A quantitative assessment of chemical techniques for detecting traces of explosives at counter-terrorist portals

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Abstract

Previous reviews have discussed in a qualitative manner the various highly sensitive analytical techniques for detecting minute traces of explosive material. However, there is no review available which compares quantitatively the sensitivities of the different analytical methods for detecting explosives. In view of the importance of this area to the present day planning of counter-terrorist strategies, this review makes a comprehensive and quantitative comparison of the analytical chemical methods which can be used for the detection of trace explosives in the luggage and on the persons of travelers. Possible directions of future development in this area are also discussed.

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1. Introduction

Concern about travelers carrying small quantities of hidden explosive material on commercial airlines has become more intense since the detonation of 250 g of plastic explosive [1] was used to bring down Pan American Flight 103 in Lockerbie, Scotland in 1988. The focus on such problems has also greatly increased since the September 11 attack on the World Trade Center in New York in 2001.

At the present time, approximately 10 million items of luggage are scanned annually [1] in a major facility such as Heathrow Airport in the United Kingdom. The demand for reliable and rapid methods for screening luggage is increasing as the threat of terrorism increases. The effective scanning for explosives in objects of various sizes, ranging from small postal parcels to large containers and trucks is now becoming an important aspect of counter-terrorism activities. Unfortunately, technologies used for screening luggage cannot always be used for screening passengers because of safety reasons [2–4]. There is thus considerable demand for the provision of safe and non-intrusive systems for detecting explosives. The analytical problems encountered in such work are unfortunately quite complex and range from the problems of remote sampling to those of non-destructive detection.

Some devices for explosive screening at airport portals are already commercially available. However, only a small number of airports have installed systems to detect vapors emitted by explosives because of the high cost [5]. Traditional methods, involving canine detectors that rely on the olfactory system of dogs have been employed for such purposes. Nevertheless, a comparison between instrumental chemical analysis and the use of highly trained dogs for explosives detection suggests some advantages of the instrumental methods over those of canines [6]. One of the major problems confronting both instrumental and canine detection in this situation relates to the problem of obtaining vapor samples from explosives housed in fully enclosed containers.

2. Major issues relating to explosives detection at entry points

A number of obvious limitations exist in the passenger screening situation. First and foremost, there will generally be no time for using many traditional analytical techniques and there will even be limitations on the time available for...
pre-concentration techniques, which are unfortunately often an important feature of ultra-high-sensitivity detection.

Secondly, quite serious technical problem emerge if a passenger chooses to place explosives in air-tight metal container, particularly if this container is impervious to electromagnetic waves at all frequencies. These problems are compounded by the enormous diversity of luggage, as a wide variety of modern chemical products accompany most travelers. These include polymers, synthetic fabrics, cosmetics, metals, and small encapsulated devices such as traveling alarm clocks, watches, mobile phones, radios, heart pace-makers and other medical accessories and prosthetic devices. Under these circumstances, it seems virtually impossible for any remote sensing device to detect explosives in sealed metal containers no matter how sensitive the detection system, unless the container, which has been detected manually or by X-ray imaging, is either confiscated or opened for more detailed inspection prior to travel.

A third issue, which needs consideration, is that with a few exceptions, detection in the vapor state is often employed where ultra-high-sensitivity techniques are used in an automated manner at transport portals. If the substance is an involatile solid, it is usually ejected into the atmosphere by a laser ablation device, which provides high detection sensitivity. Thus, even minute traces of explosives left on one’s body or clothing can be detected after vaporization by a laser beam or an intense source of heat. Unfortunately, one’s body or clothing can be detected after vaporization sensitivity. Thus, even minute traces of explosives left on the body or clothing can be detected after vaporization by a laser beam or an intense source of heat. Unfortunately, one’s body or clothing can be detected after vaporization.

Some workers have suggested the use of taggants [7] in explosives in order to provide very high detection signals. Unfortunately, this cannot be a reliable method since there is no way to guarantee that taggants will always be incorporated by clandestine manufacturers and suppliers of explosives.

2.1. Obstacles in implementing portal screening of explosives

Typical obstacles to implementation are false alarms, high cost of some of the new detection technologies, difficulties of use and the uncertainty and variability of threat scenarios are some of the factors that must be considered in the implementation of portal screening at airports. Even though most authors have reported false alarm rates between 2 and 10% and a probability of detection ranging between 88 and 98.5%, these figures are highly dependent on the detection conditions for a given technique [8–13]. The probability of a false alarm was as high as 25% at a 90% detection probability when thermal nuclear activation was used to detect small quantities of explosive molecules [14].

For the purpose of bulk explosive detection, the Federal Aviation Administration in the United States has estimated a total cost of US$ 2.2 billion for 1800 detector units that would need to be installed in 75 airports [15]. This estimated cost does not include the cost of personnel and of their training, and the evaluation and maintenance of such detectors. In contrast, Canada has spent CA$ 5 million in 2002 for the deployment of systems to detect explosives and the total budget allocated for airport security is projected to be CA$ 20 billion for the 5 years from 2003 to 2007 [16]. Detectors of bulk (solid state) explosives which are based on X-rays each cost between US$ 100,000 and several million dollars [17]. The detectors of trace explosives based on gas chromatography with chemiluminescence, electron capture or surface acoustic waves detectors and ion mobility spectrometers are sold at not less than US$ 150,000, 20,000, 25,000 and 50,000 respectively. In addition to the technology affordability, the difficulty of use of specific techniques must be taken into consideration because high speed screening at rates of less than 30 s per person is essential.

2.2. A survey of analytical techniques for the detection of explosives

Systems to detect and monitor explosives have been reviewed in the literature [2,3]. The following techniques have been used to detect bulk explosives in their solid states. X-rays detection [2,18] is well establish and in a conventional system, X-ray energy is measured after passing through an object. In some cases, two different X-ray energies are used simultaneously and this approach is capable of differentiating substances according to density and atomic number. On the other hand, X-ray scattering techniques are used to provide scatter patterns that are based on the number of the scattered X-ray photons detected. The nuclear-induced techniques use neutrons instead of photons cost more but are slow to detect explosives [2,18,19]. There are several modes of detection, either using thermal neutrons or fast (pulsed) neutrons. Nuclear magnetic resonance and quadrupole resonance [20–24] are also commonly used in the detection of traces of explosives. Other solid state analytical techniques are electron capture spectrometry, mass spectrometry, field ion spectrometry and ion mobility spectrometry. Table I provides summaries of detection techniques that explicitly reported the detection limit. X-rays and nuclear-based techniques generate the best results for the detection of bulk explosives, but the cost is high and the scanning speed is slow. Nuclear quadrupole resonance (NQR) spectrometry is used to detect explosives and drugs but weak signals in the low frequency region hinder the extensive use of this technique. The uses of immunosensors [25–28], electrochemical detectors [29–34] and spectroscopic detectors [35–50] have been well investigated and in some cases require a high level of intrusiveness. A detailed review of immunosensor technologies is available [25–28,51,52]. Polymer-based sensors [53] are susceptible to fouling and saturation. Some odors are adsorbed readily and the irreversible behavior causes polymer sensors to last only for about 10–12 h in a clean environment [54]. New approaches, using sol–gel matrix encapsulation enhance the stability towards environmental
dusturbances but cause diminished detection sensitivity [55].

On the other hand, the environmental matrices usually contain substances that either quench or enhance polymer-based fluorescence detection [54].

Gas chromatographs fitted with electron capture detectors [45,56] are useful for the detection of the vapors emitted by explosives. In this method, the high electron affinity of nitrogen atoms present in the molecules of explosives ensures the capture electrons produced by a radioactive source and thus ensures very low detection limits (see Table 1).

Another technique uses the absorption of near-infrared (NIR) radiation [65–67], reduces the interference by laser-induced fluorescence from the absorbing molecule [43]. Furthermore, infra red spectroscopy with a longer path length of 123 cm has been used for quantitative analysis of vapor from solid explosives placed in a sealed heated cell [44]. An extensive study on the scope of this method is needed.

Raman spectroscopy and Fourier transform Raman spectroscopy can also be used for detecting vapor from explosives [40–42]. A portable acousto-optic tunable filter Raman spectrometer has been suggested but the sensitivity of this method is not available for comment. One drawback of Raman spectroscopy was the laser-induced fluorescence emitted by the absorbing molecules when using shorter wavelengths of the ultraviolet–visible range for excitation.

Immunosensors can be extremely sensitive detectors and use the ability of antibodies to bind respective antigens and the ability of attached fluorescent dyes to produce signals [25,26,68,69]. The high specificity of this method is a disadvantage since it requires a specific antibody for each compound of interest. Unfortunately, poor signal discrimination results in loss of sensitivity when multianalyte immunosensors are used [25].

High-performance liquid chromatographs fitted with pre-column enrichment valves and diode array detectors have been investigated [35,36]. The major disadvantage of this method is the longer analysis time.

2.3. Detection limits

The equilibrium vapor pressure of most explosives at ambient temperature ranges between $10^{-8}$ and $10^{-9}$ Torr and corresponds to equilibrium vapor concentrations in the region of $10 \mu g/l$ down to $10 ng/l$. This vapor concentration is measured for pure samples at equilibrium in a closed
Present explosives vapor detection methods generally require pre-concentration prior to detection, because of the low vapor pressures exhibited by most explosives [3]. The pre-concentration process, which includes the use of filters and adsorbing/desorbing material, increases the detection time and may thus slow down online continuous measurements. This is because the molecules of explosives are deposited on to the adsorbing material at a low temperature and then desorbed at a higher temperature.

The mechanism of detection of explosives by canines [6] and the electronic systems to detect explosives vapor such as electronic noses [70–72] and sniff probes [73,74], which simulate the olfactory system of canines, have been described in the literature. Standards for the proficiency of explosives detection by dogs meet the expected confidence limits of 90–95% [6]. Thus, a trained dog is required to identify six different odor classes in four of five different search areas but the performance deteriorates over time.

2.4. Experimental detection limits for explosives

An extensive literature search has been carried out to produce the quantitative information in Table 1. Table 1 presents the experimental detection limits for traces of explosive using various analytical techniques. The values indicated in the Table are the lowest detectable limits claimed for each method in the literature. The variation in experimental conditions, the types of instrument, sample preparation technique and the detector systems, made comparison between these techniques very difficult [4].

From Table 1, it is clear that the lowest detection limit among the listed techniques is that of $0.07 \text{ng/l}$ using a headspace gas chromatograph fitted with an electron capture detector. In that particular experiment, 100 mg of TNT sample was placed in a vial and detection using the gas chromatograph was carried out 1 week later, assuming that an equilibrium vapor pressure had been reached. The time taken for analysis was 20 min. This highly sensitive method is thus too slow for passenger screening at airport portals.

The next most sensitive method in Table 1 involves the use of immunosensor techniques. In this experiment, dual capillaries coated with specific antibody were used; viz. anti-TNT and anti-RDX. These were saturated with fluorophore labeled antigens. Using a continuous buffer flow, the fluorescence was measured at 662 nm. These methods [25–27,75,76] have two major weaknesses if they are to be used for the direct detection of vapor from explosives. Firstly, the vapor has to be dissolved in the flow buffer and secondly, it takes several minutes to finish the analysis.

Table 1 indicates that the next most sensitive alternative for direct vapor detection is the mid-infrared cavity ring-down technique. In this technique, concentrations of explosive vapor can be directly measured down to a detection limit of 75 ng/l for TNT.

2.5. Current commercial systems

Portal limits of a commercial explosive vapor detection system are in the ng/l range and for trace solid detection are in the picogram range [3]. Some nuclear methods are well suited for the detection of hidden explosive materials in luggage [2,79]. Using a neutron source [80], 0.6 kg of the explosive RDX, was detectable in 10 s, and detection limits primarily depend on scanning time and chemical composition. Detection of the low vapor pressures (below $10^{-9}$ Torr) from the explosives RDX and PETN using ion mobility spectrometry requires initial pre-concentration by trapping the vapor and releasing by subsequent heating prior to analysis [6]. This method is capable of detecting sub-nanogram levels of TNT. Ion mobility spectrometers have been used to detect explosives and were put into production after the Lockerbie incident in 1988. Currently, techniques based on ion mobility spectrometry are the most promising and widely used analytical techniques for the detection of explosives. This is due to the fast response time and high sensitivity, which results from the high electron affinity of the nitrogen atoms [37] present in most explosives. The rapid development of ion mobility spectrometry was slowed down due to irregular responses arising from memory and humidity effects [4].

2.6. What does the future hold?

The successful development of a system for direct vapor detection in assaying explosives is critically dependent on the sensitivity of the analytical method. The absence of reliable measurements of the vapor pressures of explosives at ambient temperatures under practical (non-equilibrium) conditions is a major problem, which affects the planning of such systems. Values for the vapor pressures, which would need to be measured, have been the subject of some speculation. For example, the vapor pressures of TNT above buried land mines are claimed to be $10^7$ to $10^8$ times less than the equilibrium vapor concentration ($70 \text{ng/l}$) at room temperature. The concentration may be even in the order of $10^7$ to $10^8$ times smaller than this [81]. Such enormous ranges for these estimates indicate the unreliability of information in this area. The vapor concentration around plastic explosives could be even lower. This is unfortunately a neglected area in which the absence of reliable information severely limits the development of future systems for the detection of vapor from explosives in crucial situations such as airline portals.

Some rather new methods for detecting ultra-low concentration of chemicals are on the horizon. These include...
broadband terahertz spectroscopy [82–85], single molecule spectroscopy (SMS) [86–91] and scanning tunneling microscopy (STM) [92].

The success of the canine olfaction system to detect explosives helped in the design of the conducting polymer-based electronic nose array system that is capable of detecting explosive vapor molecules at ambient room temperature and atmospheric pressure without sample preparation. With this technique, the presence of the specific explosive vapor molecules is detected through the change in the electrical resistance of chemically sensitive arrays of conducting polymer carbon-based resistors [72,93]. The combination of conjugated polymer-based fluorescence chemosensors is capable of amplifying signals and can hence improve the detection limits [94].

In single molecule spectroscopy, the detection limit in principle might reach the ultimate sensitivity of ca. 1.66 × 10^{-24} mol (the yoctomol region). However, less optimistic detection limits of ca. 3000 molecules [95] are suggested for this technique. In this method, a laser beam is used to excite an electronic transition in a very dilute system of molecules. The fluorescence excitation spectrum of a molecule is used to obtain a highly sensitive measurement of the absorption spectrum and hence the concentration. Using an ultramicro flow-cell and excitation with a near-infrared semiconductor laser, polymethine dye could be detected in the 140–370 ag range [96] by this method. The ability of single molecule spectroscopy to reveal the inhomogeneity in a small-scale [89] could be extended for ultratrace explosives detection in a wide variety of matrices. Another method, single molecule Raman spectroscopy [90] is based on surface enhanced Raman scattering and is capable of detection to a level of ca. 100 molecules.

Scanning tunneling microscopy is another technique with very high sensitivity. It allows the investigation of electrically conducting surfaces down to the atomic scale. Thus, a single crystal of explosive material attached to a personal belonging such as a boarding pass might in principle be detected using STM technology. In this technique, the sample is either positively or negatively biased and the small (tunneling) current that flows when an electron probe is in contact with the surface is amplified and measured. This technique is very far off the stage of being a practical technique for luggage or passenger monitoring at transport portals, but its application cannot be ruled out in the long term.

Another emerging technology is broadband terahertz spectroscopy, which is mainly used in the field of imaging and sensing [97]. This non-invasive technique uses far infrared radiation in the region of 30–1000 μm (380–10 cm^{-1}) terahertz frequency [98]. This technique that uses a phase-locked microwave source to drive a picosecond transmission allows both broadband spectra and single line precision up to Hertz level [99]. The main advantages of this technique are the faster signal processing, high resolution and the capability of detecting 3–100 atoms in the gases phase [100]. Broadband terahertz techniques have considerable potential for the detection of trace amounts of explosive molecules. Unfortunately, this technique needs cryogenic systems for sample trapping. As well as increasing the cost, this slows the rate of portal detection down to an unacceptable level.

The development of multipass cells (e.g. Herriot® or New Focus®) of very long ca. 100 m path length, may allow direct detection of atmospheric gases down to the ng/l level [101–105]. Two major problems of long multipath length cells are the optical fringes that arise from scattering and chromatic aberration. The use of high precision astigmatic mirrors can reduce these problems. The improvement also allows the detection of multicomponent gases and may even allow isotopic selectivity. Currently, a 1500m path length cell involving the use of suitable prisms has been reported [106]. Direct detection of explosive vapor may be possible by using spectroscopic equipment fitted with multipass cells of such high passes.

Trace analysis by laser ablation atomic emission fluorescence spectroscopy [107] is another ultrasensitive technique, which may have application in the present area. The detection limit was 20 fg for sodium ion in pure water. Laser-induced fluorescence emission techniques are capable of detecting 10^4 to 10^5 and 10^5 to 10^7 atoms cm^{-3} with a continuous wave laser and pulsed dye laser respectively. Measurements of temporal variations of C_2 and C_3 radical densities have been demonstrated by using laser ablation of a graphite target in ambient helium gas [108]. There is thus a possibility of detecting ultratrace concentration of explosive vapor on personal belongings using a combination of laser ablation and fluorescence emission.

3. Conclusions

Direct detection of traces of explosives using instrumental analytical methods is explored. Most explosives are detected by the vapor they release and the low vapor pressures and concentrations of explosive vapor is often far below the ng/l level. There is a need for automated safe, non-intrusive, portable, low cost equipment that is more sensitive and selective for detecting traces of hidden explosives over periods of several seconds. The current approach that uses a series of processes through sampling, pre-concentration and then detection is too slow and involves high cost. A simpler and direct detection technique is required in the future and which will not only be used for aviation security but also for other public situations, such as in buses, trains, buildings, and subways. Installation of such devices at strategic locations and in the entrance portal would provide a strong counter-terrorism measure.

Since there is no single completely foolproof automated method currently available, some level of manual examination by a person is still needed. It is suggested that sealed metal containers that may interfere be removed for a manual or instrumental check. Unfortunately, there are limits to
such approaches as there is no way we can definitely predict what a terrorist’s explosive device will look like in the future.

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