Chemical sniffing instrumentation for security applications.

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**ABSTRACT**

Border control for homeland security faces major challenges worldwide due to chemical threats from national and /or international terrorism as well as organised crime. A wide range of technologies and systems with threat detection and monitoring capabilities has emerged to identify the chemical footprint associated with these illegal activities. This review paper investigates artificial sniffing technologies used as chemical sensors for point-of-use chemical analysis, especially during border security applications. This article presents an overview of a) the existing available technologies reported in the scientific literature for threat screening; b) commercially available, portable (handheld and stand-off) chemical detection systems; and c) their underlying functional and operational principles. Emphasis is given to technologies that have been developed for in-field security operations, but laboratory developed techniques are also summarised as emerging technologies. The chemical analytes of interest in this review are: a) volatile organic compounds (VOCs) associated with security applications (e.g. illegal, hazardous and terrorist events); b) chemical “signatures” associated with human presence; and c) threat compounds (drugs, explosives and chemical warfare agents).

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# Introduction to artificial sniffing for security applications

Worldwide border policing for homeland security faces major challenges due to threats from national or international terrorism and organized crime. 1, 2 The continued increase of illegal immigration and human trafficking (especially of children and women) is of particular concern as well as problems associated with illegal transportation of narcotics, explosives, chemical weapons and other restricted goods. Existing mainstream technology for bulk or trace detection of threat compounds (natural and/or chemical) and of human trafficking has limitations. Research programmes are ongoing worldwide in order to develop improved instrumentation.

Olfaction arises from the stimulation of the olfactory system by odorous compounds. It has always been and remains one of the most important biological processes providing information about the surrounding environment. In the animal kingdom especially, olfaction provides early warning against potential threats and/or other safety related issues. Both in microsmatic (human) and macrosmatic species (sniffer dogs) the sniffing processes are similar, however the differences in the anatomy of the olfactory system (e.g. epithelium structure) and in the olfactory acuity and detectability are huge. The sniffing process consists of inhaling air samples in very small quantities to detect odorants that carry certain information at low concentration levels. In this way, the analytical process depends on the morphological parameters of the particular olfactory system in question (nasal cavity, epithelium, bulb, lobe, receptor cells and neurons, etc.) including genomic factors, brain signal interpretation capabilities and species physiology.3-7 A simplified sniffing procedure may be described by the following steps:

1. pulsed sampling (inhalation) of air molecules during a certain period of time (sample collection);
2. entrapment of specific odorant substances (e.g. volatile organic compounds - VOCs) by the receptors covering the olfactory epithelium;
3. detection and odor discrimination via the olfactory receptor neurons (data acquisition);
4. data processing and signal interpretation;
5. odor recognition.

Artificial sniffing may be defined as the sum of those techniques and processes that attempt to reproduce the sense of smell originating either from human beings or from animals (e.g. canines, sniffer dogs, mosquitoes, honeybees, pigs). Artificial sniffing is a multidisciplinary field which employs, combines and integrates different areas of science, technology and engineering to explore (through mimetic and metaphoric approaches) and to replicate olfaction by developing smart systems or arrays which can exhibit trace odor sensing capabilities. Artificial sniffers (also termed artificial noses) have been successfully used in a wide range of applications such as: homeland security, search and rescue, forensics, environmental, health, medicinal products industry, food industry, doping screening, quality assurance (QA) and quality control (QC).6-11 Artificial noses can be deployed both in controlled conditions (laboratory) and in harsh (*in-situ*) environments.

This review paper investigates artificial front-end chemical sensor instrumentation and approaches especially developed for in-field border security applications. The article presents an overview of a) the existing technologies reported in the scientific literature for threat screening; b) commercially available portable chemical detection systems (both handheld and with a stand-off distance) and c) their underlying operational principles and functions. Emphasis is given on technologies that have already been developed for in-field security operations, but laboratory-developed and tested techniques are also summarized as developing technologies. The chemicals of interest include: a) volatile organic compounds (VOCs) associated with security applications (e.g. illegal, hazardous and terrorist events); b) ‘‘human chemical signatures’’ including a comparative presentation of volatile compounds identified in human body scent (produced from various parts of the human body); and c) non-volatile threat compounds (drugs, explosives and chemical warfare agents (CWAs)) including their physical and chemical properties.

# Field chemical analysis

Demands for real time or near real time accurate chemical analysis, increasingly require techniques that operate ‘‘in the field’’. Field chemical analysis eliminates sample transportation/storage costs and minimizes sample contamination risks during shipment from a distant site back to the laboratory.12 In addition to time and cost reduction, field analysis allows rapid problem-solving, decision-making and operational simplicity. Field chemical analysis is therefore a rapidly evolving and promising research area focusing on bringing the required (for each case) analytical equipment to the sampling area, instead of the traditional procedure: transportation of the sample to the laboratory.

This inversion of methodology has raised new functional and operational issues which need to be addressed. These are related to a) analytical instrumentation specifications, b) analytical performance and c) sample collection, preparation and sample introduction requirements.13 New analytical criteria have been established to evaluate instrument performance and to accommodate or fulfill essential field requirements, such as portability. This includes: apparatus size-overall dimensions, total weight, hand carry or backpack option, field-applicability, robustness (absorption of vibrations, waterproof protection, heavy duty protection), reliability (analytical stability and reproducibility), power consumption (the lower, the better), user-friendliness (minimal training requirements and simple operation via graphical user interface), low maintenance costs, fast analysis (within seconds), high sensitivity (low detection limits) and accuracy.14-16

During the last few years, the number of requests (from different research and industrial areas) for on-site chemical analysis increased dramatically. Often however, the desire for field measurements entails potential health risks or hazards for the operating personnel. To prevent and to address possible health, safety and operational issues, analytical instrumentation for *in-situ* chemical analysis (or field technology) is under continuous improvement. Currently instrument development teams can provide a range of handheld devices or stand-off distance or remote sensing devices. Concepts for field chemical analysis during security applications include: a) detection of targeted substances in the solid, liquid and gaseous phase, b) on-line chemical monitoring, c) chemical characterization, d) profiling, and e) mapping.

Major existing challenges during field operations are: a) the complexity of the background chemical environment, b) potential instrumentation drawbacks/limitations and c) the complexity of the nature of targeted sample compounds. More specifically in this review article in which artificial sniffing in border security and forensic applications is investigated, the following problems may arise on-site:

1. complex odorous chemical backgrounds interfering with target threat compounds and causing false-positive or false-negative alarms or even sometimes camouflaging/masking potential threat events;
2. threats based on extremely low levels of signal concentration (e.g. very low chemical odorous signals are emitted from the human body and are diluted in complex backgrounds with various interferences for the cases investigating illegal human trafficking, inventive terrorism and crime scenarios for concealing illegal and hazardous substances for threat transportation cases, etc.);
3. complex mass transport phenomena of threat odor plumes are usually difficult to model and to simulate;
4. lack of fully integrated threat reference substance libraries;
5. differing nature of the threat compounds (homemade, standard, etc.), quantity (trace or bulk) and properties (e.g. very low vapor pressure values make detection difficult or sometimes unfeasible);
6. geographic, environmental and weather conditions such as altitude, density of air, humidity, temperature, wind velocity and direction etc.;
7. lack of sufficient number of threat detection devices (able to detect, monitor and locate potential dangers) with fast response times and specially trained operating personnel (here the case of sniffer dogs-handlers is also included, since the current number of canines and their handlers is not sufficient to monitor all the security checkpoints);
8. the high purchase and maintenance costs of threat detection devices.

# VOCs associated with security applications

## **VOCs theory**

Volatile organic compounds (VOCs) are an important chemical class found almost everywhere in our daily lives. VOCs are found in both indoor and outdoor environments; they occur in many natural, manmade or industrial activities and can threaten human health status. VOCs are also of concern as environmental pollutants and play a significant role in photochemical smog and in global warming. Besides the interest on the effects of the VOCs upon the environment, there is a broad research focus on VOCs emanations or applications originating from the medical, security, defense, search and rescue (SaR), agricultural, pharmaceutical and R&D fields. VOCs carry pivotal information, which when decoded is of great significance. Several international organizations have tried to give a clear definition of what volatile organic compounds are:

* VOCs include all organic compounds (with key elements carbon and hydrogen), with boiling points in the range between 50°C - 260°C, excluding pesticides (WHO, World Health Organization).17
* VOCs are any compounds of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates carbides and ammonium carbonate, which participate in atmospheric photochemical reactions (EPA, U.S. Environmental Protection Agency, 1992).18
* The term VOC refers to any organic compound having an initial boiling point less than or equal to 250°C measured at a standard pressure of 101.3 kPa (EU, Directive 2004/42/CE of the European Parliament and the Council, 2004).19

An additional definition of VOCs comes in relation to the vapor pressure property (PS):

* Organic compounds which have vapor pressure PS  greater than 0.1 Torr at 25°C and 760 mmHg are considered as VOCs (EPA, US, TO-15).18

The above definitions given by the WHO, the EPA and the EU indicate the importance of the boiling point and vapor pressure in the VOCs characterization. A more comprehensive VOC definition could be the following: VOCs are defined as the organic compounds that have: a) vapor pressure PS over 0.1 Torr at 25°C and 760 mmHg and b) boiling point below 260°C. Generally, the VOCs can be defined as the organic compounds whose formation allows them to evaporate and therefore diffuse in the gaseous phase under normal atmospheric temperature and pressure conditions. Every VOC (according to its physical and chemical properties and especially its vapor pressure) is usually accompanied by the release of a specific scent.

VOCs can be produced by both indoor and outdoor sources.17 Indoor found VOCs are all the organic compounds that can volatilize under room temperature and pressure. For example, indoor VOCs can be released from paints, furniture, carpets, cleaning equipment, etc. Outdoor VOCs are those chemical compounds that affect ambient environmental conditions (e.g. photochemical oxidation) and are usually produced by industrial processes, fires, solvent use, cars, etc.

Moreover, VOCs emissions can be classified according to their origin as anthropogenic and biogenic.18 Anthropogenic VOCs derive mainly from manmade activities such as industrial processes, engines, fuel combustion processes, whereas biogenic VOCs derive from natural vegetation (plants, trees and microorganisms).

Additional VOCs’ discrimination into subcategories is based on their ease for volatilization. VOCs boiling point plays a major role in this categorization. Chemical compounds with boiling point between 1°C and 50-100°C are described as very volatile organic compounds (VVOCs). Organic compounds with boiling points in the range of 50-100°C to 240-260°C are characterized as volatile whereas compounds with boiling points 240-260°C to 380-400°C are named as semi-volatile (SVOCs).17

Another classification is from a human perspective and discriminates VOCs as endogenous and exogenous. This is especially important for health research e.g. in breath analysis for biomarker discovery and for diagnostic purposes. Endogenous compounds are those that are produced from various metabolic processes in the human body and exogenous compounds originate from the surrounding environment, usually entering the human body by inhalation.18

In order to understand the chemical behavior of a VOC of interest, it is important to investigate its physical and chemical properties such as molecular weight, chemical structure, vapor pressure, boiling point, polarity, solubility, Henry’s Law constant and Octanol-Water partition coefficient. The chemical properties of known VOCs in a simple or complex mixture establish the selection criteria of an appropriate methodology for their chemical analysis.

## **Human chemical signatures**



### **The complexity of human scent**

Chemical signs of human life are a novel and challenging research field seeking exploration. Research is being carried out to specify and establish characteristic volatile chemical compounds emitted from exhaled human breath, sweat, skin, urine and other biological excretes.20-25 Human odor as a total is a complex mixture of thousands of evolved chemical compounds which depend on personal characteristics (e.g. age, gender, diet, health condition, exercise, etc.) and has not been fully characterized. Furthermore, human body odor analysis belongs in the area of trace chemical determination, as most of the VOCs have concentration levels from low ppt to some hundreds of ppb. Complex constant or dynamic odorous chemical backgrounds (e.g. those found at cargo services, airports, security checkpoints, etc.) with various environmental conditions (e.g. temperature, humidity, altitude, etc.) make the human chemical signatures’ detection issue difficult for investigation.25-27 It is noteworthy that there is a lack of ‘‘odorprint’’ type databases storing human body odors compared to existing integrated human fingerprints, DNA or retinal scan databases. Creation of such ‘‘odorprint’’ libraries could be of great assistance for law enforcement personnel and civil security services.



### **Biological and chemical origin of human body odor**

Human skin comprises approximately 12-15% of body weight and is colonized by a vast number of both aerobic and anaerobic bacterial microflora. The main bacteria hosted include Gram-positive cocci of *Staphylococcus* and *Micrococcus* as well as a variety of Gram-positive rods, mainly *Corynebacterium*. Other known skin hosted bacteria are: *Streptococcus*, *Pseudomonas*, *Bacillus*, *Acinetobacter*, *propionibacteria* etc. Some of these are potentially pathogenic, especially if the epidermis is injured and they can find a way to have access under skin. Some others are “friendly” to individuals and simply symbiotic. Their number changes with age, gender and origin.28, 29

Human skin also contains three different types of glands (eccrine, sebaceous, apocrine), distributed in different body regions, which produce sweat. Sweat, in its primary form, is a sterile and mostly odorless biological fluid. When this fluid is metabolized by the microbiota hosted on the human skin, it is converted to an odorous liquid with hundreds of VOCs that transmit to the body’s surrounding area through a complex heat transfer mechanism.

Human body odor depends on two different factors: a) those stable over time and b) those that vary with environmental or other conditions. It is very difficult to distinguish the genetic influences from those coming from other sources such as different lifestyles, socioeconomic status, etc. Stable factors over time are the genetic factors, such as those that are responsible for human gender, color, and ethnic background. The characteristic odor originating from genetic factors is called “**primary odor**”. The term “**secondary odor**” describes constituents that are present because of diet and environmental factors. Finally, the term “**tertiary odor**” involves compounds that are present due to the influence of outdoor factors like perfumes, soaps, lotions, etc.28

The human axillae are the areas mainly responsible for personal odor. Due to the human upright stance and their position in body, the axillae are responsible for chemical communication.30 The axillary area is a complex microbial habitat, with sebaceous, apocrine and eccrine glands. The principal source of normal axillary smell is the conversion of water-soluble precursor compounds into volatile aliphatic acids by the activity of *Corynebacterium* species.

Axillary glands are more active in men than in women and give the characteristic “sweaty armpit odor”. The 3-methyl-2-hexanoic acid and 3-hydroxy-3-methylhexanoic acid are typical emanations of the axillary area. Other contributors to the axillary malodor are: produced sulfur compounds and odorous steroids. The 3-methyl-3-sulfanylhexanol is also a major component found in axillary odor. Characteristic identified odorous steroids are the 16-androsterenes, the 5α-androsterol and the 5α-androsterone.31, 32 Table 1 gives an overview of the volatile odorous emissions involved in human scent and their origin with respect to the different bodily regions.



### **Differentiation between genders**

Humans can easily be distinguished from each other through their body smell. Several studies have found male odors unpleasant, whereas female odors have been described as pleasant. The basic body odor differences between the two genders are firstly the distinct levels of sex steroid hormones (androstenes) and secondly the fact that females generally have smaller body areas than males. The second difference means that the amount of sweat produced by a woman is on average less compared to that of a man. Furthermore, women’s body odor changes more often compared to men due to the different phases of their lives (menstrual cycle, fertile phase, etc.).30

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Table 1:** Volatile compounds produced from various human body areas. | | | | | | | | | | | | | | | | |
| **Compounds identified in Human Body Scent** | | | | | | | | | | | | | | | | |
|  | **Odour Source:** | **Axilla (underarms)** | | | | | | | | **Non axillary skin** | | | | | | |
|  | **Skin Emanation:** | **Axillary area** | | | | | | | | **Hands / Arm** | | | **Feet** | **Back** | **Forearm** | **Upper Back & Forearm** |
|  | **Author:** | **Brooksbank et al., 1974 32** | **Zeng et al., 1991 33** | **Zeng et al., 1992 34** | **Zeng et al., 1996 35** | **Munk et al., 2000 36** | **Curran et al, 2005 37** | **Curran et al, 2005 38** | **Penn et al., 2007 30** | **Bernier et al., 2000 39** | **Bernier et al., 2002 40** | **Zhang et al., 2005 41** | **Kanda et al., 1990 42** | **Haze et al., 2001 43** | **Ostrovskaya et al., 2001 44** | **Gallagher et al., 2008 45** |
|  | **No of candidates:** |  | **6** | **28** | **6** | **14** | **2** | **8** | **197** | **4** | **2** | **15** | **10** | **22** | **50** | **25** |
| **Chemical Class** | **Compounds** |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **Alkenes** | Alpha-pinene |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Caryophylene |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| D-Limonene |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Pentadecene |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| **Alkanes** | Eicosane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Hexadecane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Pentadecane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Tetradecane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Tridecane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Dodecane |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| 4-phenyltridecane |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| 3-methyloctadecane |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| 3-methylnonadecane |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| **Alcohols & Phenols** | Cedrol |  |  |  |  |  |  |  |  |  |  | X |  |  |  | X |
| 2-ethyl hexanol |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| 5-methyl-2-isopropyl cyclohexanol |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Benyl alcohol |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Hexadecanol |  | X |  | X |  |  |  |  |  |  |  |  | X |  |  |
| Phenol |  | X |  | X |  | X | X |  |  |  |  |  |  |  | X |
| 2-phenylethanol |  |  |  |  |  |  |  | X | X |  | X |  |  |  |  |
| 1-tridecanol |  |  |  |  |  |  |  | X | X |  |  |  |  |  |  |
| tetradecanol |  | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Geraniol |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| 2-hexanol |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| 3-hexanol |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Butanol |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Eugenol |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| **Aldehydes** | Benzaldehyde |  |  |  |  |  |  |  |  |  |  | X |  |  |  | X |
| Decanal |  |  |  |  |  |  |  |  |  |  | X |  | X | X | X |
| Nonanal |  |  |  |  |  | X |  |  |  | X | X |  | X | X | X |
| 2-Nonenal |  |  |  |  | X | X | X |  |  |  |  |  | X |  | X |
| Hexanal |  |  |  |  | X | X | X |  |  |  |  |  | X |  |  |
| Heptanal |  |  |  |  |  | X | X |  |  | X |  |  | X |  |  |
| Octanal |  |  |  |  | X |  |  |  |  |  |  |  | X | X | X |
| Undecanal |  |  |  |  |  |  | X | X |  |  |  |  |  |  |  |
| Dodecanal |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Geranial |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| Tridecanal |  |  |  |  |  |  |  | X |  |  |  |  |  |  |  |
| Lilial |  |  |  |  |  |  |  | X |  |  | X |  |  |  |  |
| **Esters** | Methyl salicylate |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Isobornyl propionate |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Hexadecanoic acid-methyl ester |  |  |  |  |  |  | X |  | X |  |  |  |  |  |  |
| Hexadecanoic acid-dimethyl ester |  |  |  |  |  |  | X |  | X |  |  |  |  |  |  |
| Nonanoic acid-methyl ester |  |  |  |  |  |  | X |  | X |  |  |  |  |  |  |
| Tridecanoic acid-methyl ester |  |  |  |  |  |  | X |  | X |  |  |  |  |  |  |
| **Acids** | 7-Octenoic acid |  | X | X | X |  |  |  |  | X | X |  | X |  |  |  |
| Propanoic acid |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Butanoic acid |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Hexanoic acid |  | X | X | X | X |  |  |  |  |  |  | X |  |  | X |
| Heptanoic acid |  | X |  | X | X |  |  |  |  |  |  | X |  |  |  |
| Octanoic acid |  | X | X | X |  |  |  |  |  |  |  | X |  |  | X |
| Nonanoic acid |  |  | X | X |  |  | X |  |  |  |  | X |  |  |  |
| Decanoic acid |  | X | X | X |  |  |  |  |  |  |  |  |  |  |  |
| undecanoic acid |  | X | X | X |  |  |  |  |  |  |  |  |  |  |  |
| Dodecanoic acid |  |  |  |  |  | X | X |  | X | X |  |  |  |  | X |
| 3-methyl-2-hexenoic acid |  | X | X | X |  |  |  |  |  |  |  |  |  |  |  |
| 2-methylhexanoic |  | X |  | X |  |  |  |  |  |  |  |  |  |  |  |
| 2-methylheptanoic |  | X |  | X |  |  |  |  |  |  |  |  |  |  |  |
| 2-methyloctanoic |  | X |  | X |  |  |  |  |  |  |  |  |  |  |  |
| 2-ethylhexanoic |  | X |  | X |  |  |  |  |  |  |  |  |  |  |  |
| 4-ethyldecanoic |  | X |  | X |  |  |  |  |  |  |  |  |  |  |  |
| Acetic acid |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| Lactic acid |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| **Aliphatic/aromatic** | naphthalene |  |  |  |  | X |  |  |  |  |  |  |  |  |  |  |
| Nonane |  |  |  |  |  | X | X |  |  | X |  |  |  |  |  |
| Toluene |  |  |  |  |  | X | X |  |  | X |  |  |  |  |  |
| **Ketones** | 6-Methyl-5-hepten-2-one |  |  |  |  |  | X | X |  |  | X |  |  |  | X |  |
| 2-propanone (or acetone) |  |  |  |  |  |  |  |  |  |  |  |  |  |  | X |
| **Steroids** | Cholesterol |  | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Squalene |  | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5a-androst-16-en-3a-ol |  | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5a-androst-16-en-3b-ol |  | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5a-androst-16-en-3-one | X | X |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **Miscellaneous** | Diphenyl ether |  |  |  |  |  |  |  | X |  |  | X |  |  |  |  |
| tetramethyl thiourea |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |
| Acetophenone |  |  |  |  |  |  |  |  |  |  | X |  |  |  |  |



## **Threat chemistry, drugs, explosives and illicit chemistry**

Threat substances incorporate chemical components that present hazardous and/or toxic effects on human beings and other living organisms (animals or plants). They can potentially cause undesirable catastrophic effects in urban or rural environments and hamper human activities causing socioeconomic issues and concerns. They include illegal drugs, explosives, bombs, landmines and CWAs as well as their precursors or breakdown products.46-55

Illegal drugs are controlled by governments. Their use and trafficking is not permitted in any circumstances. Illicit drugs affect human senses, responses and body reactions. They are mainly categorized in three major families: a) stimulants, b) hallucinogens and c) central depressants. Stimulant drugs (e.g. amphetamine, mephedrone, methamphetamine, cocaine, 3,4-Methylenedioxymethamphetamine (MDMA), Methylenedioxypyrovalerone (MDPV), dimethylamylamine, etc.) affect the activity of the human nervous system and enhance alertness and mental or physical energy. Cocaine, γ-hydrobutyric acid (GHB) at low doses and amphetamine are stimulants for the central nervous system causing psychological euphoria. Hallucinogen drugs (e.g. lysergic acid diethylamide (LSD), psilocybin, mescaline, DMT, phencyclidine (PCP) etc.) affect the brain and cause psychedelic actions, perceptual anomalies of reality, dissociation (de-realization, de-personalization) and delirium. Central depressant agents (e.g. benzodiazepines and barbiturates) are compounds with sedative and anxiolytic effects. Cannabis and GHB at high doses belong in the category of depressant drugs.

Explosive material can be described as a reactive, usually unstable compound or mixture of compounds; which contain a large amount of energy (chemical, nuclear, etc.) that can be released after a sudden deflagration or other type of reaction. According to their rate of decomposition/burn, explosive materials can be characterized as low or high explosives. Low explosives deflagrate rapidly without causing a shock wave, whereas high explosives are produced by detonation and cause a large shock wave. Moreover, high explosives burn much faster compared to low explosives. High explosives can be classified under primary, secondary and tertiary explosives according to their sensitivity and to the shock wave that they can produce. Characteristic examples of low explosives are: propellants, black powder, fireworks, pyrotechnics, etc. Primary high explosives include: acetone peroxide, diacetyl peroxide, and nitroglycerin. Secondary high explosives include: tetryl, trinitrotoluene (TNT) and cyclotrimethylenetrinitramine (RDX), whereas a characteristic tertiary high explosive is ammonium nitrate/fuel oil (ANFO). Explosive materials can be chemically classified either as pure compounds or mixtures (ANFO, SEMTEX, C4). An interesting category of explosives is the plastic explosives or plastic-bonded explosives (PBX) such as the SEMTEX, PE-4 and C4 which are tagged with a volatile chemical that acts as a detection odor marker e.g. by sniffer dogs or artificial sniffing devices. Taggants such as 2,3-dimethyl-2,3-dinitrobutane (DMDNB), ethylene glycol dinitrate and ortho-nitrotoluene (ONT) are easily detectable in low parts-per-trillion concentration levels.16, 56

CWAs or chemical weapons employ toxic properties of some chemical agents to spread immediate or delayed terror, pain and death. The Organization for the Prohibition of Chemical Weapons (OPCW) through the Chemical Weapons Convention (CWC) defines as a CWA ‘‘*any toxic chemical or its precursor that can cause death, injury, temporary incapacitation or sensory irritation through its chemical action. Munitions or other delivery devices designed to deliver chemical weapons, whether filled or unfilled, are also considered weapons themselves*’’.57 Chemical agents, according to their effects, can be distinguished in the following main categories: a) blister agents (e.g. mustard gas – H, mustard T-mixture, Ethyldichloroarsine - ED, lewisite 1, lewisite 2, lewisite 3, b) nerve agents (e.g. sarin - GB, cyclohexyl sarin - GF, soman - GD, tabun - GA), c) precursors and degradation products (e.g. dimethyl phosphite, 1,4-dithiane, thiodiglycol, trimethyl phosphite), d) tear gases (e.g. 2-chlorobenzalmalononitrile - CS, phenacyl chloride - CN, chloropicrin - PS, bromoacetone - BA, dibenzoxazepine - CR or DBO), e) psychotomimetic agents (e.g. 3-quinuclidinyl benzilate - agent BZ) and f) arsenical irritants (e.g. diphenylchlorarsine - DA, diphenylcyanoarsine, adamsite - DM), g) choking agents (e.g. diphosgene – DP, PS, phosgene – CG, disulfur decafluoride). Representative common threat substances are listed in Table 2.

Most of the above described threats (drugs of abuse, explosives and CWAs) have vapor pressure values (and thus volatility for the same temperature) in extremely low levels, making their detection very difficult. Moreover, clever packaging methods may camouflage/mask the target threat components and confuse the detection/screening sensing systems. The technologies discussed in the sections below were developed to address this issue and render on site threat compounds detection feasible.

**Table 2:** Most common homeland security, civil defense and military related substances, classified according to their threat family.55

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Common threat compounds** | | | | |
|  | **Compound** | **CAS Number** | **Molecular Weight** | **Molecular Formula** |
| **Drug** | Cocaine | 50-36-2 | 303.35 | C17H21NO4 |
| Heroin; (Diacetylmorphine) | 561-27-3 | 369.41 | C21H23NO5 |
| Amphetamine | 300-62-9 | 135.20 | C9H13N |
| Ecstasy; (N-Methyl-3,4-methylenedioxyamphetamine) | 42542-10-9 | 193.25 | C11H15NO2 |
| LSD; (D-Lysergic acid N,N-diethylamide) | 50-37-3 | 323.43 | C20H25N3O |
| MDA; (tenamfetamine) | 4764-17-4 | 179.22 | C10H13NO2 |
| Cannabis; (THC) | 1972 08 03 | 314.45 | C21H30O2 |
| PCP; (phencyclidine) | 77-10-1 | 243.38 | C17H25N |
| GHB; (γ-Hydroxybutyric acid) | 591-81-1 | 104.1 | C4H8O3 |
| **Explosive** | RDX | 121-82-4 | 222.12 | C3H6N6O6 |
| PETN | 78-11-5 | 316.14 | C5H8N4O12 |
| TNT | 118-96-7 | 227.13 | C7H5N3O6 |
| Nitroglycerin | 55-63-0 | 227.08 | C3H5N3O9 |
| DMNB | 3964-18-9 | 176.17 | C6H12N2O4 |
| Picric Acid | 88-89-1 | 229.11 | C6H3N3O7 |
| Benzyl alcohol | 100-51-6 | 108.14 | C6H5CH2O |
| ANFO | Mixture | | |
| SEMTEX | Mixture (plastic explosive) | | |
| C4 | Mixture (plastic explosive) | | |
| **CWA** | Mustard Gas (H) | 505-60-2 | 159.08 | C4H8Cl2S |
| Ethyldichloroarsine (ED) | 598-14-1 | 174.89 | C2H5AsCl2 |
| Lewisite 1 | 541-25-3 | 207.31 | C2H2AsCl3 |
| Lewisite 2 | 40334-69-8 | 233.36 | C4H4AsCl3 |
| Lewisite 3 | 40334-70-1 | 259.39 | C6H6AsCl3 |
| Sarin (GB) | 107-44-8 | 140.11 | C4H10FO2P |
| Soman (GD) | 96-64-0 | 182.19 | C7H16FO2P |
| Cyclohexyl sarin (GF) | 329-99-7 | 180.16 | C7H14FO2P |
| Tabun (GA) | 77-81-6 | 162.13 | C5H11N2O2P |
| VX | 50782-69-9 | 267.37 | C11H26NO2PS |
| Dimethyl phosphite | 868-85-9 | 110.05 | C2H7O3P |
| Thiodiglycol | 111-48-8 | 122.18 | C4H10O2S |
| Trimethyl phosphite | 121-45-9 | 124.09 | C3H9O3P |
| Agent CS | 2698-41-1 | 188.62 | C 10H 5ClN2 |
| Agent CN | 532-27-4 | 154.6 | C 8H 7ClO |
| Agent PS | 76-06-2 | 164.37 | CCl3NO2 |
| Agent BZ | 6581-06-2 | 337.42 | C21H23NO3 |
| Agent DA | 712-48-1 | 264.59 | C12H10AsCl |
| Agent DM | 578-94-9 | 277.59 | C12H9AsClN |
| Agent DP | 503-38-8 | 197.82 | C2Cl4O2 |
| Agent CG | 75-44-5 | 98.92 | COCl2 |
| Disulfur decafluoride | 5714-22-7 | 254.11 | S2F10 |

# Sniffer animals

A wide range of domestic, semi-domestic or other animals have been specially trained and successfully used for *in-situ* border control, security and forensic applications.58 Most of them give good field performance (fast response times, trace threats detection and early localization), but usually are associated with high training time issues and cost drawbacks. For instance, sniffer dogs can easily (within seconds) detect drugs, explosives, weapons, mines, live human bodies (illegal immigrants), tobacco, cash and cadavers in the field. Dogs, usually require several months (approximately 4-6) of costly training (current estimate £10,000) before they obtain employment. The initial selection of a sniffer dog is usually done by a series of tests performed by specialist teams. Not all dog breeds are suitable for providing working dogs. The most popular breeds for security purposes use are the German, Dutch and Belgian shepherds, labradors as well as the cocker spaniels. The canines’ effectiveness depends on their training, age, experience, searching protocols, their personality, and the developed collaboration/obedience level with their handler as well as with the environmental/weather conditions of the field (e.g. canines can detect targeted substances with ease when the wind/air direction is towards them). Moreover, there are no sniffer dogs capable of versatile (i.e. universal) threat detection. Some canines are trained and able to detect explosives, others can detect narcotics, whereas others can detect live or dead human bodies. The dogs’ training is based on stimulus-reward techniques and that usually employs simulant compounds to the original energetic compounds, precursors, breakdown products or taggants. Quite often, during action, canines require breaks (for every 40 minutes of work, they require 1-hour break before they can carry on working) and sometimes retraining or conservation of their attention with additional search-reward games. The dogs’ task usually requires a dog-handler to be present and this increases highly the maintenance costs per year. In addition, canine transportation costs during overseas operational searches in the field are usually high. Large volume facilities such as airports or cargo services require a number of handler-sniffer dog teams to maintain security. The above described limitations of sniffer dogs are disadvantages from the financial and management point of view. However, from a scientific perspective, sniffer dogs have been proven to be unique in threat detection operations in the field due to their extremely delicate olfactory system and acute scent recognition-interpretation ability.58-63

Some researchers have worked closely with insects and more specifically with honey bees. Honey bees’ behavior has been studied and they have been trained using Pavlovian conditioning techniques to detect explosive materials (TNT, C4, TATP) emitted by solid or liquid bombs at very low concentrations (ppt levels). Sniffer bees’ training/conditioning can be completed rapidly within some days using relatively simple processes. Due to their speed, low-cost training and to their abundant populations, bees can be employed to fly over a certain area and scan it for potential threats within a short time. Their physiology and acute olfaction gives them the ability to sample all states of matter (liquids, gases, solids). However, honeybees are still not suitable for threat detection and localization applications in airports or confined spaces, due to practical issues, such as their interaction with humans. Moreover, honeybees are highly affected by the weather conditions and the presence or absence of light. For example, honeybees cannot work during night or in a cold and rainy or high humidity environment. Further investigation of honeybees sniffing abilities in various experimental conditions is needed.58, 64, 65

African giant pouched rats have also been used in the lab and on-site to search and alarm on vapors from explosives, landmines, bombs and drugs (e.g. cocaine).66-68 An advantage for sniffer rats’ use is that their training, maintenance and transportation costs are relatively low compared to sniffer dogs. Moreover, rats, due to their size and weight are very flexible during operations. Recently, pigs69 have been reported for their sniffing abilities to detect landmines.

Eelworms such as the nematodes *Caenorhabditis elegans* have a very well developed chemosensory receptors system that allows them to provide olfactory detection of volatile compounds associated with explosive or precursors from different chemical classes at various concentration levels. In a recent study, *C. Elegans* response to 17 explosive-related compounds was examined, providing positive detection results.70 However, they presented limited response to the original explosive materials. Finally, hard-wired moths71 have been trained, using a novel prototype system that uses electromyography, to react to specific chemical odor signatures emitted from explosives or landmines.

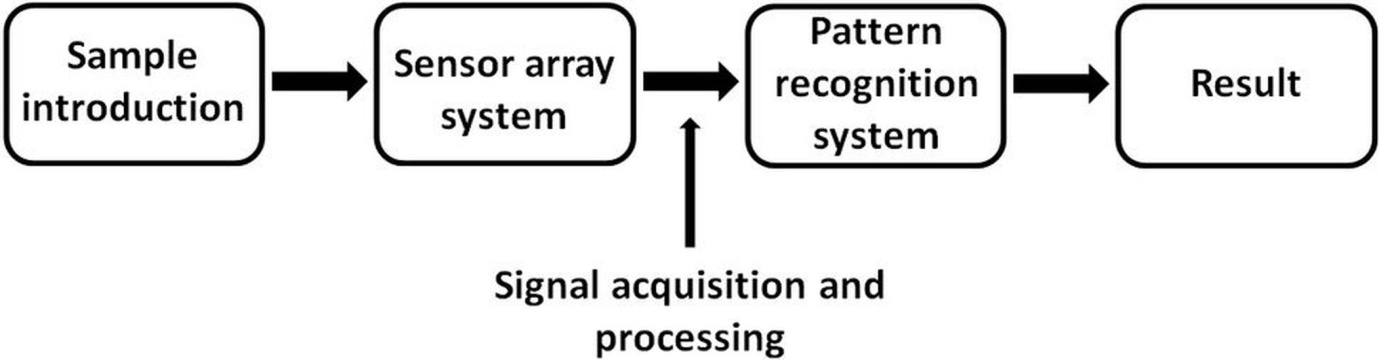
# Existing technologies for artificial sniffing

Chemical detection of target compounds related to border security applications, such as human body odor, drugs of abuse, explosives and CWAs, is still limited with existing instruments available on the market. The following sections present an overview of the existing available technologies reported in the scientific literature for threat screening, and offer brief descriptions about their functional principles. Emphasis is given to technologies that have been developed for in-field security operations, but laboratory-developed and tested techniques are also summarized.

## **Electronic noses**

Electronic noses (EN) are intelligent chemical sensor array systems, typically consisting of two major components: (a) a single chemical gas sensor or an array of chemical sensing systems and (b) a pattern recognition system.4-6, 72-74 The most commonly used sensors are based on metal oxides semiconductor (MOS) devices. Conducting polymer devices are also used. MOS sensors are mass produced, insensitive to humidity and have a long shelf-life (5 years). MOS sensor limitations include the binding with substances like sulfur compounds and weak acids and the high working temperatures. Polymer sensors are inexpensive and operate at ambient temperatures. However, their relatively slow response times (20-40 sec) and instability are their main drawbacks, resulting in non repeatable results when used over long periods of time.72, 73

The functional principles of ENs are relatively simple.6 During operation, every single chemical odorous component presented to the EN sensor system produces a response (e.g. a change in electrical properties) which can be identified as the characteristic odor signature for the examined scent. The interaction of various different gas vapors with the embedded sensor can yield the production of a library-database with range of characteristic odor signatures. The chemical detection and identification of an odorant compound in the framework of a certain application can be done by comparing EN output signals with a standard reference signal. Sensor array systems are generally better performing compared to the single sensor systems, due to the fact that they offer enhanced selectivity and multi-component identification. The basic concept of an EN is presented in Figure 1.



**Figure 1:** Schematic diagram of an electronic nose.

Traditionally, electronic noses were based on chemical gas sensors (chemiresistors or gravimetric sensors). However, demands on target threat (explosives, landmines, narcotics, chemical weapons) compounds selective detection, increased sensitivity and quantification issues, has highlighted the need for employment of new technologies. Recent advances in other scientific areas or approaches combined with miniaturization and hand-portability, has led to the development of a wide range of sensing EN systems based on different technologies. Therefore, EN have benefited from developments in optics (e.g. fiber optics based detectors75), in piezoelectrics (surface acoustic wave (SAW) detectors76), in fluorescent polymers77, in nanotechnology (gold nanoparticle based chemiresistors72), and in micro-electromechanical systems (MEMS)78, 79. From a wider perspective, electronic noses can also be considered as analytical instruments with machine olfaction capabilities (gas detection, chemical determination and quantification); alongside mass spectrometry (MS) based devices, ion mobility spectrometers (IMS), and gas chromatography (GC).72, 79, 13, 80 These technologies are described in detail below.

ENs notwithstanding their advantageous characteristics (small size, inexpensive, portable) and potential for reliable threat and illicit substance detection) still require further testing and improvements to meet the user demands (e.g. stability and specificity). In common with other threat detection technologies, ENs are prone to false positive and false negative indications/alarms. Specifically this refers to cases where ENs analyse complicated gas mixtures. Sensory output patterns derived from unknown and complicated sample sources may not accurately match with already tested single or controlled mixtures’ reference output patterns leading to false alarms. Toal and Trogler report that for ENs there are ‘many false positives’81 but do not quantify the number of occurrences. Researchers are addressing this via improvements to EN selectivity.

## **Mass spectrometry**

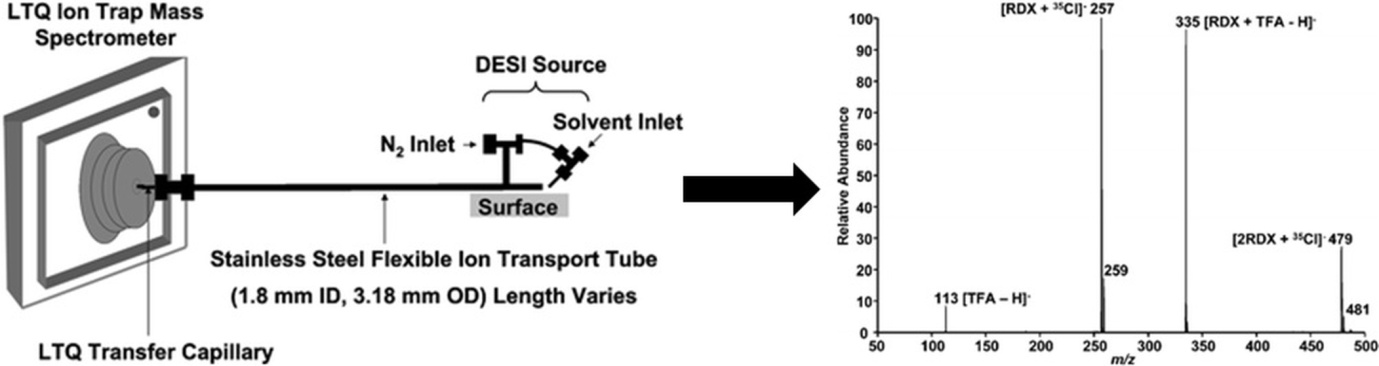
Mass spectrometry (MS) is a powerful established analytical technique widely considered to be the gold standard for chemical analysis.82, 83 It works by creating ions from neutral atoms and molecules and separating them according to their mass-to-charge ratios. Mass spectrometers can be applied for both in-laboratory measurements and on-site operations, either as standalone devices or combined with other analytical instruments. MS offers high sensitivity, low detection limits (LODs), high selectivity, fast response times and broad applicability (analysis of almost all the types of molecules; from small volatile compounds to big biomolecules and biological species). Moreover, targeted compounds for analysis can belong to all states of matter (gaseous, liquid, solid). Mass spectrometric output data carry time varying, qualitative and quantitative information that can be used for chemical detection, identification and characterization as well as for the investigation-prediction of molecular chemical structures. The main components of a mass spectrometer include:

1. Sample inlet (gas inlet, atmospheric pressure inlet, direct leak, membrane sampling probe, capillary, batch inlet, pulsed sampling system)
2. Ion source (electron impact, chemical ionization, electrospray, fast atom bombardment, field ionization/field desorption, desorption electrospray ionisation (DESI), atmospheric pressure ionization, thermospray ionization (TI), matrix assisted laser desorption ionization (MALDI))
3. Mass analyzer (quadrupole mass filter, ion trap (quadrupole, cylindrical, linear, orbitrap), time-of-flight, magnetic sector, Fourier transform ion cyclotron resonance, electrostatic analyser)
4. Detector (Faraday, electron multiplier, photomultiplier, micro-channel plate (MCP))
5. Vacuum system (usually turbomolecular pump backed by diaphragm or rotary pump)

Some decades ago, mass spectrometers were large analytical devices for only laboratory use. However, late developments in size and weight miniaturization (e.g. miniaturization of mass analyzers, detectors, vacuum system, etc.), as well as in power consumption reduction converted them into portable devices ideal for in-field operations worldwide.16 Portable mass spectrometers were specially deployed to address specific applications. This gave them, in many ways, operational flexibility and advanced analytical capabilities. A very important stage for trace chemical analysis in field conditions was the introduction of sample molecules into the MS vacuum system (e.g. via direct leak, membrane inlet or pulsed sampling systems). To address the trace detection issue and to enhance sensitivity, sample pre-concentration [e.g. with solid phase microextraction (SPME) fibers, cartridges adsorption-desorption, etc.] and collection methods (tedlar bags, wipes, etc.) were established prior to analysis. Advanced methodologies such as membrane introduction MS and ambient environment ionization techniques (described below) which require no sample preparation and provide fast analysis times have also been developed.13 These are mainly used to give the advantage of minimal sample preparation however some recent techniques also provide high sensitivity.

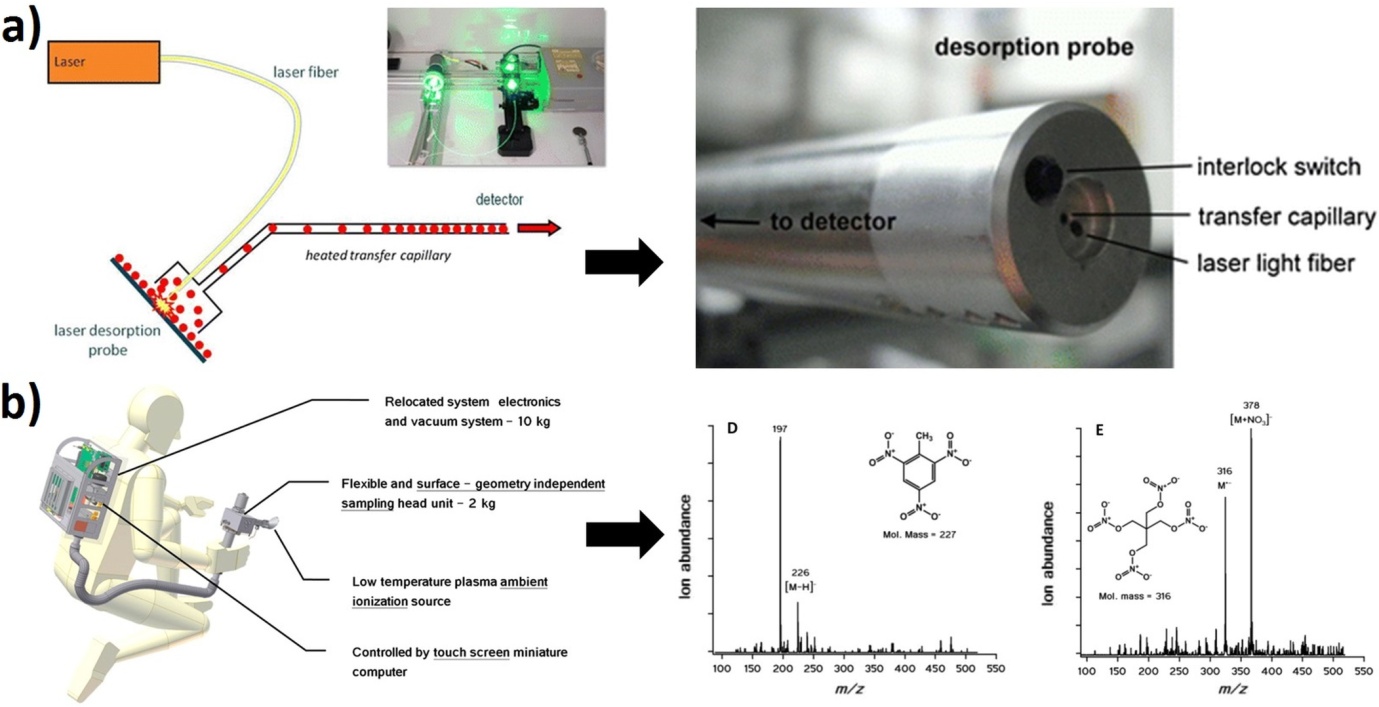
Novel ambient environment ionization techniques were also proposed, investigated, tested and evaluated to ionize substances with a range of sizes and structures as well as those with very low or extremely low vapor pressure values such as the common explosives and narcotics from complex matrices. Atmospheric pressure chemical ionization (APCI)72, 84 integrates both sample and carrier gas (e.g. acetonitrile, etc.) ionization using a corona discharge. This technique has been used to detect explosive materials such as 2,4,6-trinitrotoluene (TNT) or 2,4-dinitrotoluene (DNT) in low concentration levels emitted from the surface of human hands using sample collection swabs.

Desorption electrospray ionization (DESI)85-91 combines the basic principles of desorption and electrospray ionization and is one of the most well-known universal ionization techniques *in situ*. In DESI a stream of charged droplets splashes the surface under examination and this collision produces ions for MS analysis. Threat compounds (e.g. RDX, TNT, PETN, C-4, Semtex, TATP, etc.) were analysed and identified using this technique from various surface materials including glass, paper, clothing, metal surfaces, etc., in the low nanogram range (Figure 2). Direct analysis in real time (DART)92 was also used to ionize threat components directly from surfaces (e.g. clothing, banknotes, etc.) without prior sample preparation. DART as a technique is thus akin to DESI. In DART, (mostly) metastable atoms bombard the surface area under examination and transfer sample ionized species generated from the surface into the MS for analysis.



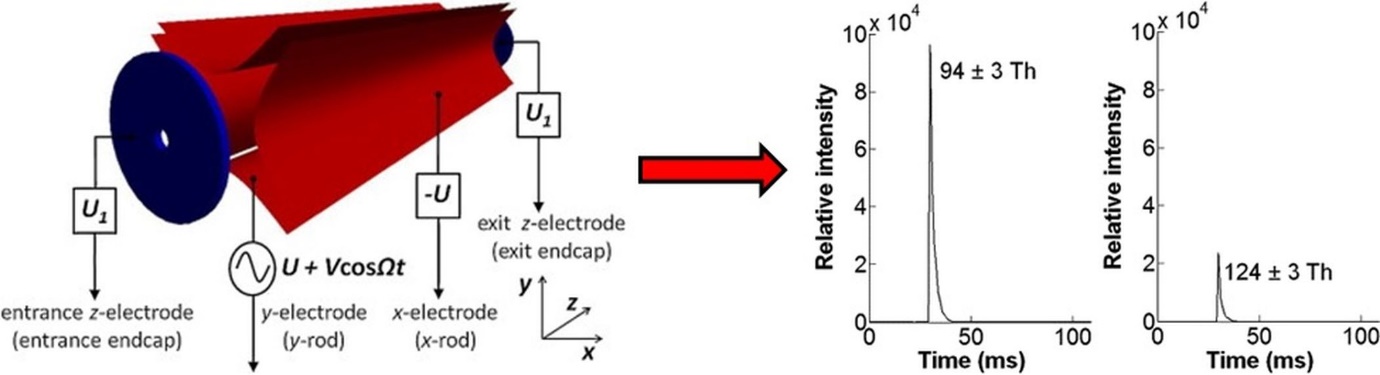
**Figure 2:** A non-proximate DESI source coupled to an LTQ MS is monitoring for explosive traces (1ng of RDX) on the surface of a laptop PC at a distance of 1 meter from the MS. Negative ion DESI spectrum of the detected RDX is shown. The spray solvent was methanol/water/NaCl/TFA (70: 30: 10mM: 10 mM). Reproduced with permission from ref 91. Copyright 2006 Royal Society of Chemistry.

In addition to the above described ambient environment ionization techniques for threat detection, the following techniques were also developed to enhance sample introduction into the vacuum system: low temperature plasma (LTP) (Figure 3)15, 93, desorption atmospheric pressure photon ionization (DAPPI)94, desorption atmospheric pressure chemical ionization (DAPCI)95-98, atmospheric pressure laser desorption (APLD) (Figure 3)99, secondary electrospray ionization (SESI)100-103, paper spray ionization (PSI)104, 105, easy ambient sonic spray ionization (EASI)106 and desorption sonic spray ionization (DeSSI)107. In general terms, each has presented positive detection results (low LOD and fast response). Moreover, proton-transfer-reaction MS (PTR-MS)108-111 and selected-ion flow-tube MS (SIFT-MS)112-115 have been also investigated successfully for real-time monitoring of explosive materials and CWAs. PTR-MS offers high selectivity, low LOD (sub-ppt) and rapid response times. PTR-MS performance has been evaluated both in laboratory and in real-life conditions. Similarly high sensitivity SIFT-MS has been tested to detect, identify and quantify in real-time solid explosive materials e.g. triacetone triperoxide (TATP). SIFT-MS is also rapid response and does not require sample preparation requirements.112



**Figure 3:** a) (*left*) Operating principle of the atmospheric pressure laser desorption (APLD) and (*right*) a prototype APLD sampling probe developed for the on-site detection of explosive materials or residues from surfaces. Adapted from ref 99. Copyright 2013 Springer., b) An autonomous man-portable mini-MS system developed in Purdue University, consisting of a backpack and a hand-held LTP source is detecting TNT and PETN traces (< 1μg/cm2) directly from glass melting tubes. Reproduced from ref 15. Copyright 2014 American Chemical Society.

Commercial portable ion trap MS systems available in the market are presented in Table 3 (classification from the heavier system to the lighter). Information regarding their mass analyzer and summarized specifications are given. GriffinTM 824 and GriffinTM 844 from FLIR Systems Inc. (Wilsonville, USA)116 uses a surface wipe sample introduction technique to inject sample molecules into the vacuum system. Sample molecules are ionized by a non-radioactive positive ionization source before they enter to the cylindrical ion trap mass analyzer for separation. TRIDIONTM-9 GC-MS and GUARDIONTM-7 GC-MS from Torion Technologies, (UT, USA)117 are man-portable GC-MS systems. Sample introduction in this case is done by an SPME fiber or a needle trap. The field-portable GUARDIONTM-7 GC-MS has been successfully examined in the analysis and in the detection of CWAs such as sarin (GB), soman (GD), cyclosarin (GF), VX and distilled mustard gas (HD).83 Mini 10, Mini 11, Mini 12 and Mini S from Purdue University118 have been tested with different inlet types (e.g. direct leak, MIMS, etc.) and ambient ionization modes (e.g. DESI, DART, DAPPI, DAPCI, LTP, PSI, etc.). PortabilityTM from Bayspec Inc. employs a membrane inlet to admit sample into the vacuum system and perform *in-situ* direct chemical analysis.119 MMS-100TM from 1st Detect (Austin, TX, USA) uses a heated membrane inlet with a pre-concentrator for enhanced sensitivity.120 The sample introduction in the M908TM is done either continuously by monitoring the gas phase/headspace area above a sample or via thermal desorption swabs.121 The palm portable MS from the Samyang Chemical Corp was presented in the 6th Harsh Environment MS (HEMS) Workshop in 2010 and uses a pulsed gas valve for direct sample injection.122, 123 A portable artificial sniffer based on non-scanning linear ion trap mass spectrometry (Figure 4) was developed within the framework of the EU research project SNIFFLES.124 Experiments with a membrane inlet showed low ppm detection of threat simulants. Recently, a vehicle-mounted membrane inlet mass spectrometer with the ability to spatially detect atmospheric effluent from illicit methamphetamine manufacture laboratories was reported.125 Research on human detection using portable MS in the field is still limited. However, recent studies have investigated volatile emissions produced from human bodies in confined conditions. The results can be used as indicators of human presence in confined spaces (e.g. shipping containers) after several hours of physical presence.25-27, 56

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**Figure 4:** Schematic diagram of a non-scanning hyperbolic linear ion trap MS detecting in the lab a 5 ppm gaseous sample of dimethyl methylphosphonate (DMMP). DMMP electron impact (EI) characteristic mass fragments *m/z* 94 and 124 are presented. Reproduced from ref 16. Copyright 2014 with permission of Elsevier.

**Table 3:** Ion trap MS systems specially developed for threat detection.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Supplier** | **Model** | **Mass analyser** | **Mass range (m/z)** | **Power (W)** | **Weight (kg)** |
| FLIR Systems Inc. | GriffinTM 824 | Cylindrical ion trap | N/A | N/A | 22.7 |
| FLIR Systems Inc. | GriffinTM 844 | Cylindrical ion trap | N/A | 110-240 VAC | 20 |
| Purdue University | Mini 12 | Rectilinear ion trap | N/A-900 | 50 | 15 |
| Torion Technologies (recently acquired by PerkinElmer) | TRIDIONTM-9 GC-MS | Toroidal ion trap | 45-500 | 80 | 14.5 |
| University of Liverpool | SNIFFLES pre-prototype | Non-scanning linear ion trap | 50-500 | 34 | 14 |
| Torion Technologies (recently acquired by PerkinElmer) | GUARDIONTM-7 GC-MS | Toroidal ion trap | 50-500 | 75 | 13 |
| Purdue University | Mini S | Rectilinear ion trap | N/A-925 | 65 | 12 |
| Purdue University | Mini 10 | Rectilinear ion trap | N/A-550 | 70 | 10 |
| BaySpec Inc. | PortabilityTM | Linear ion trap | 40-650 | 65 | 9.9 |
| 1st Detect | MMS-100TM | Cylindrical ion trap | 15-625 | N/A | 8 |
| Purdue University | Mini 11 | Rectilinear ion trap | N/A-2000 | 30 | 5 |
| 908devices | M908 TM | Microscale ion traps | 55-400 | N/A | 2 |
| Samyang Chemical Corp | Palm portable (without pump) | Quadrupole ion trap | 45-300 | 5 | 1.5 |

## **Ion mobility spectrometry**

Ion mobility spectrometry (IMS) is one of the most popular routine analytical technologies used *in-situ* for detection and monitoring of illegal drugs, explosives, chemical weapons and toxic industrial chemicals (TICs).126-134 It works by analyzing ions in the gas phase at ambient pressures. IMS offers rapid analysis, usually within some seconds. Security and military authorities use largely handheld IMS based devices during in-field and real-time applications due to their advantageous characteristics such as: portability, robustness, operational simplicity, user-friendliness, selectivity and trace levels sensitivity. The IMS operational principle is based on the separation of ionized molecules according to their mobility through a drift tube with an applied electric field and a carrier buffer gas opposing ion motion. Ion motion depends on ion size, shape and charge.

Sample collection and sample introduction techniques during border security screening can be done by various ways. Usually sample collection is performed in a non-intrusive manner. Most common sampling methods are: a) direct sampling of gaseous phase or vapor molecules, and b) sampling using a swab filter or a membrane with certain adsorption characteristics over a suspect surface (e.g. luggage, passenger hands, coat, colognes bottles, banknotes etc.) followed by thermal extraction of the molecules of interest in the IMS using desorption heating techniques or through a gas chromatography injection system. Desorption heating techniques are mainly applied and focus in the detection of non-volatile compounds or compounds with very low vapor pressure values (e.g. the majority of explosives and illegal drugs).

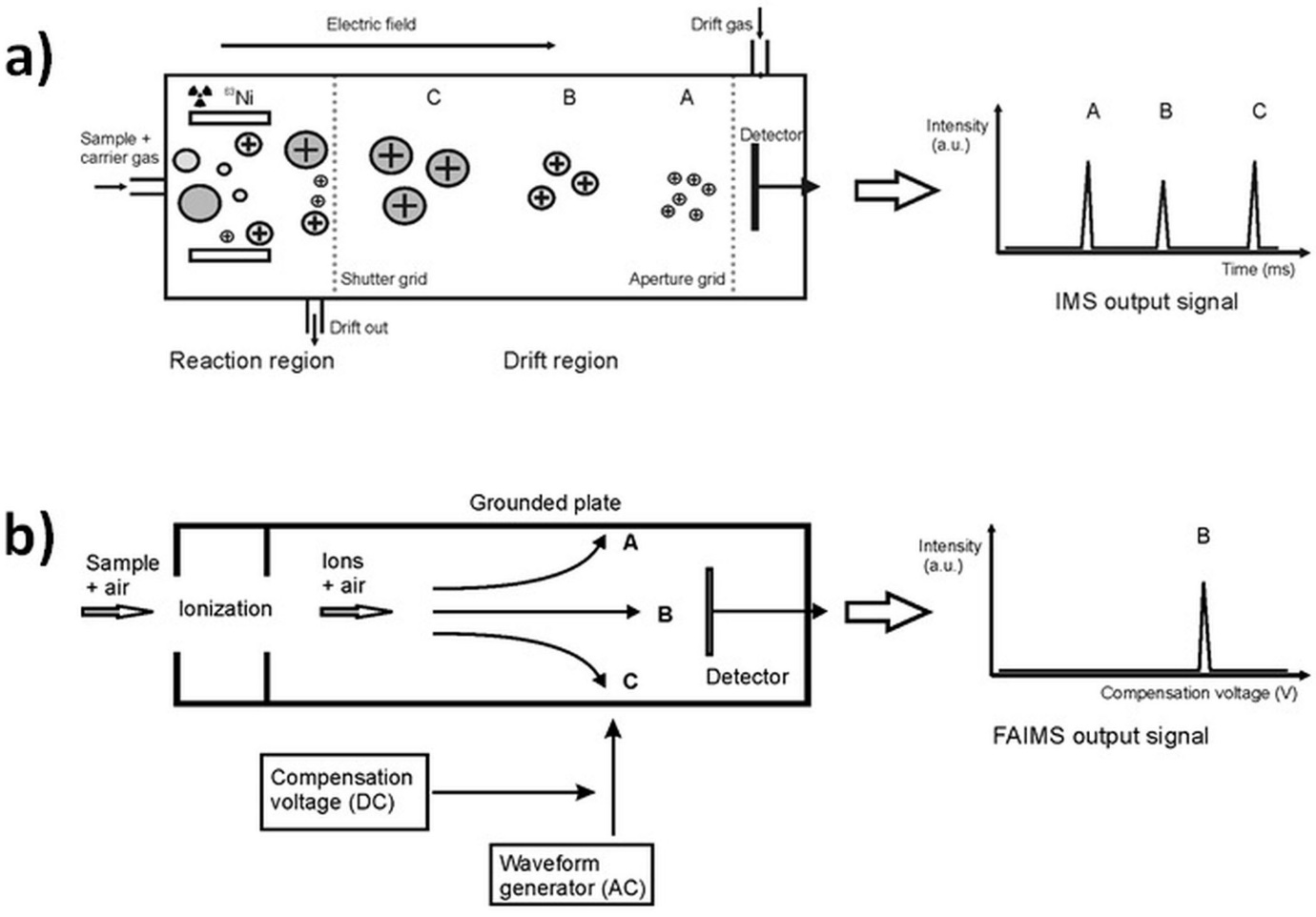
The next stage during IMS operation, after sample introduction, is the ionization of sample analytes. IMS devices employ soft ionization techniques at atmospheric pressure to create reactant ion clusters which will be mixed and interact with sample vapor phase analytes and will finally form target sample ions. The ionization source traditionally is based on the following materials 63Ni, 3H or 241Am. These materials are radioactive but maintain a stable source of ions during measurements. The radioactive nature of these sources raises safety concerns as well as often transportation issues. However, recent advances in IMS development introduced non-radioactive ionization sources79, 130, 135 based on photoionization (PI) [e.g. atmospheric pressure photoionization (APPI)136, 137], corona discharge ionization138, electrospray ionization (ESI)139 or matrix-assisted laser desorption ionization140. Ambient ionization techniques such as desorption electrospray ionization (DESI)141, secondary electrospray ionization (SESI)142, laser spray ionization (LSI)143, atmospheric-pressure solids analysis probe (ASAP)144, low temperature plasma (LTP)145, direct analysis in real time (DART)146 were initially developed for the direct analysis of sample surfaces during MS operation. The aforementioned techniques have also been successfully used with IMS.

When ions are created, they travel directly to the drift region of the IMS, passing firstly through an ion-gate. The presence of the ion-gate between the ionization source region and the drift tube region offers electronic control of ion injection as discrete packets. In the drift tube region an electric field is applied to drive the ions to the detector and separate them according to their travel time through the tube which is determined by the number of ion-neutral collisions in the drift tube. The final part of an IMS device is the detector which is usually a standard Faraday plate.

There are different types of IMS instruments available in the market such as systems working with low electric fields (e.g. 200-300 V/cm) and systems working with high electric fields (e.g. 10,000-30,000 V/cm). Also different IMS analyzers130, 131 work either in ambient pressure (e.g. drift-time, aspiration, field asymmetric ion mobility spectrometers (FAIMS)147-149) or in reduced pressures (e.g. drift-time, traveling-wave ion mobility spectrometers). IMS can also be coupled with and act as a pre-separation technique-stage to other analytical devices such as mass spectrometers, to offer enhanced analytical results. Ion mobility mass spectrometry (IMMS)150 combines the principles and advantages of both IMS and MS. IMS devices fit well with MS systems and provide clearer mass spectra due to elimination of the chemical noise background. Therefore IMS-MS instruments offer fast separation-discrimination of molecules from complex mixtures (including detection of isomers, isobars and separation of conformers due to the advantage of ion mobility separation before the mass analysis step). Figure 5 shows schematically the operating principle of a conventional IMS and a FAIMS133.

Gas chromatography (GC) can also interface with IMS devices151. This combination offers a gas chromatographic pre-separation stage of sample molecules prior to their entrance to the IMS ionization chamber and the drift tube region. GC-IMS provides better discrimination as it reduces the number of interferences or interactions of sample molecules in the ionization chamber. GC-IMS produces more reliable data because of the GC separation step (the GC retention time can be used to identify the compound). Moreover, the GC-IMS enhances sensitivity because different compounds can be separated from the GC, and get ionized sequentially, so that the ionization efficiency for the targeted compounds is improved. A GC-IMS device enables two-dimensional sample separation providing 3-D sets of data (x-y-z axis: IMS drift time - IMS intensity - GC run time). In addition to single column GC, multi-capillary column (MCC) GC152, 153 can be also used to reduce false alarms making them a good tool for in-field operations.

A solid-phase microextraction (SPME) IMS system154 was recently reported to offer pre-concentration and low LODs in explosives (nitrocellulose, RDX, PETN), in volatile constituents of explosives (2,4-dinitrotoluene, 2,6-dinitrotoluene) and in taggants (2-nitrotoluene, 4-nitrotoluene, 2,3-dimethyl-2,3-dinitrobutane) detection.



**Figure 5:** Operating principle of a) a conventional IMS and b) a FAIMS apparatus. Reproduced from ref 133. Copyright 2010 American Chemical Society.

The main advantages of IMS devices are their instrumental simplicity and high sensitivity (ppt detection limits). Moreover, ion mobility spectrometers offer real time monitoring capabilities with fast response times and low power consumption. IMS are light weight portable instruments (ranging from 520 gr to 27 kg) with small dimensions (W x D x H: 110 x 180 x 51 mm – 560 x 560 x 250 mm) and easy to operate (user-friendly). They are also very robust with low maintenance costs. The above described characteristics justify why IMS devices have great potential for in-field applications and are used widely in airport security checkpoints.

However, IMS sensors present some limitations and these are mainly related to their limited selectivity and to potential false-positive alarms usually produced by environmental or complex sample interferences. For homeland security applications, chemical compounds present in personal belongings e.g. cosmetic products, may have the same drift time as some of the threat analytes. This can ‘confuse’ the analytical instrument leading to false positive responses155, 156. Other possible sources of false alarms can come from the sample collection technique (e.g. sample swabs). Both moisture and temperature affect adversely IMS performance. Furthermore, highly contaminated chemical environments may be a serious analytical problem for IMS. Especially when high background concentrations are present, IMS can suffer from memory effects157 which can result in false positive alarms.

Commercial field-portable IMS instruments available in the market for trace threat detection purposes can be found in the Table 4 and in Figure 6. Overall device dimensions, weights and sample analysis time are also given. As can be seen, analysis time is within the range of several seconds. The presented instruments offer capabilities of both trace vapor sampling collection (e.g. SABRE 5000, MMTD, Itemiser® 3 Enhanced, Hardened MobileTrace®, MobileTrace®, RAID-M 100, μRAID, ChemPro®100i, ChemRAE, GDA-FR, Lonestar, QS-H150, IMS Mini-200, Easytec-XP, MO-2M, PKI-7315) and surface wipe sampling collection (e.g. IONSCAN 500DT, ITEMISER® 4DX, Itemiser® 3 Enhanced, DE-tector, EGISTM Defender, QS-B220, GA2100, PKI-7315).

**Table 4:** Commercially available IMS based devices for security applications.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Supplier** | **Model** | **Technology** | **Weight (kg)** | **Dimensions (mm)** | **Analysis time (s)** | **Target analytes** |
| Smiths Detection158 | SABRE 5000 | IMS | 3.2 | 363 x 110 x 130 | 20 | Explosives, Drugs, CWAs, TICs |
| Smiths Detection158 | IONSCAN 500DT | IMS | 19 | 400 x 310 x 400 | 5-8 | Explosive, Narcotics |
| Smiths Detection158 | MMTD | IMS | 5 | 483 x 216 x 203 | 10 | Explosives, Drugs, CWAs, TICs |
| Smiths Detection158 | IONSCAN600 | Non-radioactive IMS | 10.43 | 371 x 290 x 325 | < 8 | Explosives (military, commercial homemade), drugs |
| Smiths Detection158 | LCD 3.2E | Non-radioactive IMS | 0.52 | 110 x 180 x 51 | Not specified | CWAs, TICs |
| Smiths Detection158 | LCD 3.3 | Non-radioactive IMS | 0.65 | 105 x 179 x 46 | Not specified | CWAs(nerve, blood blister, choking), TICs, |
| Smiths Detection158 | LCD-NEXUS | Non-radioactive IMS | 3.1 | 184 x 165 x 270 | Not specified | CWAs, TICs |
| SAFRAN Morpho159 | ITEMISER®  4DX | Ion Trap Mobility Spectrometry | 12 | 180 x 480 x 460 | 8 | Drugs, Explosives |
| SAFRAN Morpho159 | Itemiser® 3 Enhanced | Ion Trap Mobility Spectrometry | 12 | 180 x 480 x 460 | 8 | Drugs, Explosives |
| SAFRAN Morpho159 | Hardened MobileTrace® | Ion Trap Mobility Spectrometry | 5.44 | 438 x 159 x 324 | 12 | Explosives, Drugs, CWAs, TICs |
| SAFRAN Morpho159 | MobileTrace® | Ion Trap Mobility Spectrometry | 4.3 | 409 x 152 x 315 | 8 | Drugs, Explosives |
| Bruker Corporation160 | RAID-M 100 | IMS | 3.5 | 400 x 115 x 165 | N/A | CWAs, TICs |
| Bruker Corporation160 | DE-tector | IMS | 19 | 520 x 435 x 400 | 10 | Drugs, Explosives |
| Bruker Corporation160 | μRAID | IMS | 1.2 | 130 x 64 x 223 | N/A | CWAs, TICs |
| Bruker Corporation160 | RoadRunner | IMS with no-radioactive HEPI source | 3.5 | 330 x 340 x 130 | Few seconds (not specified) | Explosives, narcotics |
| Environics161 | ChemPro®100i | Aspirated IMS | 0.88 | 230 x 101 x 57 | 2.5 | CWAs, TICs |
| RAE SYSTEMS162 | ChemRAE | Open Loop IMS | 0.8 | 228 x 102 x 50 | N/A | CWAs, TICs |
| AIRSENSE Analytics163 | GDA-FR | IMS, PID, MOS, EC | 4.2 | 395 x 112 x 210 | > 60 | CWAs, TICs, explosives |
| OWLSTONE164 | Lonestar | FAIMS | 7.8 | 383 x 262 x 195 | 1 | TICs |
| Thermo SCIENTIFIC165 | EGISTM Defender | High speed GC (HSGC) and micro differential IMS | 27 | 560 x 560 x 250 | 10-18 | Drugs, Explosives |
| Implant Sciences Corporation166 | QS-H150 | IMS | 5.1 | 493 x 127 x 188 | 5-30 | Explosives |
| Implant Sciences Corporation166 | QS-B220 | IMS | 14.6 | 396 x 366 x 412 | N/A | Drugs, Explosives |
| IUT Berlin167 | IMS Mini-200 | IMS | 6.5 | 280 x 100 x 280 | N/A | CWAs, TICs |
| Ion Applications, Inc.168 | Easytec-XP | IMS | 1.8 | NA | N/A | Explosives, Drugs, CWAs |
| Excellims169 | GA2100 | HPIMS | NA | NA | N/A | Explosives |
| Sibel170 | MO-2M | Nonlinear IMS | 1.4 | 305 x 120 x 86 | 2 | Drugs, Explosives |
| PKI-electronic171 | PKI-7315 | IMS | 4 | 430 x 113 x 205 | 5-10 | Explosives |
| Rapiscan Systems172 | DETECTRATM HX | IMS | 1.77 | 294 x 141 x 276 | 1-3 | Explosives, |
| Westminster International Ltd.173 | EVD3300 Hand Held Detector | IMS | 3.7 | 432 x 121 x 159 | 10 | Narcotics, explosives |



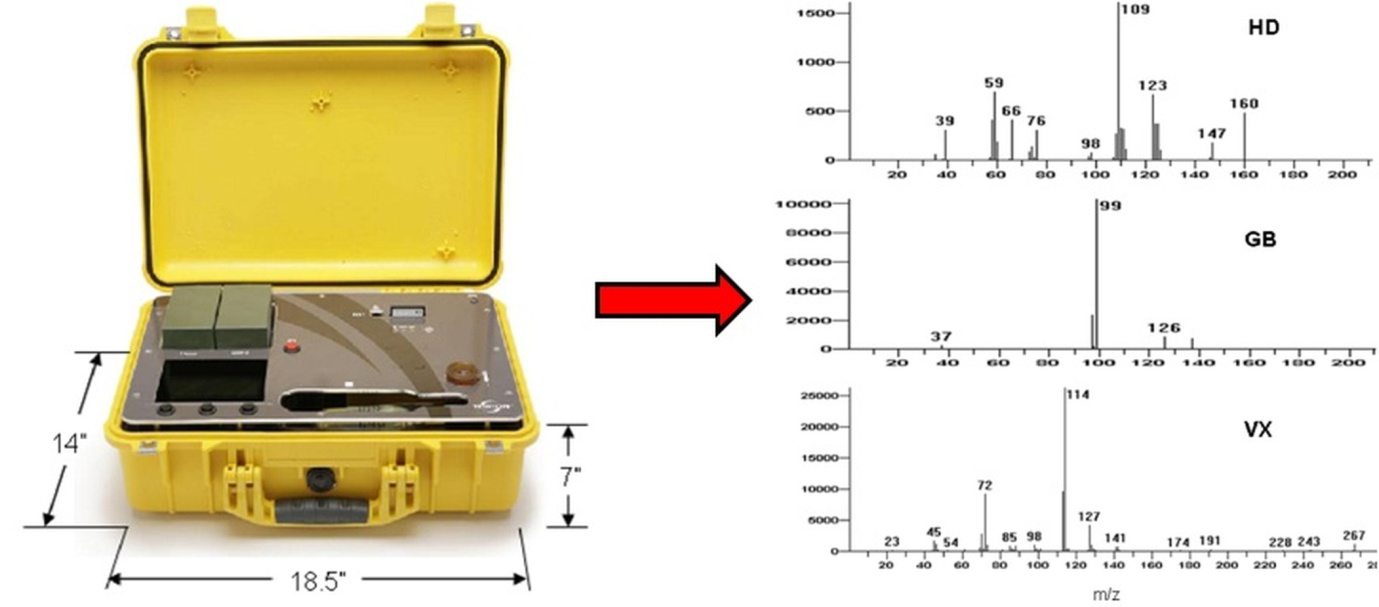
**Figure 6:** Representative hand portable IMS device (μRAID) specially developed for screening threat compounds in security applications. Reprinted with permission from ref 160. Copyright Bruker Corporation.160

## **Instruments based on other technologies**

### **Gas chromatography**

Gas chromatography (GC) is a technique that separates complex mixtures that travel through a mobile phase (gas) over a stationary phase (liquid or solid).174 The partition of each single substance and subsequently the order of elution; depends on the physical and chemical properties of each individual compound (boiling point, polarity, etc.) as well as on their interaction with the stationary phase. The most common detectors used during GC analysis are the flame ionization detectors (FID) and the thermal conductivity detectors (TCD). Usually GC is combined with other analytical techniques such as MS or IMS to offer improved chemical detection and accurate compounds identification. However, a typical GC analysis time can vary from a few minutes to more than an hour.

High-speed gas chromatography (HSGC) has been used combined with micro differential IMS and has produced a commercial drugs and explosives (e.g. TATP, HMTD, plastic explosives, nitrates, etc.) portable fast detection system (EGISTM Defender)165 provided by Thermo Fisher Scientific Inc. (Table 4). DLP-E4500 portable explosives detector from DPL-Surveillance-Equipment.com175 is a lightweight (5 kg) GC-chemiluminescence system, capable of detecting nitro based and peroxide explosives within some seconds. Chemical weapons and associated compounds were also detected using a GC system coupled to a Fourier transform infrared spectrometer (GC/FT-IR).176 GRIFFIN 400 and GRIFFIN 460 from FLIR Systems Inc.116 are GC/MS systems with MS/MS capabilities that can be used for narcotics, explosives, TICs and CWAs detection and can be both integrated in mobile lab units or in security checkpoints. Both GRIFFIN 400 and GRIFFIN 460 employ flexible sample introduction techniques such as SPME fibers, direct syringe injection and direct air-sample injection via a transfer line. The E2M and the MM2 from Bruker Corporation160 are GC/MS systems both with a heated membrane inlet that can be integrated into a vehicle or placed in a security point to screen for drugs or explosives. The WG 4500 Desktop Explosives Detector from Westminster International Ltd.173 weights less than 14 kg and is a portable GC for military, commercial and homemade explosives detection. Analysis can be completed within 15 sec. TRIDIONTM-9 GC-MS and GUARDIONTM-7 GC-MS (Figure 7) systems117, also reported in Table 3, offer rapid chemical analysis, good sensitivity and high chemical compounds discrimination on-site.



**Figure 7:** Mass spectra of three CWAs (HD, GB and VX) obtained by the portable GUARDIONTM-7 GC-MS system. Reprinted in part from ref 83. Copyright 2008 Springer.

### **Infrared spectroscopy**

Infrared spectroscopy (IR) usage has also been demonstrated in explosives detection. The principle of IR detection is based on the measurement of an infra-red beam that is absorbed from a target sample. This infra-red beam gives a characteristic fingerprint spectrum of the chemical compound under examination and provides information regarding its chemical bonds, characteristic chemical groups and its structure.177 In combination with other analytical techniques (MS, NMR, UV), it can be used for the identification of unknown chemical compounds and their structure. The traditional IR techniques present slow response times, whereas sample materials need to have pure or near pure concentrations. Moreover, water is a big contaminant during IR measurements, requiring careful manipulation. Fourier-transform Infrared (FTIR) spectroscopy was first developed in the 1970s. It offers faster measurement times (due to simultaneous scan of all target wavelengths), high sensitivity (at least one order of magnitude compared to conventional IR systems) and internal automated calibration. FTIR devices provide reliable and reproducible results that can be used for both qualitative and quantitative chemical analysis.178

A fiber optic coupled grazing angle probe reflection/adsorption IR spectrometry (FOC-GAP-RAIRS) method has been developed and tested successfully to detect and quantify high explosive trace materials on metallic surfaces.179 Detection limits of 160 ng/cm2 for TNT, 220 ng/cm2 for PETN and 400 ng/cm2 for HMX were achieved. This combined technique allows on-site measurements of nitro-explosives, however further research on the detection of other threat compound and their identification and quantification on different surfaces (glass, plastic, etc.) is required. IR imaging sensors have also been used in airports and other security checkpoints to detect human presence or movement for typical distances of several km and for different environmental conditions.

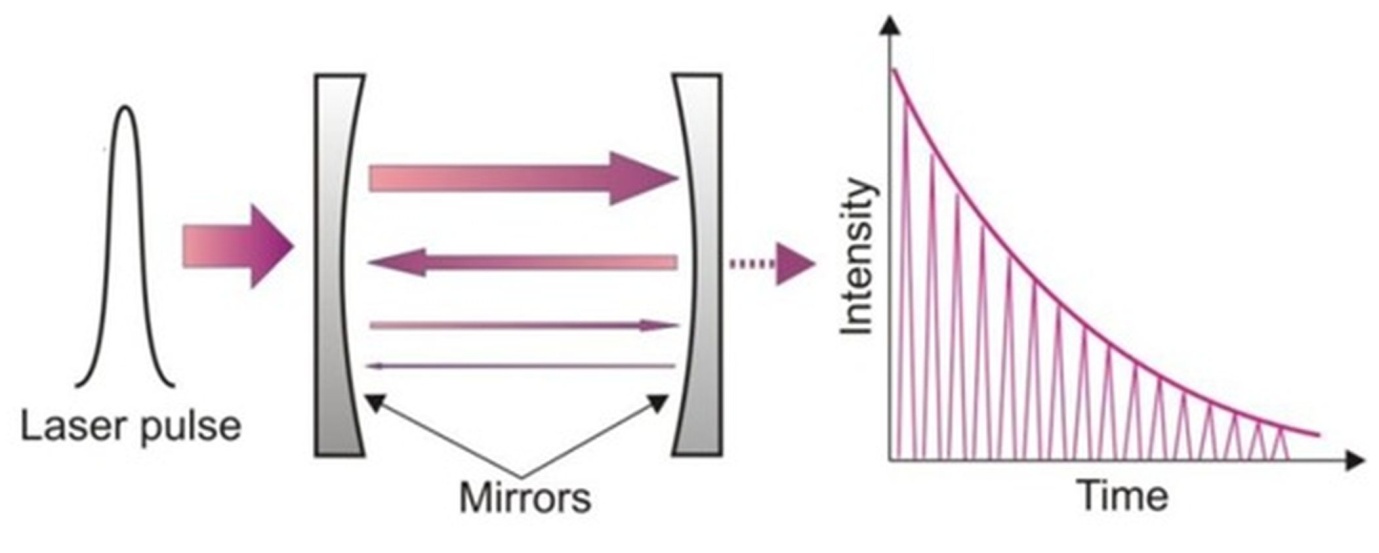
Commercially available IR device are presented in Table 5. Representatively, the MIRAN SapphIRe portable ambient multi-gas analyzer from Thermo Fisher Scientific Inc. permits non-destructive substance identification and monitoring in the sub-ppm area.165 Thermo Scientific TruDefender FT and TruDefender FTi are lightweight (1.3 kg and 1.5 respectively) handheld ergonomic FTIR spectroscopy systems for unknown chemicals and explosives identification within some seconds whereas the GeminiTM Analyser (1.9 kg) is the first FTIR and Raman spectroscopy combined handheld instrument.161 Agilent Technologies Inc.180, Smiths Detection Inc.158, Bruker Corporation160, MKS Instruments Inc.181 and Block Engineering182 are recognized suppliers with strong presence in the IR, FTIR and mid-IR market.

**Table 5:** Commercially available IR devices for threat compound screening.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Supplier** | **Model** | **Technology** | **Weight (kg)** | **Dimensions (mm)** | **Analysis time (s)** | **Library (substances)** | **Target analytes** |
| Agilent Technologies Inc.180 | 4500a FTIR spectrometer | FTIR | 6.8 | 220 x 290 x 190 | 120 | 13,000 | Explosives, drugs, white powders |
| Agilent Technologies Inc.180 | 4100 ExoScan Series FTIR | FTIR | 3.18 | 171 x 119 x 224 | Sample dependent | Available | Explosives |
| Agilent Technologies Inc.180 | 4300 Handheld FTIR | FTIR | 2.2 | 102 x 191 x 346 | 120 | Available | Explosives |
| Agilent Technologies Inc.180 | 5500 Series Compact FTIR | FTIR | 6.8 | 220 x 290 x 190 | 120 | 13,137 | TICs, white powders, drugs, explosives |
| Smiths Detection Inc.158 | HazMatID Elite | FTIR | 2.29 | 269 x 143 x 79 | N.A. | 10,000 | CWAs, explosives, narcotics, white powders |
| Smiths Detection Inc.158 | HazMatIDTM 360 | FTIR | 10.43 | 444 x 305 x 190 | < 120 | Available | TICs, nerve & blister agents, explosives, white powders, narcotics, precursors |
| Smiths Detection Inc.158 | Target-ID | FTIR | 2.15 | 255 x 156 x 98 | < 60 | 2,500 | Drugs |
| Thermo Fisher Scientific Inc.165 | MIRAN SapphIRe | IR | 10 | 144 x 193 x 553 | 20-165 | Available | CWAs, explosives |
| Thermo Fisher Scientific Inc.165 | TruDefenderTM FT | FTIR | 1.3 | 53 x 196 x 112 | few sec. (not specified) | Available | Explosives, narcotics, TICs, precursors |
| Thermo Fisher Scientific Inc.165 | TruDefenderTM FTi | FTIR | 1.54 | 61 x 196 x 112 | few sec. (not specified) | Available | Explosives, narcotics, TICs, precursors |
| Thermo Fisher Scientific Inc.165 | GeminiTM Analyser | FTIR, Raman | 1.9 | 256 x 146 x 61 | Not specified | Included | CWAs, explosives, TICs, precursors |
| Bruker Corporation160 | RAPID | FTIR, RockSolidTM interferometer | 28.7 | 500 x 331 x 386 | immediate | Included | Chemical threats, explosives, CWAs, TICs |
| MKS Instruments Inc.181 | AIRGARD® | FTIR | 34.1 | 467 x 645 x 191 | < 20 | Available | CWAs, TICs |
| MKS Instruments Inc.181 | AIRGARD®*Plus* | FTIR with ancillary electrochemical sensors | 35 | 643 x 686 x 191 | < 20 | Available | CWAs, TICs |
| Block Engineering Inc.182 | LaserScanTM | mid-IR | 4.3 | 254 x 203 x 127 | Few sec. (not specified) | Available | Chemical threats, explosives, IEDs |

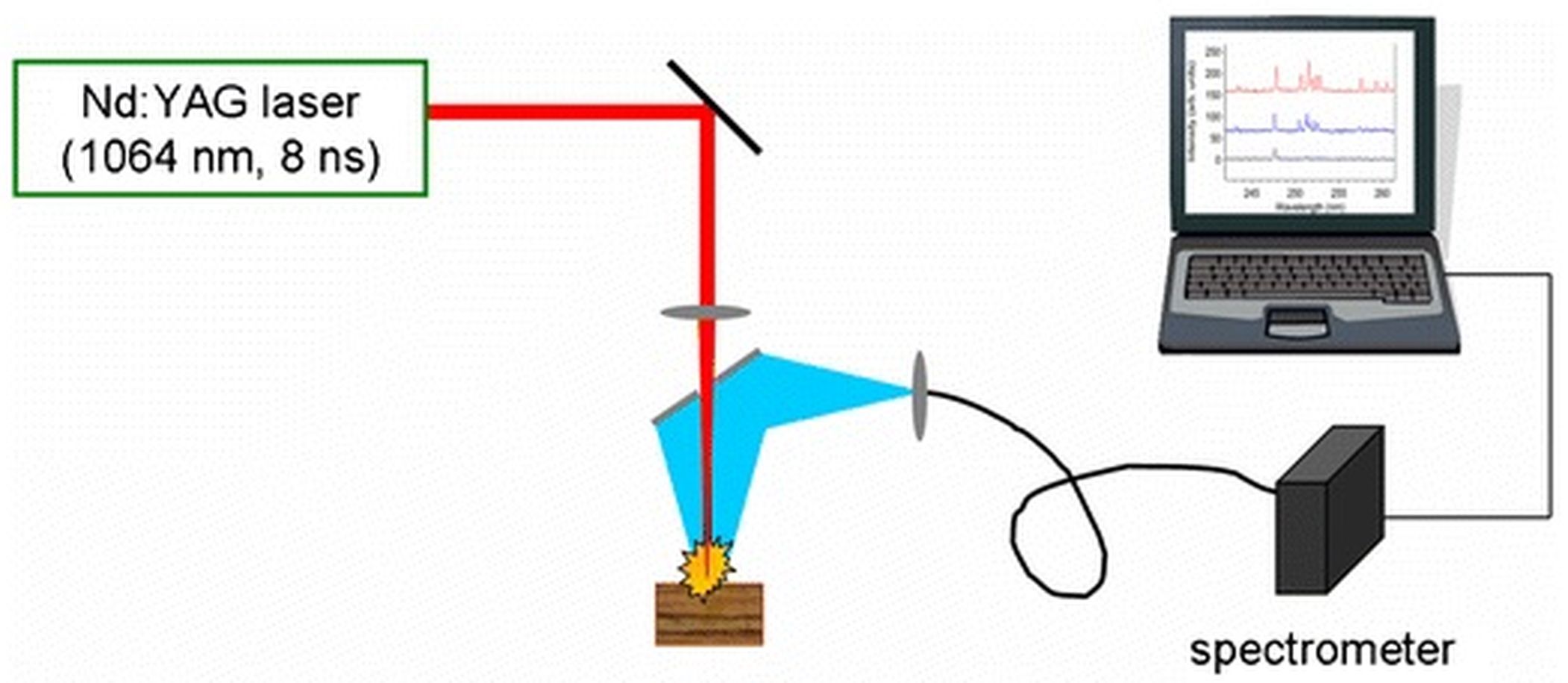
### **Cavity Ring-Down spectroscopy**

Cavity Ring-Down spectroscopy (CRDS) is based on reflectometry. A pulse of laser light is injected into a cavity with highly reflective mirrors (two or more) containing a gaseous sample material. Once the laser light is turned off, the exponential degradation is measured in correlation with the time elapsed and then compared with the laser’s exponential decay in the case when the cavity is empty. The obtained spectrum and the decay rate are characteristic of the sample compound under examination (Figure 8). CRDS offer real-time measurements and present a very high sensitivity (parts-per-trillion) with a decent selectivity in the mid-infrared region (6–8 µm).183, 184 Picarro CRDS analyser, developed by Picarro Inc. (California, USA), has been tested to detect vapor traces (low ppb) of common explosives (TNT, TATP, RDX, PETN and Tetryl).185, 186

**Figure 8:** Operating principle of cavity ring-down spectroscopy. A laser pulse is injected into a reflecting mirror cavity containing a gas sample. While the laser pulse circulates within the cavity, its intensity exponentially decays. A photodetector measures in real-time this degradation which is characteristic for the sample material. Absorption coefficient and sample concentration can be determined by the photodetector. Adapted from reference 184.

### **Laser-inducted breakdown spectroscopy**

Laser-induced breakdown spectroscopy (LIBS) utilizes a high intensity laser pulse to vaporize sample and produce a plasma plume. The emitted light from the plasma plume has a characteristic frequency and can be used for the identification and characterization of the sample material (Figure 9). Portable LIBS is ideal for *in-situ* operations as it offers direct sensitive and non-destructive real time chemical analysis with no sample preparation requirements. LIBS offers also stand-off threat detection capabilities for prevention of terrorist events at distances up to 100 m. Double pulse LIBS provides an enriched plasma plume, allowing improved discrimination of sample molecules and atmospheric components. Double pulse LIBS also eliminates false positive alarms.187, 188

**Figure 9:** Schematics of a LIBS system. A laser focused on to a sample surface causes ablation of the sample material and production of a plasma plume above it. The emitted light from the plasma is measured by a spectrometer and can be used for the characterization of the sample. Adapted from ref 187. Copyright 2009 Springer.

A representative commercial LIBS based device is the mPulse from Oxford Instruments plc.189 Applied Photonics Ltd.190 has also developed a LIBS system, the ST-LIBSTM, for remote chemical, biological, radiological, nuclear and explosive materials (CBRNE) detection with range capability in excess of 100 meters. The U.S. Army Research Laboratory in collaboration with Ocean Optics Inc. has developed a man-portable LIBS sensor for hazardous compounds (explosive, CWAs, biological agents, landmine) detection.191

### **Raman spectroscopy**

When a sample undergoes laser light excitation, the scattered photons transit up or down in the energy-level diagram. Raman spectroscopy relies on the inelastic scattering of photons and measures their vibrational transitions. In this way, identification of unknown chemicals can be done. Raman spectroscopy has the ability to penetrate various surfaces such as polymer or glass containers and identify potential threat or hazardous compounds. This can be explained by the fact that a weakly focused incident laser beam passing through varying qualities, colors and thicknesses of glass and polymers is only marginally scattered, resulting in weak Raman spectra from the substance container. Sample analysis with no significant spectral contribution from their containers is therefore possible. Raman spectroscopy is a well-established technique with fully integrated threat libraries, implemented in security checkpoints for public safety.192, 193

Field-portable Raman spectrometers for threat detection include the compact and lightweight (2.7 kg) RespondeR RCI and the ACE-ID (0.45 kg) provided by Smiths Detection Inc.158 The ACE-ID instrument can be operated with just one hand and is especially designed for harsh environments applications. The FirstDefender RM (0.8 kg), FirstDefender RMX (0.92 kg) and AhuraFD (1.8 kg) are also hand portable instruments developed and provided by Thermo Fisher Scientific Inc.165 for the same explosive and threat components identification and detection purpose. The portable i-Raman®EX from B&W Tek Inc. (Newark, DE, USA), uses Raman spectroscopy to deliver explosives, CWAs and forensic related analytes detection. SAFRAN Morpho S.A. (France)159 has developed StreetLab® Mobile (3 kg); an ergonomic, ruggedized, handheld Raman technology based device for TICs, explosives, narcotics and chemical weapons detection in the field. Cobalt Light Systems Ltd. (Oxfordshire, UK)194 used spatially offset Raman spectroscopy (SORS) to develop a fast bench top (but not handheld) liquid explosive detection system, the Insight100. SORS offers precise chemical screening of liquids concealed in non-metallic bottles or containers with various outer characteristics. Insight100 has already been deployed in many airports, offering stand-alone services or complementing other security screening systems. Table 6 gives a generic overview and summarizes the currently commercially existing Raman spectroscopy devices which were specifically developed for threat, toxic and hazardous compounds detection and monitoring. Figure 10 shows a representative Raman spectrometer currently used in security checkpoints.

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**Figure 10:** Representative hand-held Raman device (TruNarcTM) for the on-site detection of illicit narcotics in security applications. Reprinted with permission from ref 165. Copyright Thermo Fisher Scientific Inc.165

**Table 6:** Raman spectroscopy based instrumentation available in the market for the detection of threat chemicals.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Supplier** | **Model** | **Technology** | **Weight (kg)** | **Dimensions (mm)** | **Analysis time (s)** | **Library (substances)** | **Target analytes** |
| Smiths Detection Inc.158 | RespondeR RCI | Raman | 2.7 | 222 x 99 x 191 | < 30 | 15,000 | WMD, white powders, explosives, narcotics |
| Smiths Detection Inc.158 | ACE-ID | Raman | 0.45 | 127 x 89 x 56 | < 20 | 500 | Explosives, narcotics, TICs |
| Thermo Fisher Scientific Inc.165 | FirstDefenderTM RM | Raman | 0.8 | 193 x 107 x 44 | N.A. | 10,000 | Explosives, TICs, CWAs, narcotics, precursors, white powders |
| Thermo Fisher Scientific Inc.165 | FirstDefender RMX | Raman | 0.92 | 196 x 114 x 61 | < 60 | 10,000 | Explosives, TICs, narcotics, precursors, white powders |
| Thermo Fisher Scientific Inc.165 | AhuraFDTM | Raman | 1.8 | 305 x 153 x 76 | 1-20 | 10,000 | TICs, TIMs, CWAs, narcotics, white powders |
| Thermo Fisher Scientific Inc.165 | TruScreenTM | Raman | 0.9 | 208 x 43 x 107 | N.A. | Included | Explosives, precursors, benign material |
| Thermo Fisher Scientific Inc.165 | TruNarcTM | Raman | 0.57 | 51 x163 x104 | < 60 | Included | Narcotics, cutting agents, precursors |
| B&W Tek Inc.195 | Raman®EX | Raman | 3.5 | 170 x 340 x 280 | 20 | N.A. | Explosives, narcotics |
| B&W Tek Inc.195 | TacticID®-N | Raman & chemometric algorithms | 0.9 | 190 x 100 x 50 | N.A. | 1,000 | Narcotics, precursors, cutting agents |
| B&W Tek Inc.195 | TacticID®-GP | Raman & chemometric algorithms | 0.9 | 190 x 100 x 50 | N.A. | Included | Narcotics, explosives, TICs, CWAs, hazardous chemicals, precursors, cutting agents, binding agents |
| SAFRAN Morpho S.A.159 | StreetLab® Mobile | Raman | 3 | 381 x 140 x 203 | < 120 | Included | TICs, TIMs, |
| Cobalt Light Systems Ltd.194 | Insight100 | SORSTM | NA | 823 x 561 x 611 | 3-5 | Included | Explosives |
| Centice Corporation196 | Mobile Field Lab 3000 (MFL-3000) | Raman | 9.1 | 165 x 279 x 89 | < 30 | 3,800 | Narcotics, precursors, cutting agents, street drug mixtures, bath salts, explosives |
| Enhanced Spectroscopy Inc.197 | RaPort® | Raman | 2.1 | N.A. | 3 | Included | Narcotics, explosives, precursors, TICs, CWAs, nitro compounds |
| Rigaku Raman Technologies, Inc.198 | XantusTM-0 | Raman | 1 | 93 x 195 x 59 | < 300 | User library or third party vendor | Explosives, CWAs, hazardous material |
| Rigaku Raman Technologies, Inc.198 | XantusTM-1 | Raman | 2.2 | 125 x 233 x 85 | < 300 | User library or third party vendor | Explosives, CWAs, hazardous material |
| Rigaku Raman Technologies, Inc.198 | Xantus MiniTM | Raman | 1 | 61 x 176 x 82 | < 300 | User library or third party vendor | Narcotics, street drugs, explosives, CWAs |
| Rigaku Raman Technologies, Inc.198 | FirstGuardTM | Raman | 2.3 | 325 x 122 x 286 | < 300 | User library or third party vendor | Drugs of abuse, explosives, CWAs |
| SciAps Inc.199 | CHEM500 | Raman | N. A. | N.A. | N.A. | Included | Explosives, narcotics, percursors |
| SciAps Inc.199 | Inspector500 | Raman | 1.7 | 191 x 175 x 43 | N.A. | Included | CWAs, TICs, TIMS, narcotics, explosives |
| SciAps Inc.199 | ObserveRTM | Raman | 2.27 | 215 x 112 x 93 | Few seconds | Included | Explosives, TIMs, TICs |
| SciAps Inc.199 | ReporteR | Raman | 0.36 | 133 x 64 x 38 | 2-20 | Included | Narcotics, explosives, hazardous material |
| Field Forensics Inc.200 | HandyRamTM | Raman with Rapid Laser Spin (RLSTM) | N. A. | N.A. | N.A. | Included | Drugs of abuse, explosives, precursors |

### **Terahertz spectroscopy**

Terahertz spectroscopy (THz) employs electromagnetic fields with frequencies in the terahertz region (0.1 x 1012 Hz to 10 x 1012 Hz) to penetrate objects, surfaces, materials (especially non-metallic such as textiles, etc.) and through the absorbed radiation to detect concealed explosives or weapons. Threat substances give characteristic THz spectral signatures (THz fingerprints), allowing their detection through THz spectroscopy based sensors. THz radiation is not ionizing radiation (in contrast to X-radiation) so it is safe for screening humans at security checkpoints.201-203

TPS Spectra 300 from TeraView Ltd (Cambridge, UK)204 is a flexible transportable THz based explosive system. It has been successfully evaluated with Semtex, PE-4, RDX, PETN, HMX and TNT hidden beneath clothes (made from different fibre materials e.g. cotton, nylon, wool, leather, polyester, silk, etc.) and in the soles of shoes. The Ondax THz-Raman spectroscopy systems205 incorporate both THz and Raman technology to unfold important structural information and enhance chemical detection and characterization. The TeraFlash from Toptica Photonics AG.206 is a time-domain THz analytical platform with explosive and toxic gases detection capabilities. The TeraSys 4000 system from Rainbow Photonics207 is a THz spectrometer with frequency range 0.3-4 THz and resolution greater than 0.01 THz able to be used for explosives’ detection in security applications. A series of products from Zomega Terahertz Corporation208 such as the Mini-Z and the Micro-Z are lightweight portable standoff distance (1-40 cm and 10 cm respectively) THz sensors with real-time explosive detection capabilities.

### **Fluorescence spectroscopy**

Fluorescence spectroscopy comprises the manipulation of a beam of light to excite electrons in molecules and cause them to emit light. Fluorescence sensors have been deployed to detect explosive vapors at ultra-low levels.209 Recently a portable, cost-effective sensor based on the fluorescence quenching of pyrene on paper-based analytical devices was developed and tested with ten different organic explosives.210 The minimum detectable masses were in the region from 0.1 μg (for 1,3,5-trinitrobenzene - TNB) to 0.9 μg (for nitrobenzene - NB). A fluorescent nano-fiberous membrane (sensing film) was also developed, tested and evaluated to detect traces (ng) of nitro-aromatic-based buried explosive materials or residues and landmines under the use of standoff handheld UV light.211

Fido® X2 (weighs 680 gr), Fido® X3 (weighs 1.36 kg) and Fido® NXT (weighs 1.36 kg) from FLIR Systems Inc. (OR, USA)116 are lightweight, hand portable fluorescence polymer sensors for the rapid and non-invasive explosive threats detection operating in many U.S. airports. They are capable of detecting both solid and liquid explosives (homemade, commercial and military), including ammonium nitrate, plastic explosives, hydrogen peroxide and nitro-methane. Spectrum Photonics Inc.212 in collaboration with FLIR Systems Inc.116 developed an underwater chemical sensor based on amplifying fluorescent polymer (AFP) to detect unexploded ordnance and other explosives in trace-levels.

### **Optical sensor based systems**

Optical sensors for security or military purposes are classic detection systems, utilizing optics technology to locate threat components. A robust, remotely operated robot for military field use is the TALON® from QinetiQ (Farnborough, UK), which integrates optical, infrared, thermal, night vision and fisheye cameras to locate and disarm explosive devices.213 Spartacus213 is an unmanned, robotic platform with a stand-off distance up to 800 m, designed to support military missions to disable improvised explosive devices, landmines and unexploded ordnance in harsh environments. For the above applications, it utilizes six fixed focus cameras an IR camera and one pan/tilt/zoom camera. It can also support cameras with 360-degree continuous rotation with exceptional zoom capability and even thermal cameras. QinetiQ Dragon RunnerTM series213 includes the Dragon Runner 10 and the Dragon Runner 20 which are small, light and fast unmanned robots with integrated front and rear (day and night operational capabilities) as well as left and right cameras to detect, locate and disarm improvised explosive devices or bombs. Due to their size, they can be employed for fieldwork in mountains, deserts or even in urban areas. The iRobot 510 PackBot® from iRobot Corporation214 utilizes multiple high resolution, real-time, flexible cameras including a thermal camera to detect and dismount explosive materials in difficult and unsafe conditions (e.g. narrow passages, stairs, etc.).

### **Chemical sensors**

Chemical sensing systems are based on a selective chemical reaction when they interact with a threat component that yields to a characteristic distinct outcome (e.g. color variation).

EXPRAY from Plexus Scientific Inc. (VA, USA) is a commercially available portable kit for explosives and explosive residues detection. It offers nanogram detection limits within 60 sec. with high reliability and easy operation. The DropEx Plus kit from the same company has the same principles and can be applied in a wide range of explosives including: nitro-aromatics, nitrate esters and nitramines, inorganic nitrated based, chlorates and bromates as well as peroxide-based explosives.215 RAE Systems Inc.162 has also developed the MultiRAE Pro and the MultiRAE Lite Pumped, both portable multi-threat detectors (with more than 25 different chemical sensors each and auto calibration) ideal for use from Hazmat teams.

### **Electrochemical sensor based systems**

Electrochemical sensors have been developed for the fast trace detection of explosives and CWAs. They are based on the output electrical signal (voltage, current, conductivity) of a chemical reaction of a target compound of interest with the surface of a sensing electrode. For example, when a vapor sample enters into an electrochemical sensor, it firstly passes through a gas permeable membrane barrier that ensures certain sample importation. After that, the sample reacts with a sensing electrode which is either oxidized or reduced and produces a characteristic electrical signal.216-218

AreaRAE Steel Z2 multi gas system (6.3 kg) provided by RAE Systems Inc. (CA, USA) is commercially available and incorporates electrochemical, photoionization and catalytic combustion sensors to monitor toxic gases and other potential threats.162

### **Surface acoustic waves based sensors**

Surface acoustic wave (SAW) sensors utilize acoustic waves to sense and monitor chemical signatures emitted by hazardous compounds, explosives, landmines and CWAs. HAZMATCADTM Plus219 uses a hybrid technology of SAW and electrochemical sensors to detect TICs (HCN, ClCN, Cl2, AsH3, etc.) and CWAs. HAZMATCADTM Plus has fast response times (within seconds), good repeatability and high accuracy. Electronic Sensor Technology Inc. (California, USA)220 have manufactured zNose® 4600 which is a portable GC-SAW system that offers rapid (5-60 sec) field detection of narcotics (e.g. heroin, cocaine, marijuana, LSD, methamphetamines, etc.), bombs, chemical agents (e.g. GB, GD, HD, etc.) and explosives (e.g. RDX, PETN, TNT, ammonium nitrate, black powder, etc.). It works by separating sample molecules passing through the GC and then chemical detection on the SAW detector. The zNose® 4200 instrument developed by the same company is also based on the same operating principle of GC-SAW detection. Furthermore, the Joint Chemical Agent Detector (JCAD) is a lightweight hand-held device (0.9 kg) developed by BAE Systems Plc. (London, UK)221 that uses SAW technology to detect vapors arising from a broad variety of CWAs (VX, GA, GB, HD, L, AC, CK, etc.). JCAD can be used either as a mobile detection sensor or at a fixed-detection point.

### **Colorimetric sensors**

Colorimetric analysis has been extensively used in narcotics and explosives field detection. It uses visible light interactions with chromophore molecules which are able to absorb certain wavelengths of light and can reflect a color. TraceX explosive detection kit from Morphix Technologies Inc. (VA, USA) is designed to address common explosive and bomb detection issues at trace levels within few minutes222. KeDetect XD4 from KeTech (Nottingham, UK)223 is a portable swab kit for ammonium nitrate based explosives detection, whereas KeDetect XD6 was developed for high explosive detection such as PETN, RDX and TNT. KeDetect XD8 belongs in the same colorimetric test kit series and was specifically generated to detect peroxide or chlorate based explosives in less than a minute. Ex-DetectTM Mini XD-2 from Spectrex Corporation (California, USA)224 is also a compact and tested explosive and gun propellants detection kit with detection limits in the nanogram area. The Seeker XDUTM supplied by DetectaChem (TX, USA)225 is a handheld system able to detect explosives (e.g. nitroaromatics, nitrate esters, nitramines, inorganic nitrates, chlorates, peroxides, perchlorates, etc.) in both bulk and trace amounts. It utilizes a swipe-card sample collection method, which is the key element for this field chemical analysis. Swipe sampling can be applied on surfaces varying from constructive materials to textiles, body parts, etc. The ULTRATM is a series of colorimetric detection kits developed by Field Forensics Inc.200 and it includes the ULTRATM 236, theULTRATM 246 and the ULTRATM 459. These colorimetric kits are very simple to use and can be employed to detect ammonium nitrate, urea nitrate, peroxide HME, precursors, etc.

DetectaChem LLC.225 have developed a series of handheld explosives and narcotics automated colorimetric detectors such as the SEEKER and the SEEKERe. SEEKERe is only 197 gr and is able to colorimetrically detect and identify nitroaromatic explosives, nitroamines, nitrate esters, inorganic nitrates, peroxides, chlorates, perchlorates and a wide range of illegal drugs. DetectaChem LLC.225 have also developed and supply detection swipe-cards which go along with and support the SEEKER systems and allow simple and fast sample collection. CWA detection tubes from Oritest Group226 are ampoules containing some selective solutions/materials. Sample introduction can be achieved by a mini-handheld pump. If the target threat - CWA is present in the ambient air, a chemical reaction takes place within the tube and instantly the tube’s color changes allowing accurate detection.

Luxfer Magtech Inc.227 has developed the M8 and M9 chemical detection papers for CWAs detection. The M8 is used to detect nerve and blister agents in the liquid phase e.g. water, whereas the M9 detection paper is designed to detect nerve agents and mustard agents. The M256A1 chemical detection kit227 can be used to confirm the presence or absence of CWAs in large areas, while the detectability range for potential threats is expanded. Tri-tech Forensics228 and Westminster International Ltd.173 also have a strong presence in the colorimetric market for threat detection. Tri-tech Forensics offers a master kit for explosives’ detection, whereas the Westminster International Ltd. offers a wide range of portable cases and kits for narcotics detection and identification.

### **Immunochemical sensors**

Immunochemical sensors employ molecular antibody-antigen interactions to specifically detect explosive compounds. These types of sensors are still under development, so they are not yet commercially available for in-field security and military operations. Laboratory investigations have been done with various explosives such as TNT, PETN and DNT.229 Surface Plasmon resonance (SPR) biosensors have been used on immunosensing platforms to detect explosive residues with high sensitivity.230 The Analyte 2000 from Research International Inc.231 is a 4-channel, single wavelength fiber optic sensor able to perform fluoro-immunoassays. It has been remotely operated during unmanned air vehicles (UAVs) operations. Analyte 2000 has also been tested with groundwater to measure TNT and RDX.

### **Nanotechnology sensor based systems**

Nanotechnological sensors as potential detection tools have become very popular, recently. Developments in carbon nanotube technology, molecularly imprinted polymers (MIPs) and nanoparticles exhibit devices with enhanced sensitivity and selectivity threat detection and monitoring capabilities.232-234 Single-walled carbon nanotubes (SWNTs) were used to support aqueous chemical sensors and enable trace detection (sub-ppb) of DMMP and TNT.235 Such nanotechnological sensors are still under development and require continuous improvements before reaching the open market. Characteristically, Vaporsens device from Vaporsens Inc. (UT, USA),236 is based on a low-cost nano-fibre sensor able to detect trace drugs, TICs and explosives. Moreover, Tracense Systems (Hertzelia, Israel)237 has developed a miniaturized nano-wire based device for detecting chemical hazards and threats.

### **Flame spectrophotometry sensor**

Flame photometry is an atomic emission spectroscopy that is used to determine specific atoms. In the case of CWAs: sulfur and phosphorus atoms are detected. Commercial instrumentation includes the AP2C and the AP4C, both developed by Proengin Inc. (Florida, USA).238 These hand-held detectors are capable of detecting sulfur containing components (e.g. sulfur mustard) as well as phosphorus containing compounds such as all G (e.g. tabun, sarin, soman, cyclosarin, isopropyl ester) and V (e.g. Vx-agent, Ve-agent, Amiton) warfare agents. AP4C is also able to detect all the precursors of the above chemicals. Detection can be done within two seconds, in sample agents emanating from all states of matter.

### **Thin layer chromatography**

Thin layer chromatography (TLC) is an easy, rapid and low-cost standard analytical methodology that can separate, identify and characterize non-volatile chemical compounds belonging in the same family. TLC can be used during security applications for pre-screening of narcotics and explosive materials. The microTLCTM kit from Field Forensics Inc.200 is a simple to use portable kit for the onsite analysis of explosives in soil samples or drugs of abuse. It utilizes a developing chamber that allows sample separation on a TLC plate to be completed and an integrated UV light source that allows drying and visual comparison of the TLC plates. The process is completed with direct comparison of the measured spots on a TLC plate with a TLC plate with standard spots.

### **Microfluidic paper based analytical devices**

Microfluidic paper based analytical devices (μPADs) utilize colorimetric, electrochemistry, and other signal transduction methods to provide rapid, on-site detection of explosive and materials (military or improvised, inorganic and organic).239-241 Recently, a microfluidic paper based analytical platform having the capability to filter, extract and pre-concentrate explosives originating from soil samples was reported. Analysis was conducted using a lab- on-a-chip (LOC) system and eight explosive materials between 1.4 and 5.6 ng were successfully analysed.240 Since cost is an important factor in field chemical analysis; μPADs have attracted wide interest.

### **Enzyme technology based sensors**

Enzyme-based sensors have been recently employed to detect CWAs vapors from liquid and solid surfaces. More specifically, FLIR Systems Inc.116 employed a patented enzyme technology to detect and analyze nerve, blood and blister agents with their portable Fido C1 and Fido C3. Sample analysis can be completed within 5 minutes with high specificity and sensitivity.

## **Comparison of the existing technologies for artificial sniffing**

The table below (Table 7) summarizes the above described techniques and states their advantageous characteristics and their limitations when they are used during in-field security applications. Most of these methodologies (and especially in the field of human safety) are complementary, so the purpose of this comparison is to examine the analytical performance of the current techniques and how they fulfill the analytical criteria mentioned in section 2, as well as to establish research motivations for improvement of the current analytical approaches for the *in-situ* threat, illicit and hazardous materials detection.

**Table 7:** Advantages and limitations of the existing technologies for threat sniffing in security operations.

|  |  |  |
| --- | --- | --- |
| **Technique** | **Advantages** | **Limitations** |
| **EN** | 1. Simplicity 2. Fast response times 3. Portability 4. Inexpensive | 1. Unstable results 2. Specificity issues |
| **MS** | 1. High sensitivity (low LODs) 2. High specificity 3. High mass range 4. High resolution 5. Real time measurements 6. Measurements’ stability 7. Accuracy 8. Portability 9. Fast analysis times (s) 10. Qualitative and quantitative analysis 11. No sample preparation 12. Ability for MS/MS or MSn (extra confirmation steps and elimination of false alarms) | 1. Relatively high costs (purchase and maintenance) |
| **IMS** | 1. Instrumental simplicity 2. Small size 3. Light weight 4. Robustness 5. Low-power consumption 6. Fast response times 7. High sensitivity | 1. False positive alarms 2. Potential compounds’ adsorption onto the IMS surfaces 3. Limited selectivity 4. Lack of performance in highly contaminated environments 5. Humidity, temperature, and composition of the sample may affect detector’s response 6. Bureaucracy due to the integrated radioactive sources |
| **GC** | 1. Accuracy 2. Couples with other analytical techniques | 1. Long analysis times |
| **IR** | 1. Reliable and repeatable results 2. Qualitative analysis 3. Quantitative analysis 4. Non-invasive technique | 1. Lack of flexibility 2. Indoor use |
| **CRDS** | 1. Real-time measurements 2. High sensitivity | 1. Lack of selectivity |
| **LIBS** | 1. Direct analysis 2. Sensitivity 3. Non-destructive real time analysis No sample preparation | 1. False positive alarms 2. Plasma conditions vary with the environmental conditions |
| **Raman** | 1. No sample preparation requirements 2. Sensitive to homo-nuclear molecular bonds 3. Fully integrated threat libraries 4. Portability 5. Non-destructive 6. Fast response times 7. Analysis through glass and polymer packaging | 1. Cannot be used for metals or alloys 2. Fluorescence of the sample background may lead to false negative alarms |
| **THz spectroscopy** | 1. Penetrates though materials 2. Non-destructive 3. Many non-metallic or non-polar materials are transparent to THz | 1. Limited penetration in high-water content or metal objects 2. Distance limitations |
| **Fluorescence** | 1. Excellent signal-to-noise ratio | 1. Limit due to linear intensity |
| **Instruments based on various sensors (e.g. chemical, electrochemical, immunochemical, colorimetric, etc.)** | 1. Portability 2. Sensitivity 3. Reliability 4. Easy operation 5. Low LODs 6. Fast response times |  |
| **Flame spectrophotometry** | 1. Sensitivity | 1. Small number of excited atoms 2. Sample interferences 3. Reproducibility |
| **Nanotechnology** | 1. Extreme sensitivity 2. Rapid analysis 3. Selectivity 4. Small size 5. Accuracy |  |
| **TLC** | 1. Simplicity 2. Sensitivity (high) 3. Low cost 4. Fast separation | 1. Humidity and temperature effects on the sample |
| **Enzyme based sensors** | 1. Simplicity 2. Specificity 3. Sensitivity 4. Low false positive or negative alarms 5. Speed of analysis | 1. Lack of stand-off detection |

# Summary

This review paper investigated the current status and recent advances in the area of artificial sniffing instrumentation for in-field security applications. A wide range of technologies and systems with threat sensing (detection, characterization and online monitoring) capabilities has emerged to identify the chemical footprint associated with illegal, hazardous, toxic and terrorist activities. Target compounds include human chemical signatures (for cases involving illegal immigration and human trafficking), drugs of abuse, explosives and CWAs.

The paper consisted of two main parts. The first part was a comprehensive presentation of the chemical compounds which are associated with homeland security and civil defense operations. The second part gave an overview of the existing and well-established technologies for threat detection including under development technologies. It summarized their main characteristics, functional principles and presents commercially available chemical sensing systems. The article concludes with a comparative feature study for each of the discussed technologies.

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**Stamatios Giannoukos** received a M.Eng. degree in Chemical Engineering from the National Technical University of Athens, GR, and a Ph.D. degree in Electrical Engineering and Electronics from the University of Liverpool, UK. He is currently a Research Associate in the Mass Spectrometry group at the University of Liverpool. The area of his specialization is in analytical chemistry, in instrumental methods for chemical analysis with emphasis in mass spectrometry and gas chromatography, in VOCs chemistry and in field chemical analysis.

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**Dr. Guido F. Verbeck**, Associate Professor of Chemistry and Biochemistry, is an expert is mass spectrometry, specifically instrument design and development. Dr. Verbeck has developed ion cyclotron resonance, time-of-flight, and ion trap mass spectrometers over the past 17 years, and has been a member of the analytical community for 22 years. Dr. Verbeck’s appointment is currently at the University of North Texas where he continues to design novel ion optical devices for miniaturization, preparative, and analytical mass spectrometry, and is the Director for the Laboratory of Imaging Mass Spectrometry.

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