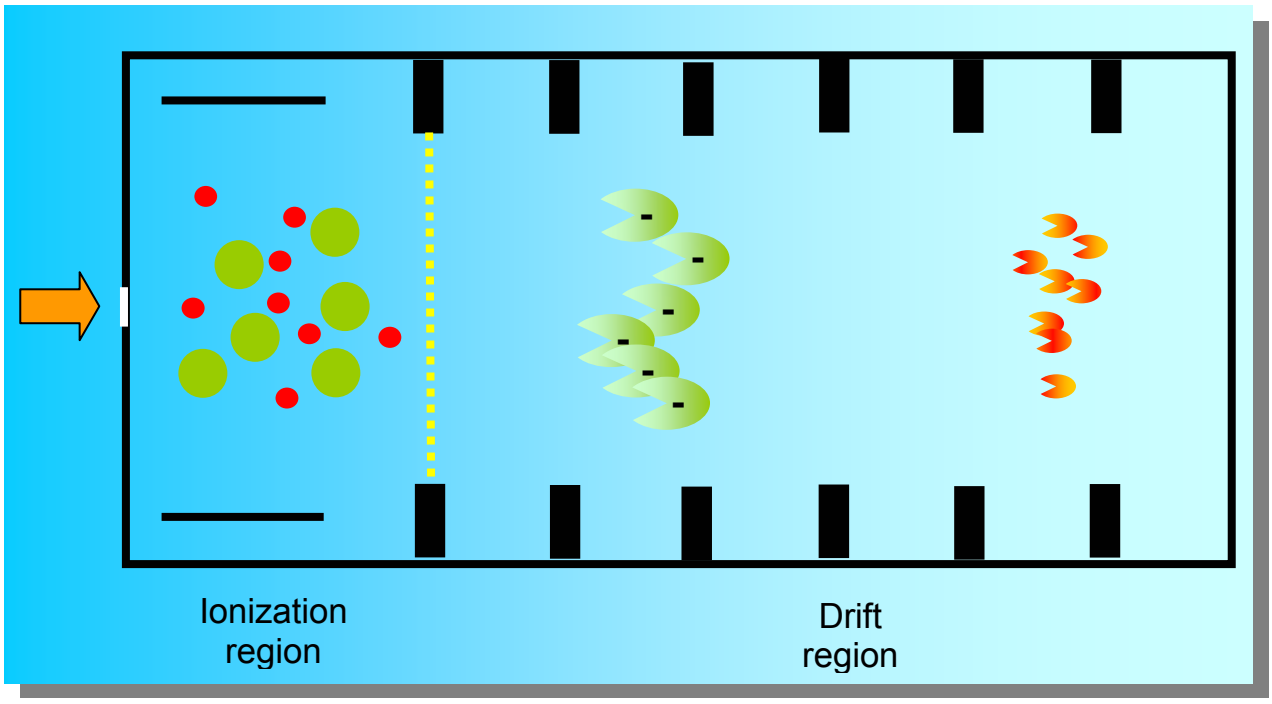


*Figure 23 Schematic of an IMS spectrometer.*

A complicating factor for the use of IMS for explosives detection is the need to use high temperatures for surface desorption and transport to a heated drift tube versus the thermal instability of explosives that leads to fragmentation. Most successful is the ionization of TNT and other nitrotoluenes because of reasonably uncomplicated gas phase chemistry. The ionized analytes form stable molecular or molecular plus adduct ions. Other explosives decompose thermally more easily. This can lead to formation only of fragment ions at higher temperature, and to autoionized molecular adduct ions or clusters at lower temperatures [98]. Difficulties arise when the optimal desorption temperature vary between explosive target molecules.

There are implications that laser ionization IMS (LIMS) is a new trend. The benefit is the increased selectivity that can be achieved by using two photon or REMPI ionization. By using a molecular specific excitation energy level as the first step of two in the ionization process, background and interferences can be reduced. No articles giving quantifying data has been found, but web pages suggesting development of LIMS exist [99,100].

Example of a commercial IMS using opto/electrical ionization technique is the Quantum Sniffer from Implant Sciences. Specifications claim ppt detection of vapours and pg-ng levels for particles detection in 1-5 seconds. Identifiable substances are RDX, NC PETN, EGDN, TNT, dynamite, ANFO, TATP, smokeless power, black powder, Semtex and C4 [101].

Limit of detection: ppt stated for vapor, pg-ng levels for particles [101]
Speed: High, 1-5 s
Selectivity: Good if a limited number of target molecules are attempted
Applicability: RDX, NC, PETN, EGDN, TNT, Dynamite, ANFO, TATP, smokeless powder, black powder, Semtex, C4
Cost:
Sample type: vapour and particles
Skill: Low
Fieldability: Good, exists for field use
Size: Small, can be handheld

### 4.4.2 High Field Assymetric Waveform Ion Mobility Spectrometry – FAIMS

To further increase the selectivity of IMS, the method has been refined through FAIMS (High Field Assymetric Waveform Ion Mobility Spectrometry). FAIMS is also known as acronyms IMIS (Ion Mobility Increment Spectrometry) or Field Ion Spectrometry.

In strong electric fields, with field strengths over 5000 V/cm, the ion mobility (K) is not directly proportional to the electric field (as is the case for weak fields), but varies as a function of applied electric field strength. The high field mobility is thus a non constant term. It is the change in ion mobility, and not the absolute ion mobility, that is being monitored.

The working principle for FAIMS is the following: The ions in the drift region are affected by an assymetrically varying, high electric field. The gas stream in the drift tube passes between two spaced-apart parallel plate electrodes. Often, a first plate is maintained at ground potential while the second plate has an asymmetric waveform, V(t), applied to it. The asymmetric waveform V(t) is composed of a repeating pattern including a high voltage component, $V_1$, lasting for a short period of time $t_2$ and a lower voltage component, $V_2$, of opposite polarity, lasting a longer period of time $t_1$. The waveform is synthesized such that the integrated voltage-time product, and thus the field-time product, applied to the plate during each complete cycle of the waveform is zero, for instance $V_1t_2+V_2t_1=0$; for example +2000 V for 10 µs followed by -1000 V for 20 µs [102]. Also applied is a DC voltage that compensates for translational drift. This allows only ions of certain mobility terms to pass through the drift region. Other ions are neutralized at the electrodes. The selectivity can be further increased by coupling the FAIMS to a mass spectrometer to give ion mass information.

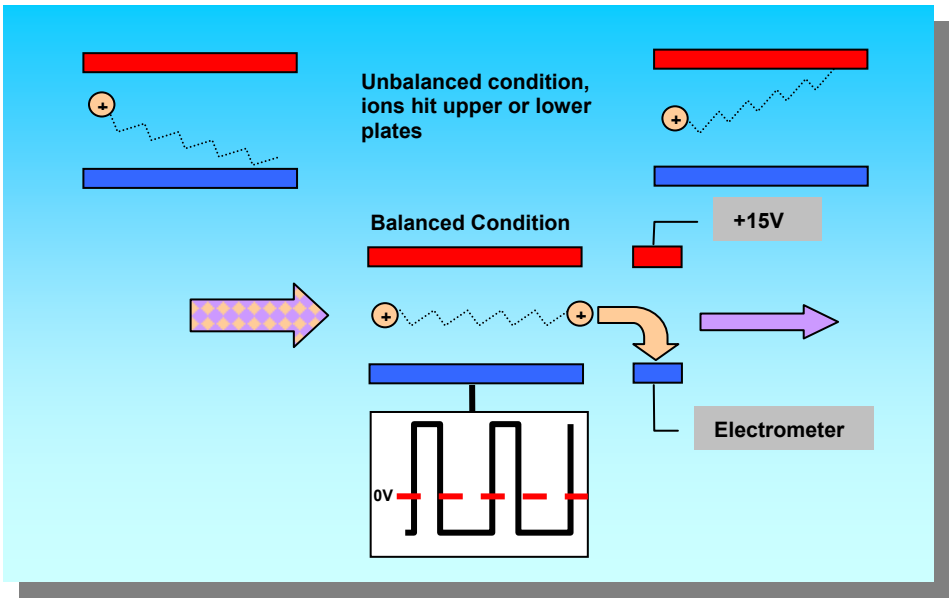


*Figure 24 Schematic of drift tube for high-field, asymmetric, ion-mobility spectrometry. Ions are moved through the drift region by gas flow and not by an electric field, as in traditional ion-mobility spectrometry. Ion separation is accomplished using an electric field applied to the drift region. Ions emerging from the drift region are sampled at a Faraday plate detector.*

A commercial detector based on FAIMS in combination with MEMS and microfabrication technology is the EGIS Defender from Thermo Electron Corporation. Stated specifications are ng levels of nitrates, (EGDN/AN), NG, DNT/TNT, PETN, RDX, TATP, HMTD and tetryl in 10-12 s time [103].

Limit of detection: ng levels for particles [103]
Speed: Fast, 10-12 seconds
Selectivity: High selectivity
Applicability: According to manufacturer nitrates (EGDN/AN), NG, DNT/TNT, PETN, RDX, TATP, HMTD

Cost: n/a
Sample type: Particles
Skill: Low
Fieldability: Good
Size: Small, available for handheld use

### 4.4.3 Quantum Cascade Lasers and IR spectroscopy

Until recently, coherent, tuneable light sources in the mid IR wavelength region has not been available. With the emerging quantum cascade (QC) laser technology, pulsed and semi continuous laser sources of narrow linewidth that can be operated at room temperature and with peak power reaching 500 mW are appearing on the market today. The lasing region is from 3 to 20 μm, covering the two atmospheric windows at 3-5 μm and 8-14 μm. This is also a wavelength region with fundamental transitions for the majority of molecular species. Therefore, with the development of QC lasers follows the possibility of developing selective IR spectroscopic detection methods. Methods that are currently being explored for explosives detection in the mid IR region are for example continuous wave CRDS based methods[104] absorption spectroscopy and evanescent-field spectroscopy[105].

### 4.4.4 Evanescent Field Spectroscopy

Evanescent field spectroscopy is based on the interaction of an electromagnetic field that penetrates from a totally reflecting surface into the surrounding space – giving rise to the so-called evanescent field. In the case of a coinciding molecular transition in the medium surrounding the total reflector, a small portion of the energy is absorbed by this medium. The loss of laser intensity with wavelength then identifies the absorbing media. To give measurable response, multiple reflections are needed. An optical fibre stripped from cladding makes a good multi reflecting element. However, for mid IR evanescent field spectroscopy, low cost, standard fibres are not available. Instead, other materials consisting of mineral oxides can be used. No detection levels of explosives have been found for this spectroscopic technique.

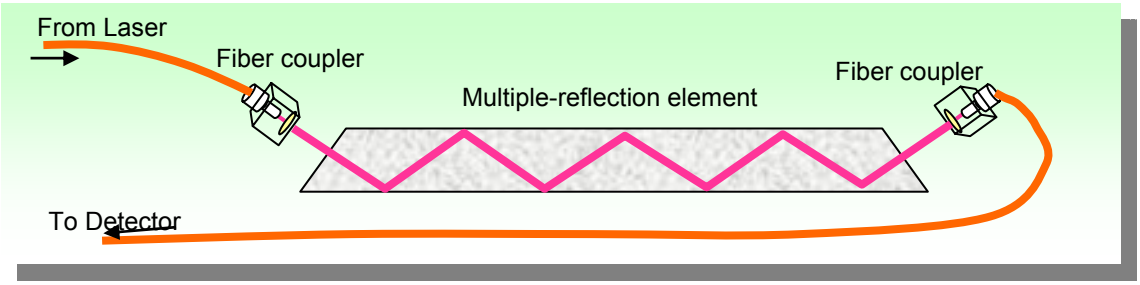


*Figure 25 Left: Schematic of a fiber-coupled multiple-reflection element. Right: Photograph of a coiled fibre optic laser sensor (This specific sensor was used for monitoring volcanic gases.) From Willer*[105].

Limit of detection: n/a
Speed: fast – online monitoring possible
Selectivity: Depending on possibility to use multiple measuring wavelengths. Possibly moderate to good. No data for explosives detection found.
Applicability: n/a
Cost: n/a
Sample type: gas phase, liquid phase
Skill: n/a
Fieldability: Can be used in rough environments
Size: Possibly small if further developed

### 4.4.5 LI-MS

Ions produced by laser ionization (LI) in general are ideally detected using a time-of-flight mass spectrometer (TOF-MS) or an ion trap mass spectrometer (IT-MS), which both takes advantage of the pulsed nature and well-defined temporal character of laser ionization. LI (Laser Ionization) is a "soft ionization" method, which produces exclusively or predominantly the parent molecular ion; i.e., fragmentation of the ion into smaller pieces is negligible in most cases. Ionization can be done with varying degree of selectivity depending on the actual ionization scheme chosen.

Some selectivity can be achieved with SPI – Single Photon Ionization. In this technique, a laser wavelength that will ionize a good number of explosive compounds with a single photon is used. The photon wavelength typically corresponds to an energy of ~10.5 eV. Many other chemical compounds will not be ionized by single photon processes in this energy regime. The mass spectrum from SPI-MS will reveal characteristic fragmentation of the explosive molecules. This method has been demonstrated for nitrobenzene, 1,3-dinitrobenzene, *o*-nitrotoluene, 2,4-dinitrotoluene, and 2,4,6-trinitrotoluene, as well as the peroxide-based explosive triacetone triperoxide in the gas phase[106]. Sensitivity is in the low ppb region. The authors report limits of

detection for nitrobenzene and 2,4-dinitrotoluene to be 17-24 (S/N ~2:1) and ~40 ppb (S/N ~2:1), respectively.

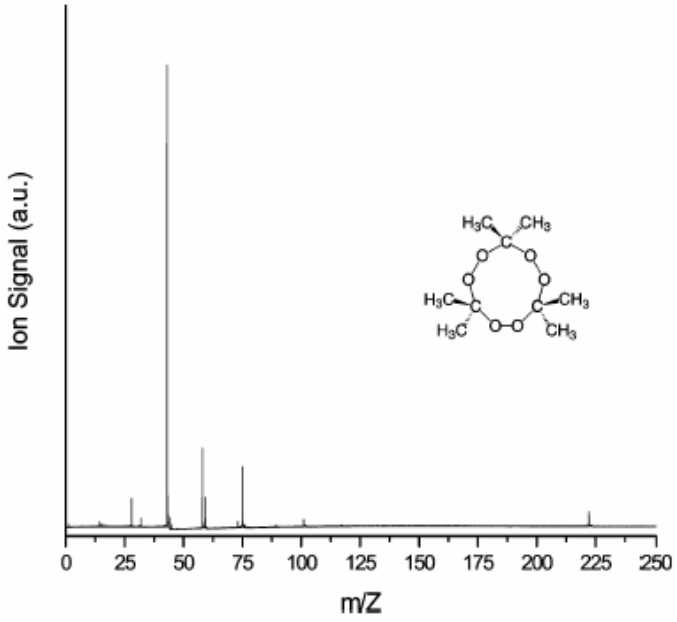


*Figure 26 SPI mass spectrum of TATP. From Mullen*[106].

A more selective LI-MS detection method is Jet-REMPI-MS. This method combines the two different physical principles of optical spectroscopy and mass spectrometry, giving information about two different molecule-specific properties: their mass and the energy of a molecular specific level. The REMPI technique performs the laser ionization in two steps. Figure 27 shows the simplest form of REMPI, which uses two photons of the same energy. Absorption of a first photon excites the molecule from the ground state to a molecule specific energy level, and absorption of a second photon ionizes the molecule.

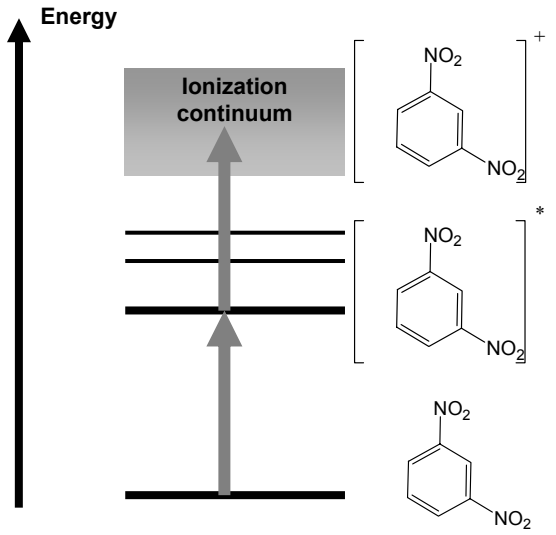


*Figure 27 The REMPI process.*

For a molecule to be ionized, the energy of the laser photons must match the first excitation step. Therefore, the laser ionizes only molecules with a matching molecule-specific energy level. Since mass measurement is exclusively possible with ions, no molecules other than the targeted molecules will be detected; thus there is no interference from the surrounding environment.

The REMPI technique results in a higher degree of chemical selectivity than SPI due to the resonance of the first step. By proper choice of the laser wavelength for REMPI, only molecules having a level resonant at the energy of the laser photons will be ionized. This method has proven effective for the detection of one trace compound at ppt levels in the midst of others, including molecular isomers in the gas phase[107-110]. REMPI is also a very effective ionization method, which makes it highly sensitive. Ionization efficiencies from 1% to 10% have been reported[110].

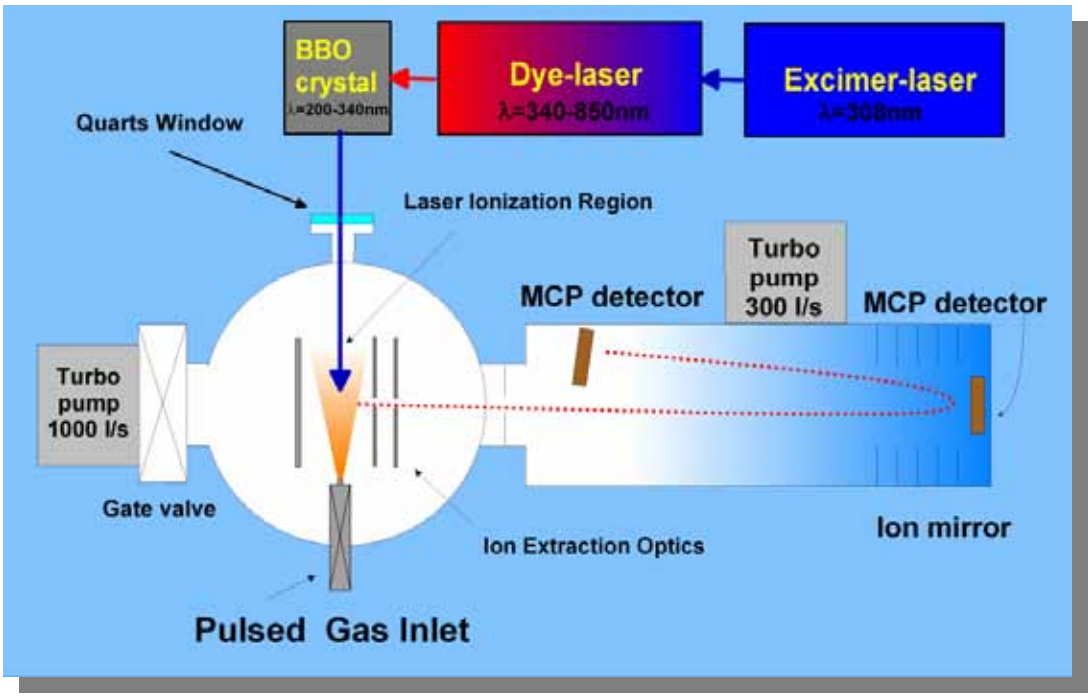


*Figure 28 Lab setup for LI-MS detection, intended for research activity. A laser beam from the Excimer laser pumped, frequency-doubled Dye-laser ionizes the molecules from the sample inside a vacuum chamber. The sample gas is introduced into the chamber through a pulsed valve. The ions are extracted into the TOF-MS. At the end of the MS, an ion mirror reflects the ions towards the detector.*

The sensitivity and specificity for REMPI is dramatically improved when performed using gas cooling via a supersonic jet (jet-REMPI). In a supersonic jet, the adiabatic expansion leads to dramatic cooling, providing temperatures down to approximately 18 K[111]. This cooling greatly simplifies the spectra, producing narrower and stronger electronic transitions. The lower gas temperatures lead to population of fewer rovibrational levels, which in turn produce larger peak signals in the REMPI spectra, thus sensitivity is improved. Also, selectivity is improved because

there are fewer absorption lines of other molecules that might interfere with the absorption lines of the target molecules.

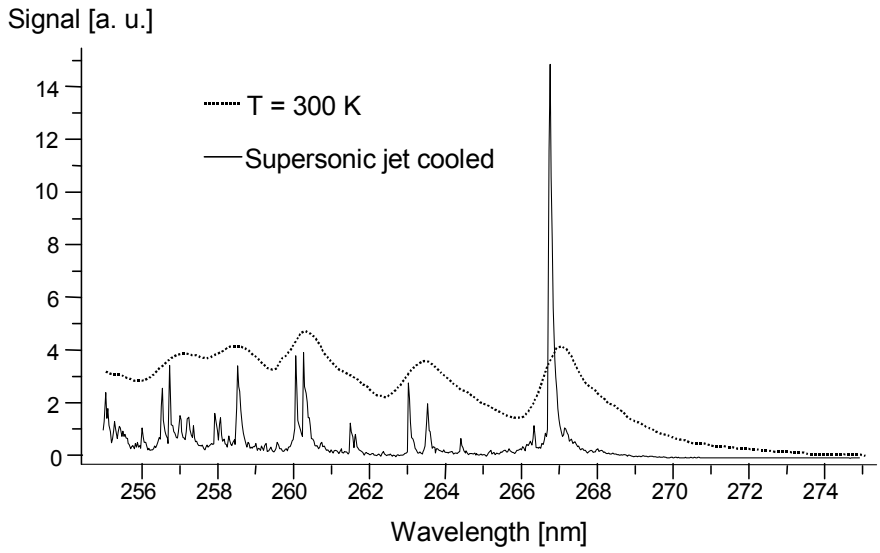


*Figure 29 REMPI spectra of toluene at 300°K and supersonically jet cooled. Cooling of internal molecular degrees of freedom (rotation, vibration) in a supersonic beam results in a very narrow line allowing high-resolution gas-phase UV spectroscopy to be performed (Courtesy of SRI International).*

Figure 29 provides an example of the improvement in ionization selectivity due to cooling. The figure shows optical spectra for toluene with cooling, where air is the carrier gas, and without cooling. With cooling, a tremendous reduction in the spectral line widths is observed.

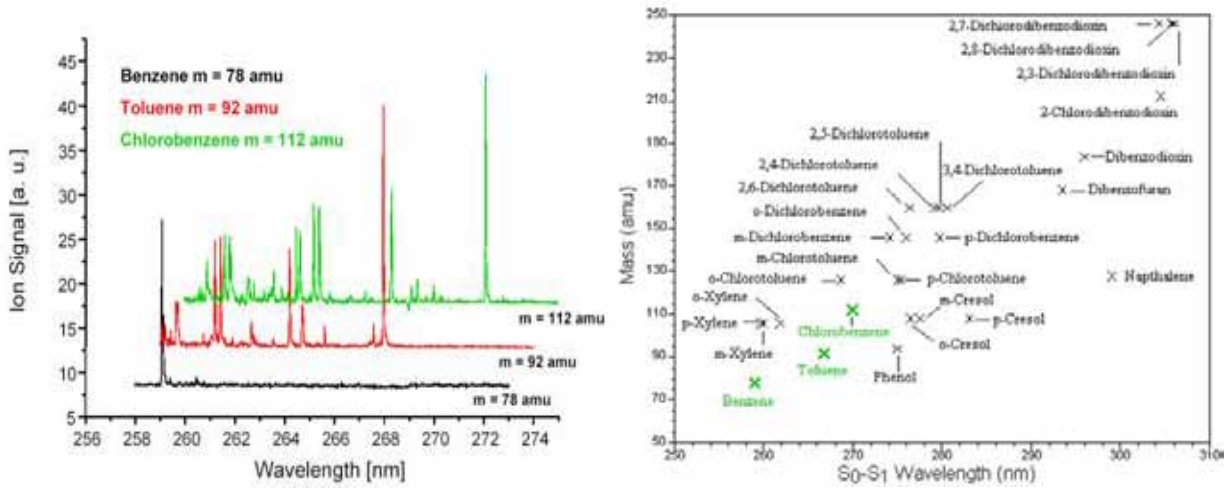


*Figure 30 REMPI spectra are measured in two dimensions. The simultaneous detection by mass and wavelength yields a two-dimensional detection scheme based on wavelength and mass. An extremely high chemical selectivity is obtained. This is crucial when identifying one trace compound in the midst of many other similar ones. (Courtesy of SRI International.)*

Limit of detection: Estimated to ppt range
Speed: Potential for about one substance per second
Selectivity: Excellent
Applicability:
Cost: Expensive
Sample type: Vapour and particles (with particle collection)
Skill: N/A (At the moment only available as research instrument)
Fieldability: Good
Size: Stationary to mobile depending on configuration and technical development. Unlikely to be handheld with current technological status.

### 4.4.6 SERS

Directing a laser beam towards a substance causes the photons of laser light to be scattered. Most of this scattering is Rayleigh scattered, an elastic scattering that does not change the energy of the photons (wavelength of the light). About one out of a million photons is inelestically scattered so that the photon looses or gains energy in the collision. This is called Raman scattering. The energy that the photons loose or gain corresponds to differences in the molecules vibrational energies (Figure 31). This results in spectra that fingerprint the analysed molecules since all molecules have different structure and hence different vibrational structure.

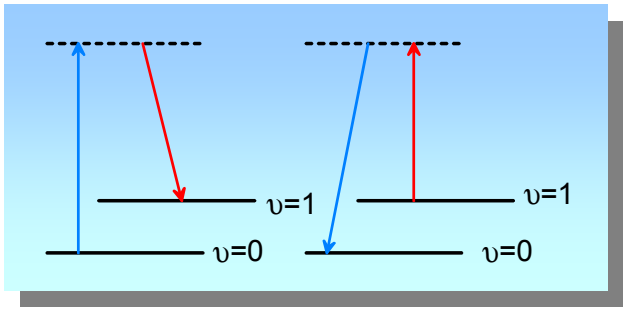


*Figure 31 Schematic level diagram of Raman Spectroscopy. Raman scattered light either loses or gains energy corresponding to a vibrational quantum of the molecule.*

The fact that most of the light is Rayleigh scattered means that Raman spectroscopy is intrinsically an insensitive method. However, there are other, more sensitive variations to Raman Spectroscopy. One of them is Surface Enhanced Raman Spectroscopy, SERS. The surface on which the analyte is adsorbed used is normally silver, copper or gold of a special surface structure. The Raman intensities with SERS are enhanced $10^2$ to $10^{14}$ times compared to ordinary Raman.

For Raman spectroscopy in general, the choice of wavelength is important since the Raman response is competing with fluorescence. The fluorescence is stronger with shorter wavelengths so

longer wavelengths are preferred. Wavelengths of 785 nm or 830 nm are preferred for portable instruments[112].

The vibrational modes corresponding to the part of the molecule that is involved in the adsorption process are the most enhanced modes. For nitroaromatics NO2 is the adsorbing moiety which means that the two key spectral regions are around 1350 and 820 $cm^{-1}$. SERS is able to detect picogram to femtogram levels of analytes of interest. EIC Laboratories have reported measurement of 2,4-DNT at 5 ppb concentration in less than 10 seconds, and the detection of actual buried landmines with their prototype equipment[113].

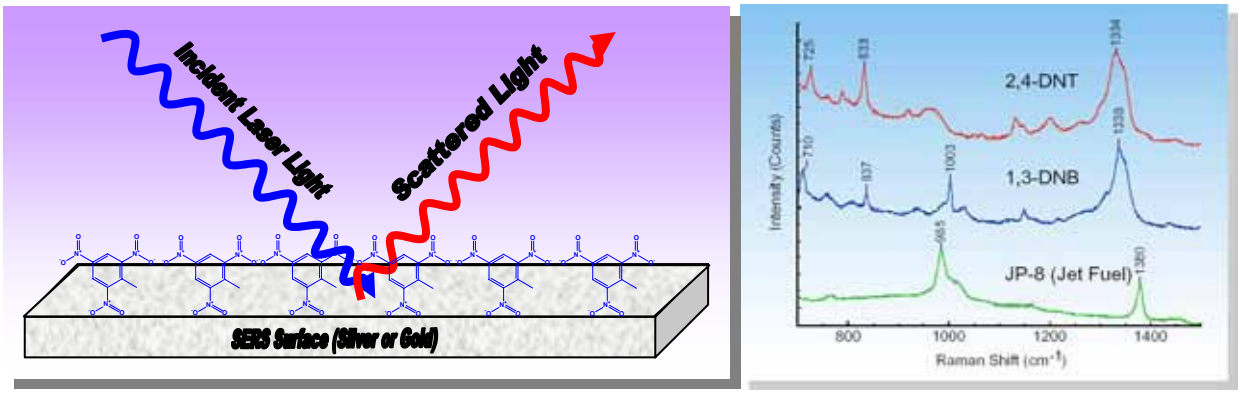


*Figure 32 Left: Schematic illustration of SERS. Right: SERS data demonstrating selectivity of the technique for explosives, From EIC Laboratories*[113]

Limit of detection: ppb

Speed: 10 s

Selectivity: n/a

Applicability: n/a

Cost: n/a

Sample type: n/a

Skill: n/a

Fieldability: good

Size: portable

### 4.4.7 Electrochemistry

Electrochemistry is an analytical method useful for analysis of trace amounts of a substance in an electrolyte. A potential is applied between two electrodes in the electrolyte and measured relative to a reference electrode. The potential is varied with time and the current response is measured. The result depends on the properties of the electrolyte and any traces of other substances in it thereby providing an identification of these traces.

Sakovich et al. have presented an electrochemical sensor (Figure 33) in which the electrolyte is directly on the surface without separation by a membrane. The sensitivity is in the range 10-100 ppb. This sensor is intended for detection on vapour phase.

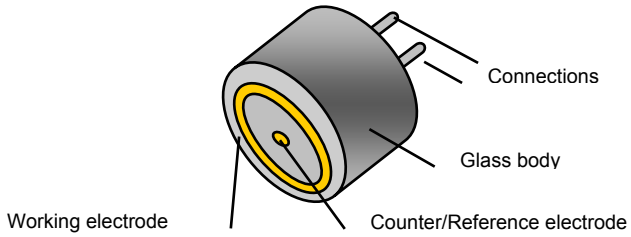


*Figure 33 Electrochemical sensor with 25 µm gold wire and electrolyte direct on the surface without separation by a membrane. The reference electrode coincides with the counter electrode. (From Sakovich [114])*

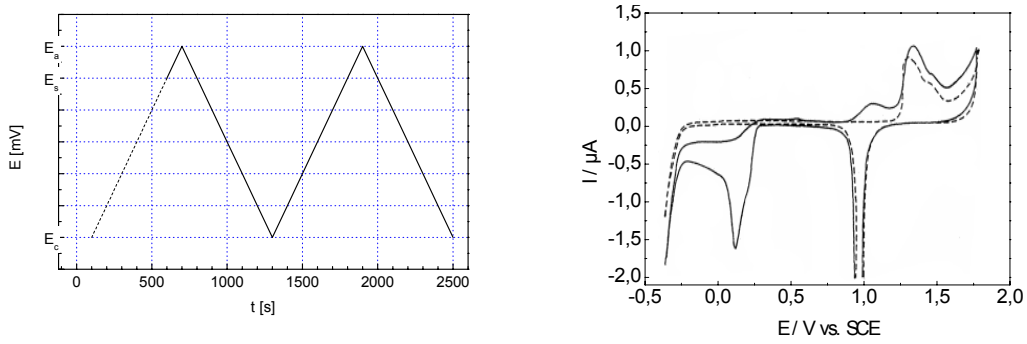


*Figure 34 Left: Variation of applied potential. Right: Dashed line is Au electrode in 0,5M $H_2SO_4$, solid line is with 50 mg/l TNT. (From Sakovich [114])*

Another example of the use of electrochemistry in detection of explosives has been presented by Wallenborg and Bailey[115]. They used a dye as a visualizing agent to obtain indirect laser-induced fluorescence from the analytes. A mixture of 14 explosives was analysed. They were separated using electrophoresis using 1-4 kV. A 750 nm laser diode was used for the indirect laser-induced fluorescence and a photomultiplier tube for detection. Using 1 ppm each of TNB, DNB, NB, TNT, Tetryl, 2,4-DNT, 2,6-DNT and NT they obtained the electropherogram in Figure 35.

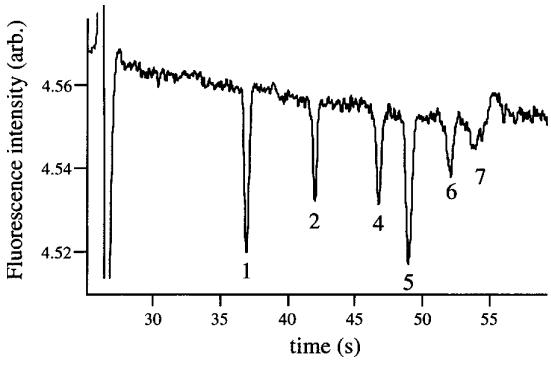


*Figure 35 Electropherogram of a mixture of explosives: TNB (1), DNB (2), NB (3), TNT (4), tetryl (5), 2,4-DNT (6), 2,6-DNT (7), 2-, 3-, and 4-NT. (From Wallenborg[115])*

The sensitivity of electrochemistry, at least in these forms is far too low for detection of low vapour pressure explosives. However, there is an interesting technique called Spectroelectrochemistry in which electrochemical measurements are combined with a spectrometric method such as Raman spectroscopy, SERS, IR absorption or UV-Vis Spectroscopy for identification. Improved sensitivity and selectivity may be the result of a suitable combination of techniques.

Limit of detection: ppb
Speed: n/a
Selectivity: medium
Applicability: n/a
Cost: n/a

Sample type: n/a
Skill: n/a
Fieldability: good
Size: small

### 4.4.8 Spot tests

This has not been a focus of this study. However, the existence of spot tests should be mentioned. Spot tests use a combination of chemicals to identify a substance by its colour change when subjected to these chemicals. An example is found in Figure 36. The sensitivity is in the ng-region. Spot tests are not available for all explosives.

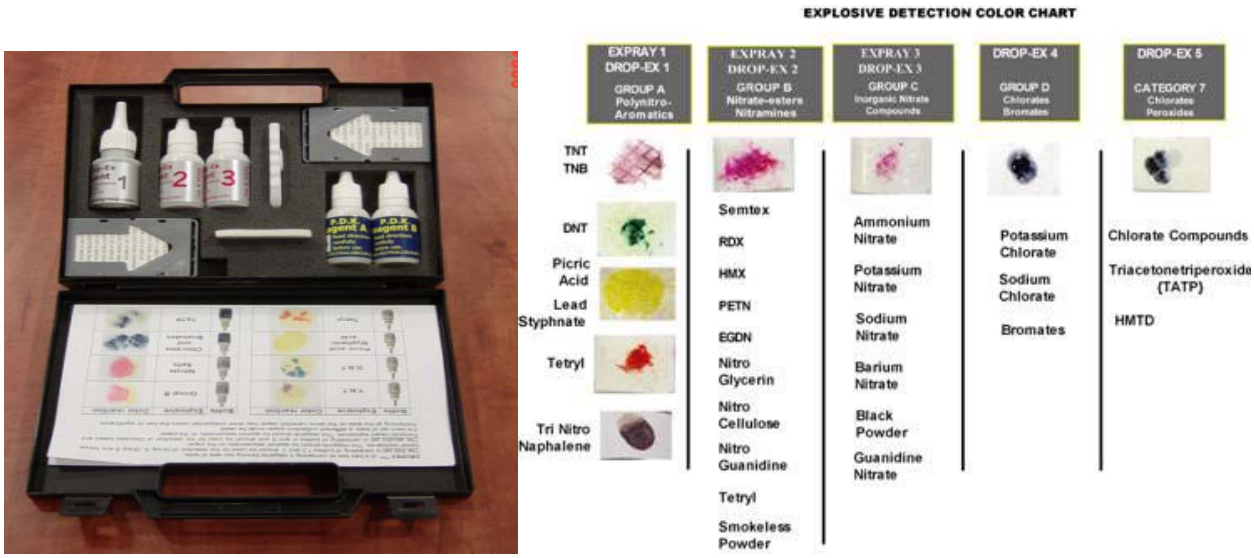


*Figure 36 Example of a spot test, Drop-ex plus. Courtesy of Mistral Security Inc.*

# 5 Standoff detection

In the report "*Existing and Potential Standoff Explosives Detection Techniques*"[27] the authors defined standoff detection of explosives in the following way:

> *Standoff explosive detection involves passive and active methods for sensing the presence of explosive devices when vital assets and those individuals monitoring, operating, and responding to the means of detection are physically separated from the explosive device. The physical separation should put the individuals and vital assets outside the zone of severe damage from a potential detonation of the device.*

The zone of severe damage varies with scenario and bomb type but they chose 10 m for a pedestrian suicide bomber and 100 m for a vehicle based bomb.

Standoff detection is important when finding suicide bombers, roadside bombs, and for wide-area-surveillance. The problem involves detection of a weak signal in a noisy environment and high detection speed is important when the threat is rapidly approaching like eg. for roadside bomb detection. To prevent suicide bombers it is important to find the bomber before he reaches the intended target and since the bomber does not need to leave the bomb behind, there is less time opportunity to find the bomb. Another important factor when detecting suicide bombs is to do it without alerting the suspect since this may trigger an attack even if not at the intended target.

Some detection methods with potential for standoff detection are described in this chapter. Bulk detection methods have already been treated in Chapter 3. Therefore only their potential for standoff detection is summarised in Chapter 5.1.1.

## 5.1.1 Bulk detection methods for standoff detection

X-rays have good potential for imaging at standoff distances of 10 to 15 m[27]. It has the advantage of high image resolution but may cause concern about health hazards when imaging people. High cost and size of x-ray systems are also problematic for many applications.

THz spectroscopy has a fundamental limitation on image resolution at frequencies above 1 THz. For imaging purposes the region 100 GHz to 1THz is better. Even then resolution poses a problem. To resolve 1cm at a distance of 20 m when using 1mm waves (300 GHz), a collecting antenna of nearly 2m in diameter is needed[27]. A general constraint for spectroscopic methods at standoff distances is absorption by water vapour, but in the 100 GHz to 1 THz region, this absorption does nor constitute a problem.

Neutrons and γ-rays both have limited sensitivity for standoff applications and pose health hazards. Magnetic resonance techniques are ill suited for standoff detection since they require close proximity (<1m) to the explosive[27].

### 5.1.2 LIBS

Laser Induced Breakdown Spectroscopy (LIBS) is a detection method that uses a laser with high enough energy to break down the sample into plasma. This plasma emits light with characteristic frequencies from ionic, atomic and molecular species that can be detected with a spectrometer, allowing identification of the elemental composition.

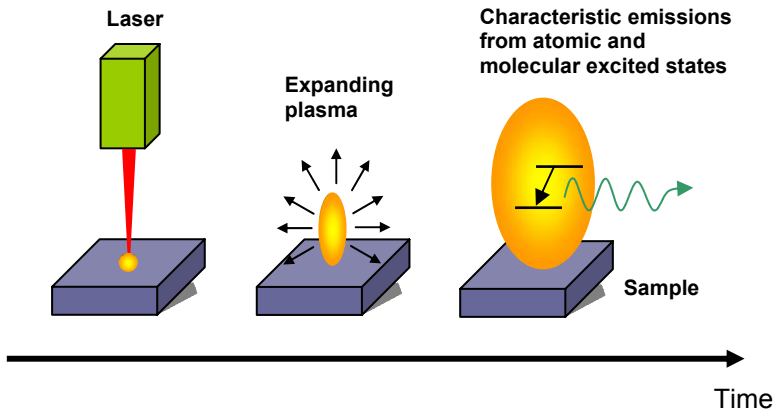


*Figure 37 Illustration of the LIBS principle.*

An important question to answer to assess the usefulness of LIBS for explosives detection is whether it is possible to accurately identify the detected species in a real environment. In a real environment there will be many interfering substances. The explosive surface may not be exposed so the detection may be made on trace particles on a surface. Therefore other dust particles and dirt as well as parts of the surface may be interfering with the result. There can also be contributions from nitrogen and oxygen in the air. Another possible problem is peak intensity variations depending on plasma temperature variations from shot to shot. Some of these issues have been investigated by De Lucia et. al[116]. They identify two possible ways to identify the origin of a LIBS spectrum. The first is to make a spectral matching with a predetermined spectral library and the second is to use the stoichiometry of the compound by taking the intensity ratio between peaks of interest. For explosives these ratios would be C:H and N:O.

There is a European patent pending[117] describing how temporal resolution of the LIBS emission can be used to discriminate between e.g. explosives and plastic materials (Figure 38).

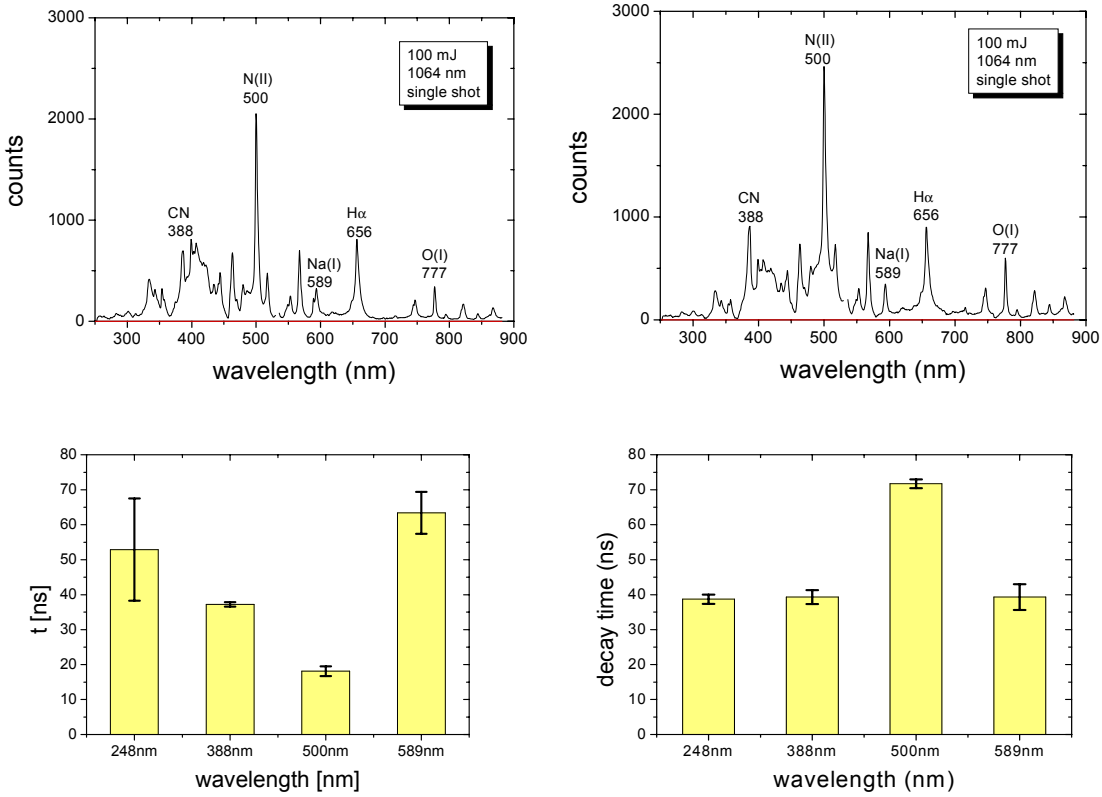


*Figure 38 Temporal resolution of the LIBS emission helps discriminate between different materials. Left: HMX, Right: TNT (From Schade[118]).*

Limit of detection: ng to pg

Speed: fast

Selectivity: high, at least in the lab. n/a in a real environment

Applicability: Stand-off detection

Cost: "*A LIBS system is fairly inexpensive- approximately $50,000 for a system that can detect a wide range of substances, and less than $20,000 for a LIBS system optimized for specific threats*"[119]

Sample type: solid, liquid, gas, aerosol

Skill: n/a

Fieldability: n/a

Size: possible to make rugged and filed portable

### 5.1.3 Multiplex CARS (Coherent Anti-Stokes Raman Spectroscopy)

This technique typically has its use in combustion diagnostics because of its good spatial and temporal resolution. Raman is a fluorescence spectroscopic technique that, in contrast to conventional FT-IR spectroscopy, has the advantage of being able to probe homonucleus species ($O_2$, $N_2$, $C_2$ etc.). Conventional Raman spectroscopy has the disadvantage of the inherent weakness of the incoherent scattering effect, sometimes leading to spectral interference from stronger

processes. In Coherent Anti-Stokes Raman Spectroscopy, the signal is enhanced by non-linear optical effects, and the interference from other processes can be overcome. CARS uses two or more intense laser beams to generate a third, narrowband beam that is coherent and blue shifted relative to the input beams. By gradually changing the frequency of one or more of the incoming beams, spectra can be obtained. However, the process of generating a full vibrational spectrum is time consuming, because of the slow process of shifting the frequency of incoming light.

In [120], a technique of using one broad band laser as two broad band sources is presented. A third narrow band source then defines the spectral resolution. In this way, a spectrum covering the full range of the broad band sources (> 3000 $cm^{-1}$) can be collected in a single laser shot. The authors report spectral resolution of < 1$cm^{-1}$, spatial resolution <0.05 $mm^2$ and temporal resolution < 1s.

Advantages with multiplex CARS compared to conventional Raman and include:

- Ability to achieve 3D spatial resolution (crossed beams)
- Raman signal generated as an intense beam
- Non resonant background
- Signal intensities vary with the square of the concentration
- No trade off between spectral resolution and throughput.

No work aimed at explosives detection has been reported. However, it might be considered for fast and well resolved IR spectroscopic detection/quantification.

Limit of detection: n/a
Speed: Fast
Selectivity: Has potential to be very good
Applicability: References to explosives detection not found.
Cost: High

Sample type: Vapour and particles
Skill: Probably requires a certain degree of skill
Fieldability: n/a
Size: n/a

### 5.1.4 Non-linear wave mixing

When two laser beams overlap they interact with each other. Non-linear effects can yield very specific response to what happens in the overlapping region. Molecules present in the overlapping region interact with the laser beams and the chemical information is transmitted to the detector as a laser-like beam. Laser wave mixing is a very sensitive detection method (ppq levels) and work to investigate its applicability to stand-off detection of explosives has only recently been started [121].

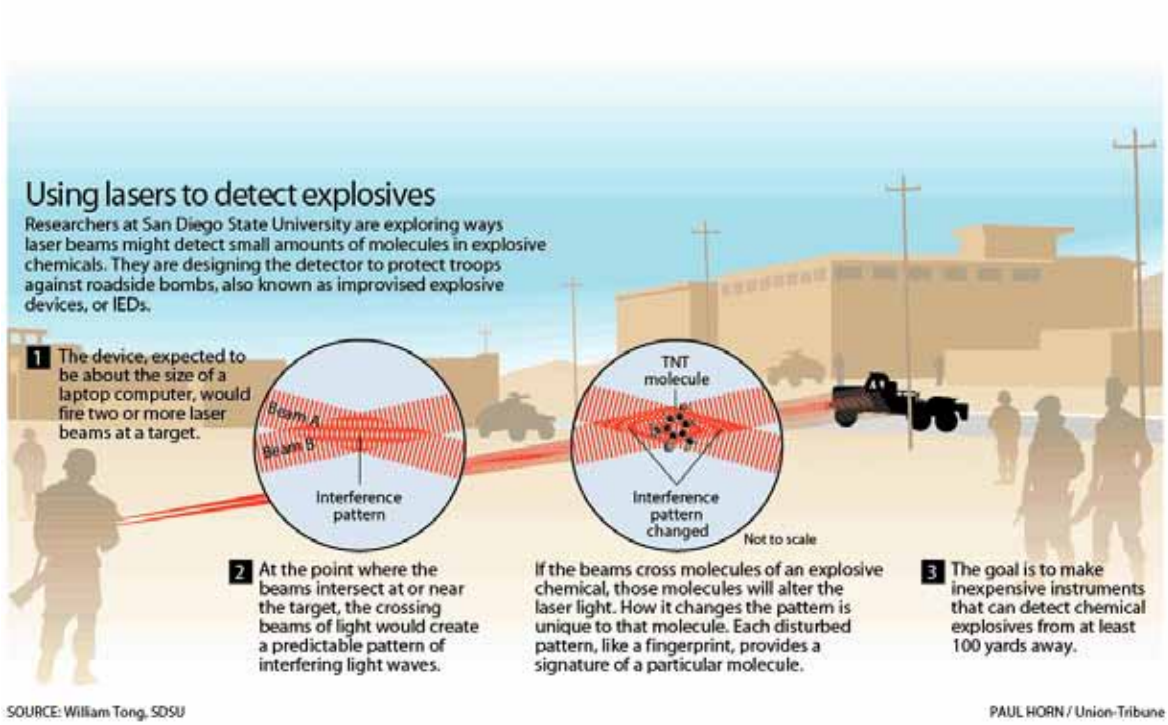


*Figure 39 Detection principle for non-linear wave mixing of laser beams. From Lieberman*[121]

Limit of detection: ppq-levels (very sensitive)
Speed: Fast
Selectivity: High
Applicability: Stand-off detection of explosives

Cost: n/a
Sample type: Vapour
Skill: n/a
Fieldability: n/a
Size: Relatively small, portable.

### 5.1.5 PLP/LIF or PF /LIF

For nitro compound based explosives, it is possible to combine photo fragmentation and the detection of photo dissociated NO radicals. A laser pulse is used to fragment the explosive (Pulsed Laser Photodissociation, PLP, sometimes also referred to as PF, Photo Fragmentation). The fragmentation of nitro based explosives leads to the formation of NO-radicals. Thus the explosive can be detected through monitoring of NO-concentrations. This is not a species selective detection method, rather it will alert for any nitro containing compound. Since NO is frequently present in the atmosphere, interference of background NO and explosives originating NO can cause a sensitivity problem.

The monitoring of NO-radicals is managed with LIF (Laser Induced Fluorescence), which is a spectroscopic detection method of high sensitivity. LIF can be used to monitor NO by probing its vibrational levels in the ground electronic state. A reported method [122] uses the same laser pulse,

wavelength 248 nm, for fragmentation and LIF-spectroscopy. The monitoring is done by excitation in the $A_2\Sigma^+(\upsilon'=0) \leftarrow X^2\Pi(\upsilon''=2)$ transition. The fluorescence originates from $A_2\Sigma^+(\upsilon'=2) \rightarrow X^2\Pi(\upsilon''=0, 1)$ transitions. This means that the excitation is done from a vibrationally exited level of the NO radical.

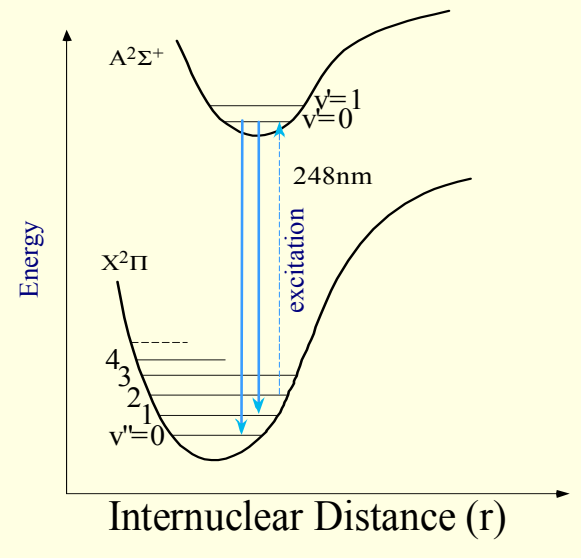


*Figure 40 (From Arusi-Parpar[123])*

Since the atmospheric NO is not excited above $\upsilon'' = 0$ to any noticeable extent at room temperature, atmospheric NO interference is significantly reduced (Boltzmann distribution gives the relative populations of NO in the $\upsilon'' = 0, 1, 2$ states as 1, $10^{-4}$, $10^{-8}$, respectively, at room temperature). In dissociated TNT molecules, at least 30% NO is produced with a $\upsilon'' = 0, 1, 2$ ratio of 1, 0.5, 0.1, respectively. Thus, in this detection scheme, interference from atmospheric NO is greatly reduced. Another contributing factor for interference reduction is that the fluorescence is measured at shorter wavelengths than the excitation wavelength, rejecting fluorescence from TNT and other molecules in the air.

The authors of [122] reports a sensitivity for 2,4,6-trinitrotoluene of 15 ppb at near ambient conditions (atmospheric pressure and explosive sample holder at 28 ºC) and at a range of 2.5 meters.

Other publications has reported sensitivities of 40 ppb [124] or low ppm [125] levels. The detection schemes used were however not chosen for suppressing background interference and measurements were conducted in a low pressure, controlled environment.

This method has potential for remote detection (Figure 41). However the sensitivity needs to be enhanced.

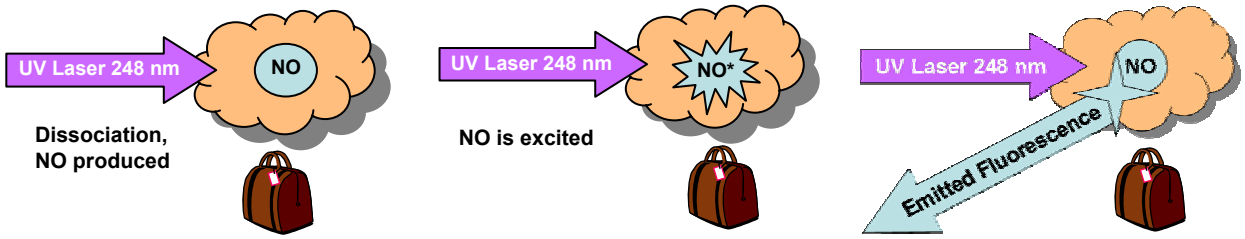


*Figure 41 Detection principle for remote detection by PLP/LIF.*

Limit of detection: low ppb

Speed: fast

Selectivity: poor – detects nitro containing compounds

Applicability: n/a

Cost: n/a

Sample type: gasphase, liquid, solid

Skill: n/a

Fieldability: n/a

Size: n/a

### 5.1.6 LIDAR

The basic principle of LIDAR (LIght Detection And Ranging) is similar to RADAR (RAdio Detection And Ranging), i.e. a short laser pulse is emitted from the laser and the echo (reflections) from objects in the light path is recorded. The position of the object is given by the time delay of the echo. The echo from each laser pulse is recorded at multiple times, thus giving information along the beam path.

This basic form of LIDAR does not give any information about the object that is scattering the light. There are however different variations to the LIDAR principle that can give more information. For example, DIAL (DIfferential Absorpion Lidar) uses two different laser wavelengths, selected so that one of the wavelengths is absorbed by the molecule of interest while the other wavelength is not. The difference in intensity of the return signals is used to determine the concentration of the molecule being detected.

Raman LIDAR detects the Raman scattered light and Fluorescence LIDAR uses a laser wavelength resonant with the investigated species and detects the fluorescence. Raman LIDAR is restricted to detection of a species in high concentrations since Raman scattering has very low cross-section.

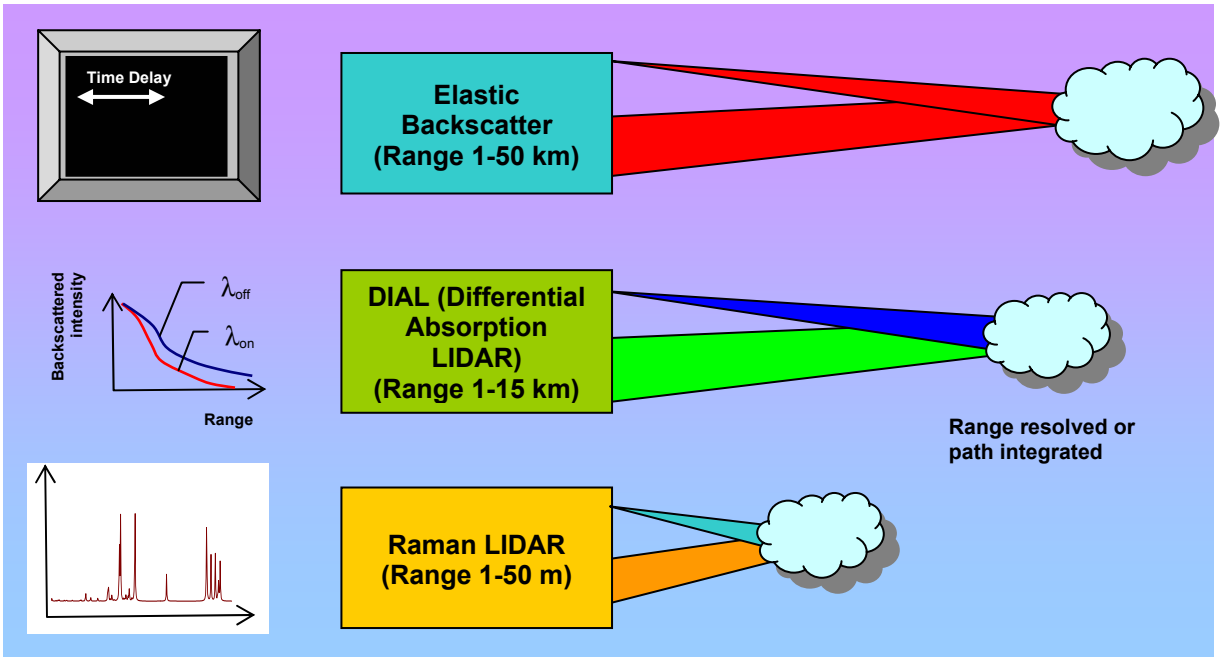


*Figure 42 Some LIDAR measurement techniques. Distances are not applicable to explosives. (After Highdon[126]).*

LIDAR has many uses. The types of LIDAR that give specific information about the detected species are normally used for environmental monitoring. The detected substances are then present in much higher concentrations than explosives vapour around a bomb. LIDAR has however been mentioned as a possible detection method for explosives provided that the sensitivity can be improved[27].

| | |
|---|---|
| Limit of detection: Needs improvement to be useful for explosives detection | Cost: |
| Speed: | Sample type: |
| Selectivity: | Skill: |
| Applicability: Standoff detection potential | Fieldability: |
| | Size: |

### 5.1.7 Resonant Raman Spectroscopy

Two problems with Raman Spectroscopy are solved with Resonant Raman Spectroscopy in the UV. The low sensitivity of Raman spectroscopy is due to its non-resonant nature. With a tuneable laser the wavelength can be chosen to match or nearly match a resonant absorption in the investigated species leading to an intensity enhancement in the order of $10^6$, i.e. significantly lower detection limits.

Another problem with Raman spectroscopy in certain wavelength regions is fluorescence which mask the weaker Raman signal. Even if the investigated substance does not fluoresce, real world samples are likely to contain impurities that fluoresce when illuminated by visible light. Infrared radiation can be used to eliminate this fluorescence since it does not have enough energy to excite the fluorescence. The other approach is to use UV light which will cause fluorescence in the visible – well out of the region where the Raman signal will be.

Using Resonant Raman Spectroscopy in the UV also simplifies spectra since they will be dominated by the resonantly enhanced peaks. A careful choice of excitation wavelength will enhance the Raman spectrum from the target molecules relative other molecules present.

Lacey et al used UV resonant Raman spectroscopy to study explosives and some of their results are shown in Figure 43.

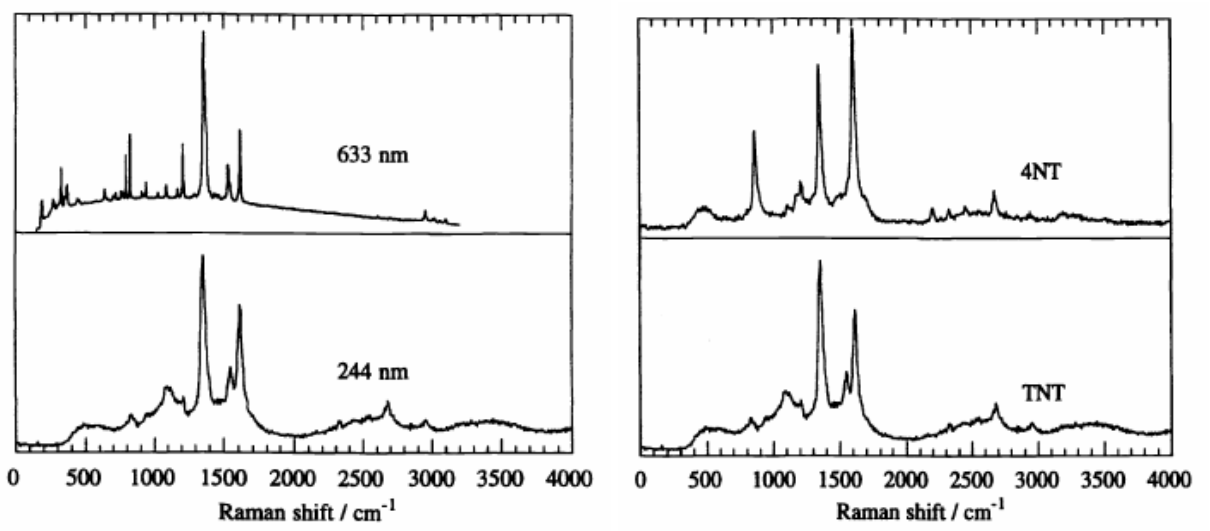


*Figure 43 Left: Comparison of excitation wavelengths for TNT. Right: Comparison between 4-nitrotoluene and 2,4,6-trinitrotoluene. (From Lacey[127])*

Limit of detection: n/a

Speed: n/a

Selectivity: good

Applicability: Standoff detection

Cost: n/a

Sample type: n/a

Skill: n/a

Fieldability: n/a

Size: n/a

# 6 Analytical Methods

## 6.1 Effects of Physical and Chemical Properties of Explosives on Chemical Analysis.

With explosives and related compounds as the analytical targets, GC (Gas Chromatography) and LC (Liquid Chromatography) are two fundamental chromatographic techniques. They are currently the most used methods. They are reliable and well established since decades. Depending on physical properties of the molecules of interest, LC or GC is used.

A wide range of detectors have been developed for both techniques. Again, physical properties govern the choice of detector device. Electro-negativity, adsorbtivity, thermal stability and frangibility are very important properties that are shared by the most frequently used organic explosives. These four properties strongly affect their behaviour in sampling and analysis by all analytical techniques in use today. Another crucial property is the vapour pressure of each compound. The vapour pressure of a molecule is very important when air sampling techniques are used, with low vapour pressure only a small number of molecules are available for sampling.

To be able to detect a molecule it is crucial that the analyte is possible to ionise. A positive or negative charge has to be created on the target molecule[128]. The most commonly used explosives with nitramino and nitro groups in the molecule have a strong electron affinity. Thanks to this property, electron capture or other negative ionisation techniques are the methods of choice.

Very polar molecules, e.g. explosives, adsorb to a wide range of different surfaces, such as glass, quartz, wood, steel, fused silica, and even Teflon. Once adsorbed, explosives must be desorbed and vaporised in order to be collected and analysed. When a surface with adsorbed explosives is heated, it is very important to increase the temperature slowly to prevent thermal degradation of the explosive molecules[129].

Chromatographic systems connected to an appropriate detector can be and are used in order to verify and validate new analytical systems. They are also important chemical tools to use when different sampling techniques and detection devices are investigated.

## 6.2 Gas Chromatography (GC)

Gas Chromatography (GC) is a very useful analytical technique for the separation and identification of organic compounds, including some of the most common explosives e.g. TNT and related molecules. The drawback of GC is that the molecule must be thermally stable, and have a distinct boiling point.

Generally, a GC system utilises a carrier gas, helium, nitrogen or hydrogen, to transport the molecules (analytes) from the injection port, through the column and finally into the detector, where a specific molecule gives a specific response as the compound passes.

Separation of complicated mixtures is possible by using the differences in boiling points. The interactions between the molecules and the analytical column are also used to separate the analytes. The analyte mixture solution is injected to the system by the injection device. The analytes are in solution on the beginning of the column with carrier gas flowing through. The initial column temperature (50 to 100 °C) is maintained below the boiling points of the compound to be analysed and above the boiling point of the used solvent. After a short time (a few minutes) the oven temperature increases. When the temperature reaches the boiling points of the molecules they will vaporise and be carried into the detector retained and separated with different retention times.

In most applications, the injection port has a higher temperature (250 to 300 °C) than the boiling points of all analytes and the column temperature alone is used for separation. However, when the molecules of interest are explosives another injection technique is required. The sample is injected directly onto the column that has a temperature of 50 to 100 °C. This is to avoid thermal decomposition of the analytes due to their frangibility properties.

GC separation of analytes is often used together with various detection devices, e.g. IMS and SAW detectors to increase their specificity.

## 6.3 Liquid Chromatography (LC)

LC (Liquid Chromatography) is a chromatographic method where the sample is dissolved in a solvent and injected into an HPLC (High Performance Liquid Chromatography) system via an injection port[130]. The injection port of an HPLC commonly consists of an injection valve and a sample loop. Typically, a sample is dissolved in the mobile phase before injection into the sample loop. The sample is then drawn into a syringe and injected into the loop via the injection valve. Then, a rotation of the valve rotor closes the valve and opens the loop in order to inject the sample into the stream of flowing solvent. Loop volumes can range between 10 µl to over 500 µl. In modern HPLC systems, the sample injection is typically automated.

The mobile phase in HPLC refers to the solvent being continuously pumped through the analytical column. The mobile phase acts as a carrier for the sample in solution. A sample solution is injected into the mobile phase through the injector port. As the sample solution flows through a column with the mobile phase, the components of that solution migrate according to interactions of the compound with the analytical column. The chemical interactions of the mobile phase and

sample with the column, govern the migration and separation of components in the sample. For example, those samples that has stronger interactions with the mobile phase than with the analytical column will elute from the column faster and thus have a shorter retention time, while the reverse is also true. The mobile phase can be varied to manipulate the interactions of the sample and the analytical column.

## 6.4 Detectors used in GC analysis of explosives

The detector is used to continuously analyse the carrier gas that is eluting from the analytical column and to generate a signal in response to variation in its composition due to eluted components. The GC detector has to respond very fast to concentration gradients of different molecules as they elute from the column. Stability, linear response, ease of operation is together with a uniform response to a wide range of molecules very important properties that are required. GC systems are connected to different detectors in order to create optimal sensitivity and specificity for the molecules of interest. Detectors most frequently used for explosives are, ECD,NPD and MS.

#### *6.4.1.1 Electron Capture Detector (ECD)*

The ECD has a limited dynamic range and is most often used in analysis of halogenated compounds. The ECD is extremely sensitive to molecules containing highly electronegative functional groups such as halogens, peroxides, quinones and nitro groups. ECD is therefore a widely used detector for trace level determinations of explosive residues in environmental samples[131]. It is insensitive to functional groups like amines, alcohols and hydrocarbons.

Sensitivity: 1-100 pg (nitro compounds)

#### *6.4.1.2 Nitrogen Phosphorous Detector (NPD)*

In the literature there exist several names for the nitrogen-phosphorus detector and the terminology is quite ambiguous. The term thermo ionic detector (TID) principally describes the function of the ionization process, where the sample molecules are converted to negative ions in the detector by extraction of electrons emitted from a hot solid surface[132]. This detector is used mainly for TNT and other explosive related aromatic molecules.

Sensitivity: 1 pg (nitrogen and phosphorus)

#### *6.4.1.3 Mass Spectrometer (MS)*

With the use of a mass spectrometer, it is possible to obtain information about the weight of a specific molecule. GC combined with MS, is a powerful analytical tool. An analytical chemist can take an organic solution with an unknown mixture of explosive molecules, inject it into the instrument and then separate, identify and quantify the different components.

The MS as a detector gives an additional method apart from retention times (GC) to use in the identification process. The weight of each molecule in combination with the retention time gives a very powerful identification technique.

The detector is operating under vacuum. When an individual molecule elute from the analytical GC column, it enter the electron ionisation (mass spectrometer) detector. There, the analyte is bombarded and ionised with a stream of electrons causing it to break apart into fragments. These fragments can be used to identify the original molecule. The fragments are charged ions with a certain mass. The mass of the fragment divided by the charge is called the mass to charge ratio (*m/z*). Since most fragments have a charge of +1, the *m/z* usually represents the molecular weight of the fragment.

There are two ionisation techniques used to analyse explosives, EI (Electron Ionisation) and CI (Chemical ionisation). The EI ionisation method is suitable for thermally stable compounds. Molecules in vapour phase are bombarded by electrons, usually of 70 eV energy. This results in ion formation (ionization). Some of these molecular ions decompose into fragment ions. The quantities needed for an experiment is usually less than a microgram of material. The major problem with EI is that when explosive molecules are analysed, the molecular ion peak is often very weak. In these cases, the softer method CI can be used to obtain information about the molecular ion[131]. Reagent gas (e.g. ammonia, methane or butane) is initially subjected to electron impact. Sample ions are formed by reactions of reagent gas ions and sample molecules. Reagent gas molecules are present in the ratio of about 100:1 with respect to sample molecules.

Sensitivity: 1-10 pg (Neg CI)

## 6.5 Detectors used in HPLC analysis of explosives

There are a number of detectors that can be used with HPLC. Two of the most common detectors used for explosives are absorption of Ultra-Violet light (UV) and Mass Spectrometer (MS).

### *6.5.1.1 Ultra-Violet light absorption (UV)*

UV detectors measure the ability of a molecule to absorb light. This can be achieved in different ways. A fixed wavelength measures at one single wavelength. Variable wavelength measures at one wavelength at a time, but can scan over a wide range[130]. The diode array detector measures a spectrum of wavelengths simultaneously. Most of the organic explosives contain nitro groups and are therefore possible to analyse with a UV detector[133]. Figure 44 illustrates a UV chromatogram collected at 290 nm.

Detection limit: 1 to 10 ng

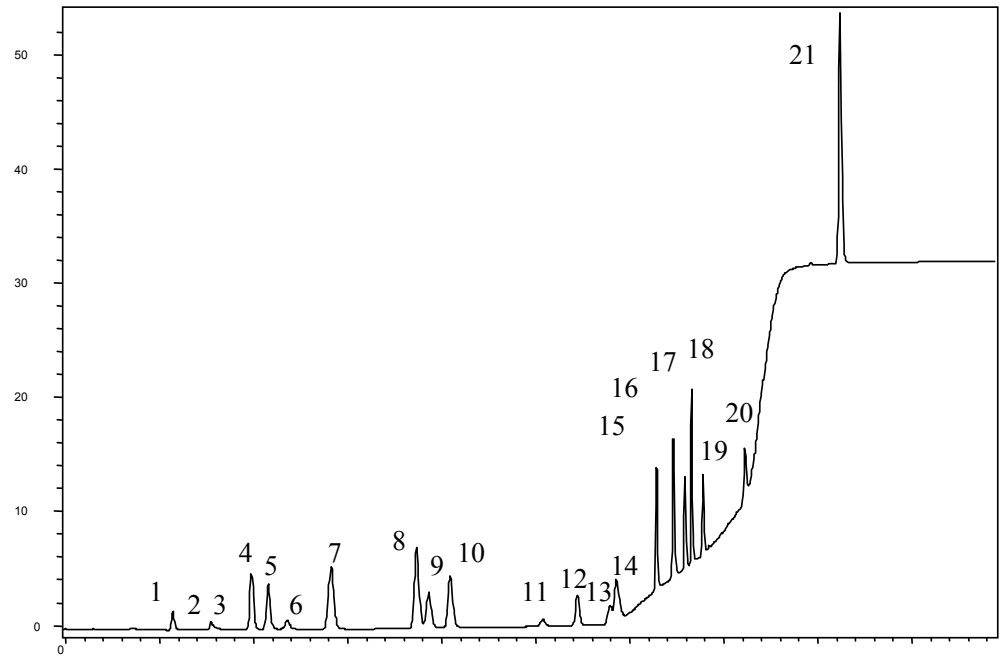


*Figure 44 UV Chromatogram collected at 290 nm. 1)RDX; 2) PETN; 3) HMX; 4) 1,2-DNB; 5) 2,4-diamino-6-NT; 6) CL 20; 7) Tetryl; 8) 3,4-DNT; 9) 2,3-DNT; 10) 2,6-DNT; 11) 2,6-Diamino-4-NT; 12) 4-Amino-2,6-DNT; 13) 1,3-DNB; 14) 1,4-DNB; 15) 2,5-DNT; 16) 2,4-DNT; 17) TNT; 18) 2-Amino-4,6-DNT; 19) 3,5-DNT; 20) TNB; 21) HNS.*

### *6.5.1.2 Mass Spectrometer*

Interfacing an HPLC system with a mass spectrometer is quite complicated. The analyte has to move from a solvent mixture into a gas phase and finally ionise. The solvent has to evaporate while an acceptable vacuum level in the mass spectrometer is maintained, and to allow the generation of gas phase ions. Most analyses of explosives are currently done with electro spray (ESI) and APCI ionisation. ESI and APCI are both API (Atmospheric Pressure Ionisation) techniques[128]. The ionisation step takes place at atmospheric pressure and both are considered to be quite soft ionisation methods. The mass spectrum produced gives mainly information about the molecular weight, unless fragmentation techniques are used. The three possible fragmentation

techniques are in source CID (collision induced dissociation), CID in the collision cell of a triple quadropole type instrument and fragmentation in an ion trap[128]. Figure 45 illustrates an MS chromatogram.

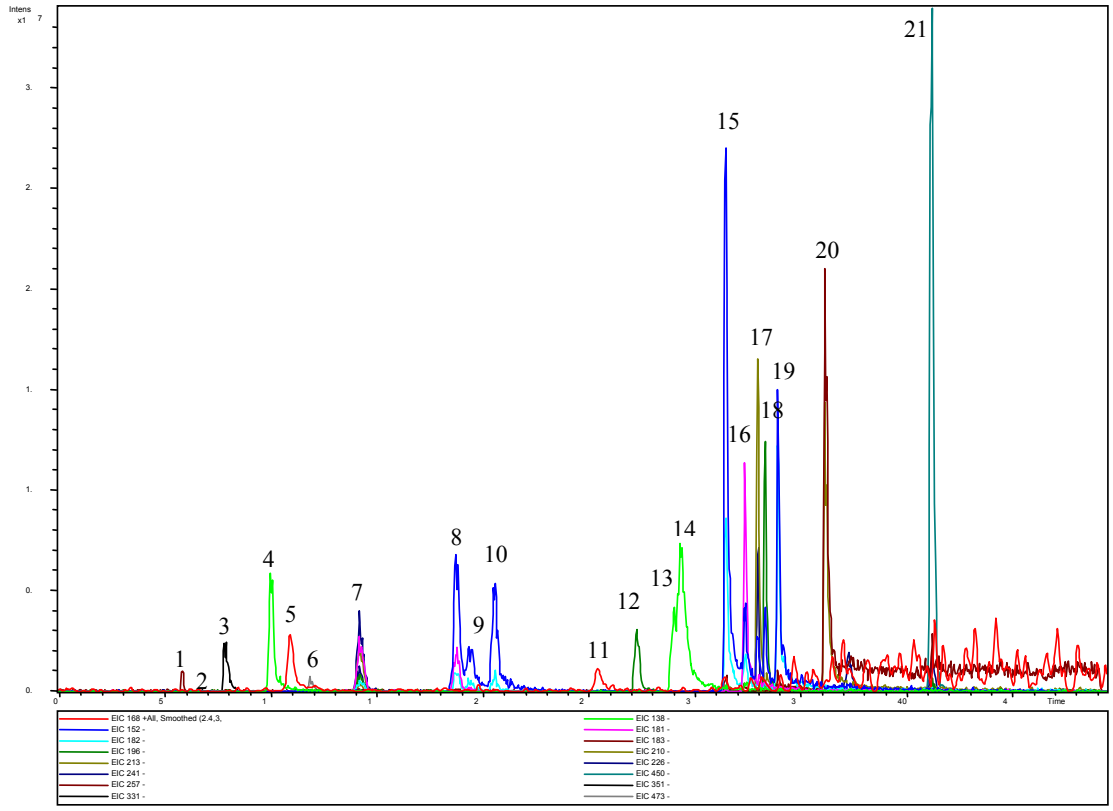


*Figure 45 MS chromatogram (APCI). 1)RDX; 2) PETN; 3) HMX; 4) 1,2-DNB; 5) 2,4-diamino-6-NT; 6) CL 20; 7) Tetryl; 8) 3,4-DNT; 9) 2,3-DNT; 10) 2,6-DNT; 11) 2,6-Diamino-4-NT; 12) 4-Amino-2,6-DNT; 13) 1,3-DNB; 14) 1,4-DNB; 15) 2,5-DNT; 16) 2,4-DNT; 17) TNT; 18) 2-Amino-4,6-DNT; 19) 3,5-DNT; 20) TNB; 21) HNS.*

### *6.5.1.3 Applications in summary:*

The application field of LC/MS regarding explosives and related compounds are covered by two major ionisation techniques - ESI and APCI. In recent years, powerful techniques have been developed and new analytical tools are available. In the area of LC-MS, there has been an explosion of new products that has solved a lot of analytical problems. Explosives which are non volatile, labile or have a high molecule weight are now possible to analyse with fewer problems[133,134]. Analysis by the use of GC connected to detectors like ECD, NPD or MS is limited to explosives that are stable enough and have a distinct boiling point. TNT and related compounds are stable enough to be analysed by GC and detectors such as ECD, NPD and MS gives detection limits for these compounds in the fg to low pg level[131,135]. New miniaturised GC systems are now commercial and will maybe result in new possible applications for analysis outside the laboratory facilities[136]. RDX, HMX, PETN, Tetryl is preferably analysed with LC-MS due to their

frangibility[133]. Water soluble energetic salts are analysed and detected by the use of LC-MS[137]. LC-MS generally gives higher detection limits, in the high pg to low ng level. LC-UV is often used when only a few analytes are analysed, soil samples and other complicated sample matrices, which has a lot of other species are very difficult to analyse due to unspecific UV absorption. When LC-UV is possible to use the detection limit is in the ng level[137]. A new technique UPLC is a development of HPLC. Compared with HPLC, UPLC performs an analysis much faster. For a general application, UPLC is about 4 to 5 times faster, gives better separation, lower detection limits and consumes less solvent[138]. This technique is possible to apply on the analysis of explosives and UPLC will probably be the dominating LC system used in the future.

# 7 Conclusions

A number of important conclusions can be drawn from this survey:

- Sensors need to be specific, fast and able to detect many substances, as well as provide an identification of the threat.
- No single sensor exists today that is capable or even has the potential to solve all explosives detection scenarios.
- Sensors need to be chosen to suit the chosen scenario application.
- Multiple sensor systems will be necessary to solve many problems.
- Bulk detection sensors need to be developed to detect specific chemical information rather than physical properties like density and nitrogen content. (Eg. there are explosives with low density and no nitrogen content.)
- Sampling of both vapour and particles is an underdeveloped and very important area for trace detection methods.
- Standoff detection methods are desperately needed but far away in technical development. A lot of effort is needed in this area.
- Research and development is needed in trace detection methods and sampling, bulk detection and standoff detection.
- It is desirable to have common standards for certification of explosives detection equipment as well as independent testing and certification authorities.
- Explosives detection is a very challenging problem but also a very important problem to solve considering developments in both military threats and threats by terrorists. This is a technology area which should be one step ahead of the threat development but is currently several steps behind. It becomes increasingly important to develop detection capabilities for many purposes, both military and civilian. It will take a lot of effort to solve and it is important to work with both research and development in this area for a long time to come.

# 8 Abbreviations

| | |
|---|---|
| AN | Ammonium Nitrate |
| ANFO | ammonium nitrate + fuel oil |
| APCI | Atmospheric Pressure Chemical Ionization |
| APPI | Atmospheric Pressure Photo Ionization |
| C4 | plastic explosive containing ~ 91% RDX, 5% bis(2-etylhexyl) sebacate and 2% polyisobutylene |
| CARS | Coherent Antistokes Raman Scattering |
| CFI | Continuous Flow Immunosensor |
| CI | Chemical Ionization |
| CL | Chemiluminescence |
| CRDS | Cavity Ring Down Spectroscopy |
| DESI | Desorption Electrospray Ionization |
| Detasheet | plastic explosive based on PETN, plasticizer and elastomeric binder |
| DIAL | Differential Absorption LIDAR |
| DMNB | 2,3-Dimethyl-2,3-dinitrobutane |
| DNT | dinitrotoluenes |
| Dynamite | |
| ECD | Electron Capture Detector |
| EGDN | ethylene glycol dinitrate |
| ESI | Electrospray Ionization |
| FAIMS | High Field Assymetric Waveform Ion Mobility Spectrometry |
| FID | Flame Ionization Detector |
| FOB | Fiber Optic Biosensor |
| FT-IR | Fourier Transform Infrared |
| GC | Gas Chromatrography |
| HMX | cyclotetramethylene-tetranitramine, octogen |
| HPLC | High Performance Liquid Chromatography |
| IED | Improvised Explosive Device |
| IMS | Ion Mobility Spectrometry |
| IR | Infrared |
| IT | Ion Trap |
| LC | Liquid Chromatography |
| LIBS | Laser Induced Breakdown Spectroscopy |

| | |
|---|---|
| LIDAR | Light Detection and Ranging |
| LIF | Laser Induced Fluorescence |
| LIMS | Laser ionization IMS |
| LI-MS | Laser ionization mass spectrometry |
| LOD | Limit of Detection |
| MALDI | Matrix Assisted Laser Desorption Ionization |
| MNT | mononitrotoluene |
| MS | Mass Spectrometry |
| NG | nitroglycerine |
| NMR | Nuclear Magnetic Resonance |
| NN | nitronaphtalenes |
| NP | nitropyrene |
| NPD | Nitrogen Phosphorous Detector |
| NQR | Nuclear Quadrupole Resonance |
| NT | nitrotoluenes |
| PETN | pentaerythritol trinitrate |
| PF | Photo Fragmentation |
| PFTNA | Pulsed Fast/Thermal Neutron Analysis |
| PLP | Pulsed Laser Photodissociation |
| ppb | Parts per billion ($10^{-6}$) |
| ppm | Parts per million ($10^{-3}$) |
| ppq | Parts per quadrillion ($10^{-12}$) |
| ppt | Parts per trillion ($10^{-9}$) |
| PTFE | Polytetrafluoroethylene |
| QC | Quantum cascade |
| RDX | cyclotrimethylenetrinitramine, hexogen |
| REMPI | Resonance Enhanced Multi Photon Ionization |
| SAW | Surface Acoustic Wave |
| Semtex | plastic explosive based on RDX and PETN, in equal amounts, antioxidant, plasticiser, dye, oil and binder |
| SERS | Surface Enhanced Raman Scattering |
| SIM | Selected Ion Monitoring |
| SOP | Semi conduction organic polymer |
| SPI | Single Photon Ionization |

| | |
|---|---|
| SPR | Surface Plasmon Resonance |
| TATP | triacetone triperoxide |
| TEA | Thermal Energy Analyzer |
| THz | Teraherz |
| TIC | Total Ion Count |
| TID | Thermo Ionic Detector |
| TNB | Trinitrobenzene |
| TNT | Trinitrotoluene |
| TOF | Time of Flight |
| UPLC | Ultra Performance Liquid Chromatography |
| UV | Ultra violet |
| UXO | Unexploded Ordnance |
| XRF | X-Ray Fluorescence |

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**Abstract**
This report is a literature survey of explosives detection methods, bulk and trace detection sensors as well as standoff detection techniques. Sample collection for trace detection is not a priority for this survey although it is of outmost importance for a complete overview. This report attempts to cover not only existing techniques but also emerging technologies and technologies with possible future potential for explosives detection. However, the area is so wide spread so it cannot be presumed to be complete in any way.

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**Rapportens titel**

Explosivämnesdetektion - en teknisk inventering


**Sammanfattning**

Denna rapport redovisar en litteraturstudie om metoder för explosivämnesdetektion – sensorer dör bulk och spårmängdsdetektion liksom avståndstekniker. Provinsamling för spårmängdsdetektion är av yttersta vikt för en komplett översikt, men är inte en prioriterad del av denna studie. Rapporten strävar efter att inte bara behandla existerande tekniker utan även nya tekniker under utveckling och tekniker med möjlig framtida potential för explosivämnesdetektion. Området är dock så stort att sammanställningen säkerligen inte kan kallas komplett på något sätt.



**Nyckelord**

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