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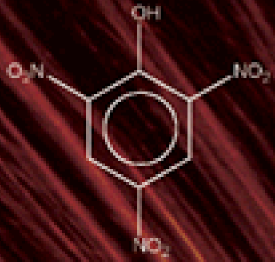

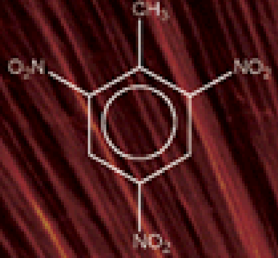

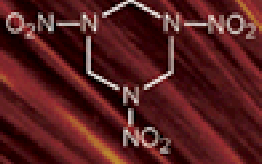

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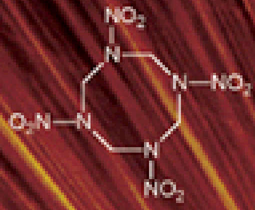

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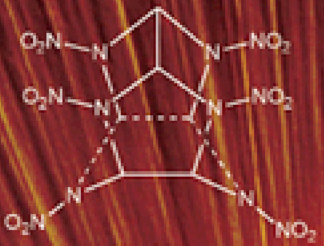

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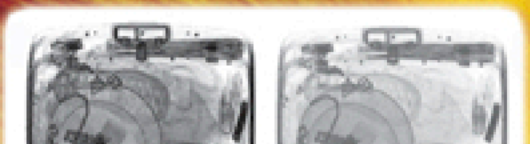

ASPECTS OF EXPLOSIVES DETECTION

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Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2009

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British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

ISBN: 978-0-12-374533-0

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Printed and bound in Great Britain
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PREFACE

Detection and quantification of trace chemicals are a major thrust of analytical chemistry. In recent years, much effort has been put into developing detection systems for priority pollutants. Less mature are the detections of substances of interest to law enforcement and security personnel: narcotics, chemical agents, and explosives. This volume will discuss the detection of the latter, emphasizing explosive detection both because of its public importance and because it has undergone remarkable developments in the last decade.

Terrorist events in the late twentieth century, for instance, airplanes blown out of the sky, such as PanAm 103 over Lockerbie and UTA 772 over Africa, and attacks on U.S. cities, for example, on the World Trade Center in New York in 1993 and the Murrah Federal Building in Oklahoma City in 1995, emphasized the danger of concealed explosives and led to calls for new technology to protect the public. However, because most explosives release little vapor, it was not possible to detect them by technology widely used on other organic substances. After PanAm 103 was downed over Scotland, the U.S. Congress requested automatic explosive detection equipment be placed in airports.

Given the breadth of the field of explosives detection, we have had to be selective; nonetheless the group of distinguished contributors has dealt with a broad spectrum of the key technologies as well as some of the operational and legal issues. Many aspects of explosives detection, for instance, ultimate technical capabilities, operational tactics and limitations, are quite properly kept secret by government agencies. Particular care has been taken in the preparation of this work to ensure that no such material is improperly disclosed. This volume outlines the history of explosive detection research, the developments along the way, present-day technologies, and what we think the future holds. Written at graduate level and heavily referenced, we hope it will be of value and interest to practitioners, researchers, and students of this important and rapidly evolving subject.

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CHAPTER 1

THE DETECTION PROBLEM

M. Marshall *and* J.C. Oxley

Contents

1. EXPLOSIVE DETECTION TECHNOLOGY – THE IMPETUS

There has always been a need to detect the presence of threats. The classical threats from smuggled weapons and poisons remain, but new threats from explosives as well as from chemical and biological agents must also be considered. Threat must be defined rather broadly, to include both immediate threats, for example, a bomb on an airplane, and longer term threats, for example, smuggled drugs. To prevent explosions requires the detection of bombs, bomb makers, and bomb placers.

The functional components of a bomb are a control system, detonator, booster, and a main charge. Such threats can often be recognized from their shape. These can be viewed as bulk detection issues, historically addressed by imaging techniques such as sight or touch. Other threats may take no particular physical form and can only be recognized by their chemical composition. These are often trace detection issues, historically detected by the sense of taste or smell.

In modern times, many techniques have been investigated for the detection of explosives and illicit chemicals. The main impetus has been for military applications. For example, a great deal of work was carried out in the period 1970–1990 to develop rapid methods and instruments for battlefield detection of chemical warfare agents. There was the development of colored test papers (e.g., the M256 detection kit introduced into US Army service in 1978), the UK deployment of nerve agent-immobilized enzyme alarm and detector, and the production of early models of ion mobility spectrometers (IMSs) for identification of a range of chemical warfare agents (e.g., the Chemical Agent Monitor adopted by the UK Armed Forces in the late 1980s) [1]. Similarly, instruments for breath alcohol were developed to aid law enforcement officers in the fight against drunken driving [2], and a number of simple field tests and kits for the rapid screening of suspect illicit drugs [3] were produced.

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Table 1 Terrorist attacks influencing US explosive detection efforts

Date	Target	Method	Killed	Wounded
1983	US Marine Barracks, Beirut, Lebanon	~5000 kg bomb	241	
1988	Pan Am 103, Lockerbie, UK	~400 g bomb	269	
1993	World Trade Center, New York, USA	~500 kg bomb	6	~1000
1995	Murrah Building, Oklahoma City, USA	~2000 kg bomb	168	~1000
1996	Khobar Towers, Saudi Arabia	~7000 kg bomb	19	Hundreds
1998	US Embassies in Kenya & Tanzania	~1000 kg bombs	224	Thousands
2000	USS Cole, Yemen	~500 kg bomb	17	39
2001	World Trade Center, New York, Pentagon & Pennsylvania	Hijack & crash airliners	~4000	Thousands

Throughout the latter part of the twentieth century the UK experienced a ferocious campaign of Irish terrorism, Israel was the target of frequent Palestinian bombings, and Spain suffered from attacks by Basque terrorist group ETA (an abbreviation in the Basque language: "Euskadi Ta Askatasuna", which translates into English as "Basque Homeland and Freedom"). In Eastern Europe, Chechen terrorists conducted a number of horrific attacks in Russia, whereas in Asia numerous terrorist bombings took place in Sri Lanka. At the same time, attacks against US interests continued around the world (Table 1).

Although both the UK and US military had supported some developmental work on explosive detection, the event that launched new efforts in explosive detection was the downing of Pan Am Flight 103 over Lockerbie on 21 December 1988. Shortly afterward the US Congress passed the Aviation Security Improvement Act (Public Law 101–604), directing the Federal Aviation Administration (FAA) to set standards for acceptable detection (covering not only the type and amount of explosive, but also sample throughput) and "certify" instruments that met those standards. Other countries also mounted similar programs, notably the UK and Israel.

The investigation into the sabotage of Pan Am Flight 103, which left 269 dead, indicated that the explosive used was Semtex H, a plasticized mixture of hexahydro-1,3,5-trinitro-s-triazine and pentaerythritol tetranitrate, and that the amount used was half the quantity that the fledgling technique of Thermal Neutron Analysis (TNA) was designed to detect. Although the placement of the explosive device was fortuitous (from the terrorists' point of view) and the suitcase had not been screened by TNA, this event killed the TNA prototype program.

Progress toward setting certification standards was slow so that in 1991 the Office of Technical Assessment was quite critical of the FAA's efforts [4, 5]. One of the FAA's responses was to create the first of many National Research Council committees to review and advise [6]. By 17 July 1996, when TWA 800 crashed taking off from New York, one system, the InVision CTX 5000, had obtained certification but appeared nowhere near deployment. The crash of TWA 800 and the accompanying suspicion that it was an act of terrorism changed the paradigm. Congress mandated deployment of non-certified detection systems and, more importantly, supplied the funding to support their purchase. The influx of money provided by Congress spurred the industry, which had previously only dabbled in explosive detection, to spend serious money on research. Furthermore, the terrorist attacks on US soil on 11 September 2001 made the threat sufficiently real to the American public that stringent security measures, once thought to be intolerable, could be put in place. The ensuing Afghanistan and Iraq wars provided a massive increase in government funding for explosive detection and defeat. Further impetus was provided to research in the UK by the attacks against public transport in London in July 2005 and threats in the summer of 2006.

2. THE PROBLEM

In considering detection issues, we need to find ways of narrowing down the scope so as to focus on questions that can be addressed and solved in practice. This involves making some assumptions about what a terrorist or other bomb maker might do and why they might do it.

The problem of threat detection can be considered on several different axes, as follows:

1. the malefactors;
2. the location – airports, public buildings, vulnerable high-value facilities;
3. the target – airplanes in luggage, in cargo, on people; and
4. the threat – weapons, drugs, explosives, bombs.

We can reasonably divide such malefactors into the following four groups: (1) state-sponsored actors; (2) non-state-sponsored actors; (3) criminals; and (4) mentally disturbed or immature persons. Each of these groups has individual characteristics that impinge on our strategy for bomb detection. However, each also requires the same basic four requirements, namely, motivation, knowledge, capability, and access.

Criminals and mentally disturbed or immature persons are both likely to be limited by the availability of materials and knowledge. In addition, criminals are quite likely to be more susceptible than the other groups to deterrence by visible and effective security measures. Thus, the first two groups – state-sponsored actors and non-state-sponsored terrorists – are the main threats on which explosives detection needs to focus. Unfortunately, this conclusion implies the need for detection of military, commercial, and improvised explosives and does not greatly help in narrowing down the issues.

The geographical location, such as an airport or building, whether the threat is on (or in) people or objects, the target mobility, and whether the target is moveable or fixed are all factors that impose constraints on the detection techniques employed and influence the operational deployment. For example, high-energy X-rays might be used to screen baggage containers but most certainly could not be used to screen thoroughbred racehorses. In many instances, the location and nature of the target will be the predominant factor in choosing a detection strategy. This is a multidimensional problem. The issue needs to be viewed as a whole; different approaches are needed depending on the scenario, and what works in one arena may be operationally impractical in another. For example, the installation of security screening and explosives detection systems at airports has had significant physical impacts in terms of the space required for equipment and also upon the flow of passengers through facilities. Quite detailed studies of traffic flows need to be conducted to ensure that security procedures do not impair the overall function of a facility. Such considerations are of course much easier to resolve in new buildings when the requirements can be built into the design, as opposed to existing buildings where modifications can be costly and difficult.

Related to the issue of threat detection is that of threat resolution. We can distinguish the following three types of positive detection: (1) false alarms where an innocent substance is incorrectly identified as a threat; (2) innocent detections where a threat substance is correctly identified but is not a threat, for example, traces of explosive on members of the security forces or other persons who legitimately work with explosives; and (3) genuine threat detections. This implies a need for an understanding of the environment, that is, what background levels of target species may be present in the public environment from legitimate activities, and what potentially interfering species may be present. Background surveys to answer these questions would assist in the difficult decision as to where to set alarm levels for instruments. And, of course, operators need a plan and a system for resolving alarms when they occur.

A general issue is the need to design detectors against a specific set of threat scenarios or target materials. It is important not to be driven by the technology but to address the operational requirement by whatever means is most effective. An explosives trace detector is unlikely to be the right solution if the threat is from smuggled knives.

Human factors need to be properly considered in the design and application of any detection system. Studies have shown that explosive detection systems generally perform less effectively in realistic field trials than in laboratory tests and that one of the biggest causes of this shortfall is failure to properly consider the operator/system interface.

3. DETECTION TECHNOLOGIES

Apart from explosives there is a great deal of interest among law enforcement agencies in both the detection of caches of illegal drugs and in determining whether a person has taken an illegal drug. There is also a medical requirement for the diagnosis of unconscious patients admitted to hospital emergency rooms where treatment depends on diagnosis and delay may be fatal. Typically, this latter requirement is met by laboratory analysis rather than field portable detectors. In the drug field there are potentially many thousands of possible drugs of abuse, whereas in the explosives field there are also theoretically very many potential threat materials. It is one thing to design an instrument to detect a single compound with great sensitivity, selectivity, and speed, but quite a different proposition to achieve the same performance against a range of compounds, particularly if they have rather disparate characteristics. And, of course, the example of roadside breath testing for alcohol demonstrates that the technical challenges can be substantial even in the single-compound scenario.

If we consider equipment for drug detection, outside the hospital scenario, it is likely to be required to be portable so that it can be used at crime scenes, to be sufficiently robust, safe, and easy to operate so that it can be deployed with individual police officers, to have adequate sensitivity and selectivity so that false positives and false negatives are avoided, to provide rapid results and to operate in a way that does not infringe subjects' civil rights (see Chapter 12). Given that any results are likely to be used in court proceedings, the methodology must be subject to thorough scientific peer review and validation. The techniques used must be open and susceptible to ready explanation. Finally, the technology must be affordable so that it can be deployed on an operationally useful scale. Many of these same requirements also apply to portable explosives detectors for use by either law enforcement officers or military forces engaged in anti-terrorist operations.

Imaging techniques such as radiography are quite good for recognizing bombs either visually or by computer-aided image recognition, but as they are not particularly sensitive, they will only detect suspect items of a certain minimum size. And, of course, the imaging equipment does have to look at the right thing, which may also be disguised to avoid recognition.

Detection of explosives is divided into "bulk" and "trace" technologies. Bulk detection looks for a mass with certain properties considered indicative of an explosive. High nitrogen and/or oxygen content and high bulk density are the properties usually targeted. Naturally, there will be explosive compounds that do not match these target characteristics, for example, triacetone triperoxide; and there will be innocuous materials that do, for example, sausage. In detecting the presence of an explosive compound at trace levels, the general approach is to look for a specific chemical from a library of target compounds rather than for a general property. This means that the probability of false alarm is significantly lower than for bulk detection techniques, which are generally based only on typical properties. However, a positive trace detection provides no spatial information, is limited to the explosives provided in the library, and makes no immediate allowance for terrorist innovations. A positive detection may also be misleading. The example that comes to mind is the reported positive detection on the wreckage of TWA flight 800. In that case, it was explained that explosives had been present in the aircraft many days earlier for purposes of a training exercise but that none were present upon takeoff. In theory, many chemical detection schemes should be applicable to trace detection of explosives, but the realities of explosive detection require a degree of rapidity and robustness that limit the type of useable instrumentation.

To date, only two technologies have reached the original goal of "certification", namely, X-ray computer tomography (CT) in 1996 and X-ray powder diffraction coherent Compton scattering in 2004. In fact, since 1996 this has not been a requirement for deployment. The FAA/Transportation Security Agency (TSA)/ Department of Homeland Security (DHS) now use the term Explosive Detection System (EDS) for instruments that have attained certification.) It is not an accident that both EDSs are bulk detection techniques. Trace techniques have the drawback both of being limited to an input library and of the need for some "trace" of the explosive to be available to the detection equipment.

Probably the oldest need for trace detection was for the detection of poisons. Food tasters fulfilled that role, as did canaries when used by miners to warn of poisonous atmospheres underground. In more recent times, society has required the detection of other chemicals. Often a trained dog meets that need. Canine olfaction will be discussed in Chapter 3.

Generally, trace techniques are based on matching some chemical property of the molecule in the detector to a library of properties of targeted threat materials. This should result in lower false alarms than bulk detection but requires constant expansion of the instrument library as the threat changes. Nuisance alarms (detection of background levels of explosive where the threat quantity is not present) are high, and malicious contamination could result in denial of service. Unlike bulk detection techniques, trace detection offers no spatial or quantitative information to aid in decision-making. A typical technique involves thermally driving a sample into a detector. Samples with low volatility, for example, nitrocellulose and black powder, are lost at this point – a missed detection or false negative. After the sample components have been separated, a number of detectors may be used. Major problems with trace detection are as follows: (1) the collection of vapor or particulate is inefficient; (2) it is difficult to obtain the sample to the detector; and (3) countermeasures are obvious.

Although trace detection has its drawbacks, a vast number of applications, other than explosive detection, support its continued development [7]. In the laboratory environment, the most sensitive detection instrument is the electron-capture detector (ECD). The ECD is sensitive to electronegative species such as nitro groups and chloride. This detector is usually connected to a gas chromatograph (GC) to provide separation of components. It was the use of this type of instrument that was envisioned when the International Civil Aviation Organization (ICAO) taggants were proposed. However, laboratory GC proved too slow for FAA requirements so that the first trace instruments to be fielded were the IMS and a chemiluminescence detector marketed as explosive detection system (EGIS) by Thermedics Inc. Technology for the EGIS was based on that developed for a laboratory analytical instrument – the Thermal Energy Analyzer. Thermedics developed an extremely fast GC to couple to the front end. Unfortunately, the detector required a vacuum pump, and the original system required frequent maintenance. The IMS is the instrument seen in most US airports since 11 September 2001. It is usually used as a backup for the metal detectors screening carry-on luggage and for the CT screening checked baggage. IMS is discussed in Chapter 9. It does not require a GC on the front end or a vacuum. Species are ionized and then separated in a drift tube by size. Like most trace detection instruments, it is set to detect only the FAA-required species. Although IMS is the state of the art as of 2006, mass spectrometry (MS) has so much potential that within this decade it may become the foremost technique in trace detection. MS offers much better discrimination than IMS but to date has poor sensitivity relative to IMS or chemiluminescence. Furthermore, in the past, MS was much too difficult to maintain. Now, sample introduction has been simplified, the whole instrument downsized, and separation of the ionized species can use a number of approaches, namely, quadrupole, magnetic sector, ion trap, time of flight, or ion cyclotron resonance (Chapter 8). JEOL introduced the direct analysis in real-time high-resolution, time-of-flight MS in 2005. It seems to the authors that this may revolutionize the field of detection. Another well-developed laboratory technique expected to emerge in field portable detectors is Raman spectroscopy. It offers the possibility of remote explosive detection. Development of specific polymers for detection has been sufficiently successful that it has already been commercialized and is discussed in Chapter 10.

Unlike trace detection, which requires an explicit library, most bulk detection techniques key on supposedly unique properties of explosives. Those supposedly unique properties are high density, high amounts of oxygen and/or nitrogen, and fast energy release. Unfortunately, it is the first two properties that are usually targeted, and there are a number of exceptions to these as characteristics of an explosive (see Chapter 2). Fast energy release would be a better indicator of an explosive than the other properties. Direct chemiluminescence [8] would be one possible way to detect this for some compounds, but to date the technique has not been sufficiently developed. In general, bulk detection schemes use characteristic emission or attenuated signal from a sample to identify explosives. Emission is usually elicited by bombarding the sample with particles or rays. Passive millimeter wave detection is an exception. That technique distinguishes the unique thermal energy of human flesh versus the lack of such from inanimate objects. Emission from a sample is usually the result of properties specific to a general class of explosive or drug.

Nuclear Quadrupole Resonance (NQR) has been successful for limited applications, but baggage with metal contents cannot be inspected; this is a serious practical limitation being addressed by current research. Although having some basic similarities to the well-established technique of nuclear magnetic resonance, NQR requires no external magnetic field. Splitting of the nuclear spin states is by electrostatic interaction of nuclear charge density with the electric potential of electron cloud. The nuclei to be detected must have a spin quantum number greater than or equal to one. This means that potentially ^{14}N, ^{35}Cl, ^{37}Cl, and ^{39}K could be targeted. Depending on the number of equivalent nuclei and their relaxation time, the number, properties, and sequence of pulses are adjusted; in addition, sophisticated signal processing and enhancement techniques are employed to improve the sensitivity of the technique. NQR provides detailed information about the chemical structure of materials and so is compound specific. This means that identification depends on matching the signals with a library of known threat materials with the concomitant disadvantage that materials not in the library, that is, new threats, are not immediately identified. Potential applications of NQR to the detection of both drugs and landmines have also been studied. The field is very active; Refs. [9–15] give a flavor. Interestingly, as we write, this technique is being fielded in the US on a test basis to screen shoes.

Another very active field of research is terahertz detection. This technology employs electromagnetic radiation in the frequency range from 3×10^{11} to 3×10^{12} Hz, that is, wavelengths of 1–0.1 mm, at the extreme of the far infrared spectrum. Development of improved radiation sources and detectors at the end of the twentieth century has enabled considerable progress to be made. Although absorbed when passed through substantial distances of air, terahertz radiation is only weakly absorbed by most non-conductive materials. This offers the exciting possibility of a technique that provides a chemically characterized image at moderate standoff distances [16–18].

Like NQR, coherent X-ray diffraction is compound specific and so requires libraries of threat materials for identification and detection. Because high density together with high nitrogen and oxygen content are characteristics of, but not unique to, explosives, false alarms tend to be higher than with trace detection; missed detections are also possible. Bulk detection has the advantage of gathering spatial and quantitative information. Positive detection means a device is present, not just trace contamination.

The requirements for an explosive detection system are set out in certification standards issued by the FAA/TSA/DHS. Key issues are as follows:

1. explosive detectability;
2. detection limits (lowest quantity detectable);
3. configuration of explosive (i.e., is sheet-explosive detectable);
4. probability of detection (P_{d}) and probability of false alarm (P_{fa}), that is, the receiver operation curve;
5. throughput;
6. vulnerabilities or susceptibilities to countermeasures;
7. robustness and maintenance;
8. operational ease of use;
9. costs, initial investment, maintenance, space requirements; and
10. alarm resolution.

In terms of bulk detection, X-ray (Chapter 6), specifically computer tomographic detection (Chapter 7), was the first to meet the FAA certification requirements. X-ray interaction with a material depends on the energy of the X-ray and the type of material. The X-ray may (a) transit without interference; (b) be absorbed giving energy, at low energy, to an electron (photoelectric interaction) or, at high energy, to an electron and positron (pair production); or (c) be scattered either coherently (Compton unmodified) or incoherently (Compton modified). Conventional X-ray scanners operate at low energies, that is, 50–75 keV. At such low energy, the important interaction is photoelectric absorption, which reduces the transmitted X-ray beam. (Absorbed X-rays are sometimes re-emitted as lower energy X-rays – X-ray fluorescence.) Below a few hundred keV, the photoelectric absorption cross-section increases rapidly with increasing atomic number (Z). Thus, transmitted X-rays are most sensitive to high Z materials (e.g., medical X-ray machines show high contrast for the calcium in bones but not between different types of soft tissues). In conventional airport X-ray scanners, the transmitted X-rays clearly differentiate between high Z (metal) and low Z (organic) materials. At all energies, the Compton scattering cross-section mainly depends on density and only weakly depends on atomic number. Thus, materials with low Z_{eff} are imaged by scattering, but not by transmission; high Z materials show up in both the transmitted and scattered image. (Z_{eff} is the effective atomic number, a combination of all contributing species.) Dual-energy X-ray takes advantage of the different degrees of discrimination. Using energies, for example, 75 and 150 keV, the difference between the photoelectric (sensitive to high Z_{eff}) and Compton attenuations (sensitive to both low and high Z_{eff}) yields information about density, average atomic number, and high-resolution two-dimensional images. The two-dimensional spatial resolution obtained using X-rays is much better than that achieved by nuclear techniques; but unless high-energy X-rays are used, X-rays do not have the penetrating power of the nuclear techniques.

To achieve the depth of penetration into a container, for example, cargo containers, the container must be interrogated with neutral species, such as neutrons or high-energy photons (high-voltage X-rays or γ-rays). Nuclear techniques (Chapter 5) encompass an alphabet soup of technologies. Most have in common the advantages of penetration power and determination of chemical information – detection of nitrogen or oxygen, usually high in explosives, or chlorine from the hydrochloride salts of heroin or cocaine. However, the advantages of nuclear techniques are offset by the disadvantages of high cost, large size, shielding requirements, resolution significantly worse than X-ray, and severe operational impact. Except for TNA, the techniques require a special accelerator to create neutrons or photons (γ-rays). The neutron beam is usually collimated; this wastes most of the neutrons. If a monoenergetic beam is used, a target material must be used, and this results in problems with heat loss and erosion. Neutrons (5–15 MeV) or γ-rays (1–6 MeV) have mean free paths on the order of tens of centimeters; thus, severe attenuation can occur in cargo. Complex discrimination algorithms must be used to compensate for cluttered background. Nuclei with which the neutrons collide inelastically are excited and return to their lower energy state by emitting a series of characteristic γ-rays. The lighter the nucleus with which a neutron collides inelastically, the greater the energy imparted to the nucleus and the greater the loss of energy from the neutron. This process is called "modulation". For most techniques, residual activation (e.g., neutron activation) is not a problem. Modulation is a problem for nuclear techniques. Modulated neutrons usually have diffused far from the incident beam before detection; thus, they give no spatial or timing information. Thermal (low-energy) neutrons produce an abundance of γ-rays that can overwhelm the detection of the γ-rays from the desired fast neutron interactions.

Many of the original puzzles and concerns considered before initial deployment of explosive detection equipment have not been resolved, but less than optimal solutions have had to be accepted. For example, an alarm is usually resolved by re-screening of the object, hand examination of the alarming item, or questioning of the owner. None of the presently fielded techniques address the need to determine whether a liquid threat material has been sealed in a bottle. There was a short period of time after the terrorist attacks of 11 September 2001 when people wishing to carry a bottle of liquid on board an airplane were required to take a sip of it to demonstrate it was innocuous. Since the threat from liquid explosives in the summer of 2006, much funding has been allocated for research into this problem. We can expect to see developments in this area, but as of this writing, liquids in airline hand baggage are limited to 100 ml bottles in a clear plastic bag.

Quality control on detection equipment presents problems from improvements and modifications to the original instrument to the question of how to check the performance of a deployed instrument. In an airport or seaport environment, screening of cargo remains an unsolved problem. In areas of conflict or terrorism, remote (standoff) detection remains a much sought-after goal [19–20].

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CHAPTER 2

EXPLOSIVES: THE THREATS AND THE MATERIALS

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Contents

1. DEVICES AND EXPLOSIVES

A bomb can be considered to contain four functional blocks, namely, a control system, a detonator, a booster, and a main charge. Although a simple ignition fuse can be used as a control system and timing device, the control system is usually more mechanical or electrical in nature. The detection of control systems may be visual, or by magnetometry, or by X-ray. It must be remembered that many of the items involved in the ignition system, that is, clockwork, batteries, or electronic circuitry, are commonplace in ordinary items, such as cameras, mobile telephones, and personal stereos, and are not unique indicators of the presence of a bomb. In fact, it is the presence of explosives that is the key indicator of a bomb.

In this chapter, we will consider some fundamentals of explosive technology, the properties of some common explosives, including any detection-related aspects, their availability, performance, and any feature that might lead a terrorist to choose one over another.

2. FUNDAMENTALS OF EXPLOSIVES

2.1. Usage of explosives

Large quantities of explosives are used every year. In the United States, for example, the annual consumption exceeds over 2 million tonnes. Most are used for commercial purposes and are ammonium nitrate-based formulations. There are less than a dozen chemical explosives that are manufactured in bulk quantities, and most of these were "discovered" in the 50-year period between 1850 and 1900. New explosives have been synthesized but optimization of the formulations takes decades and is very expensive. Consequently, any new material has to offer very significant advantages, either in terms of unique performance for military applications or in terms of cost and safety for commercial applications.

2.2. Detonation and deflagration

With proper initiation, chemical explosives (as opposed to mechanical or atomic explosives) undergo violent decomposition to produce heat, gas, and rapid expansion of matter.

The practical effect will depend on the speed at which the decomposition takes place as well as on the amount of gas and heat released. We can distinguish two important cases, as follows:

1. Chemical reaction proceeds through the material at a rate less than or equal to the speed of sound in the unreacted material. This is known as a "deflagration".
2. Chemical reaction proceeds through the material at a rate greater than the speed of sound in the unreacted material. This is known as a "detonation".

Both deflagrations and detonations can produce what a lay observer might describe as an "explosion". Nonetheless, a detonation is a special type of explosion with specific physical characteristics. It is initiated by the heat accompanying shock compression; it liberates sufficient energy, before any expansion occurs, to sustain the shock wave. The shock wave propagates into the unreacted material at supersonic speed, typically 1500–9000 m/s. We discuss the practical differences between the effects of detonation and deflagration in Chapter 11 on post-blast issues.

2.3. Primary and secondary explosives

Explosives are classed as primary or secondary. Typically, a small quantity of a primary explosive would be used in a detonator (known colloquially as a "cap"), whereas larger quantities of secondary explosives are used in the booster and the main charge of a device. This collection of explosives is known as an "explosive train" in which a signal (mechanical, thermal, or electrical) from the control system is converted first into a small explosive shock from the detonator, which in turn initiates a more powerful explosion in the booster, which amplifies the shock into the main charge.

Primary explosives are sensitive to modest stimuli such as heat, spark, or friction; application of the correct stimulus will lead to a detonation. The primary explosives used in detonators are typically extremely sensitive but not particularly powerful; common examples are mercury fulminate, lead azide, and lead styphnate. In principle, the heavy metals present in most primary explosives should be a good cue for detection; however, there are primary explosives that do not contain such elements.

It should be noted that there are modern detonators that are designed to function without primary explosives. These usually rely on an electrically generated shock to produce detonation in a small charge of a specially prepared and sensitive charge of a secondary explosive.

In general, secondary explosives cannot be caused to detonate without the input of a strong shock. For example, they do not burn to detonation if unconfined. Nonetheless, there are substantial and practically significant differences in sensitivity between the various common secondary explosives. Those secondary explosives, which can be caused to detonate using only a cap, that is, a detonator, are termed "cap-sensitive". Some common military explosives are cap-sensitive; indeed, some are specifically formulated to achieve this particular property. Other military explosives, particularly those intended for use in large main charges, are chosen and formulated to be relatively insensitive, requiring a powerful booster to bring them to detonation. Similarly, the commercial explosives used in bulk applications are generally formulated to require a booster.

The requirement for an explosive train, that is, a primary explosive to initiate the secondary explosive, is a safety feature. In the past, people wishing to illegally use explosives usually had to steal the detonators (e.g., Timothy McVey). Consequently, the effective control of access to detonators has been widely regarded as a key public safety measure by many governments and law enforcement agencies. However, recently, triacetone triperoxide (TATP) has been used as the primary explosive (e.g., Richard Reid's shoe bomb) and TATP is readily, although hazardously, synthesized from acetone, hydrogen peroxide, and acid.

2.4. Energy release, explosive output, and critical diameter

For most explosives, where a small volume of a solid is converted into a large volume of gas, a good approximation of the energy release ΔG is dominated by the enthalpy change ΔH: $\Delta G = \Delta H - T\Delta S$, where ΔH is given by the heat of formation of the products minus the heat of formation of the reactants [see Eqs. (1) and (2)]. Hence, it is desirable that chemical explosives have as positive a heat of formation as possible.

$$\mathrm{RDX: C_3H_6N_6O_6 \rightarrow 3\,N_2 + 3\,H_2O + 3\,CO} \tag{1}$$

$$\mathrm{TNT: C_7H_5N_3O_6 \rightarrow 1.5\,N_2 + 2.5\,H_2O + 3.5\,CO + 3.5\,C} \tag{2}$$

To maximize the working fluid (i.e., gas) generated in an explosion, chemical explosives are designed to be dense and to have high oxygen and/or nitrogen content. It is this requirement for gas formation that favours explosives having C, H, N, and O atoms. To react with sufficient rapidity, an explosive must contain its own source of oxygen.

Energy release and gas formation are not unique to detonation. Detonation is distinguished from combustion by its rapidity. The energy released by an explosive is not dramatic; detonating dynamite produces about 5 kJ/g, which is around/approximately one-tenth of the amount produced by burning petroleum. Much more important, in terms of functioning as an explosive, is the rate of heat release in Joules per second, that is, Watts. Detonating high explosives produce around 10^{10} W/cm^3. Detonation is so rapid that external oxygen, for example, in the air, does not contribute to the initial heat-producing reaction. The oxidation is sufficiently rapid to support the detonation wave only if the explosive has oxygen readily available.

For optimal energy release, an explosive should convert all its atoms into gaseous products. For most explosives this means having sufficient oxygen to convert every H into H_2O and every C into CO, for example, RDX [Figure 1, Eq. (1)]. However, many explosives are oxygen deficient, for example, TNT [Figure 1, Eq. (2)]. Although not as “powerful” an explosive as RDX and HMX ($C_4H_8N_8O_8$), TNT is a very effective explosive, despite being oxygen deficient.

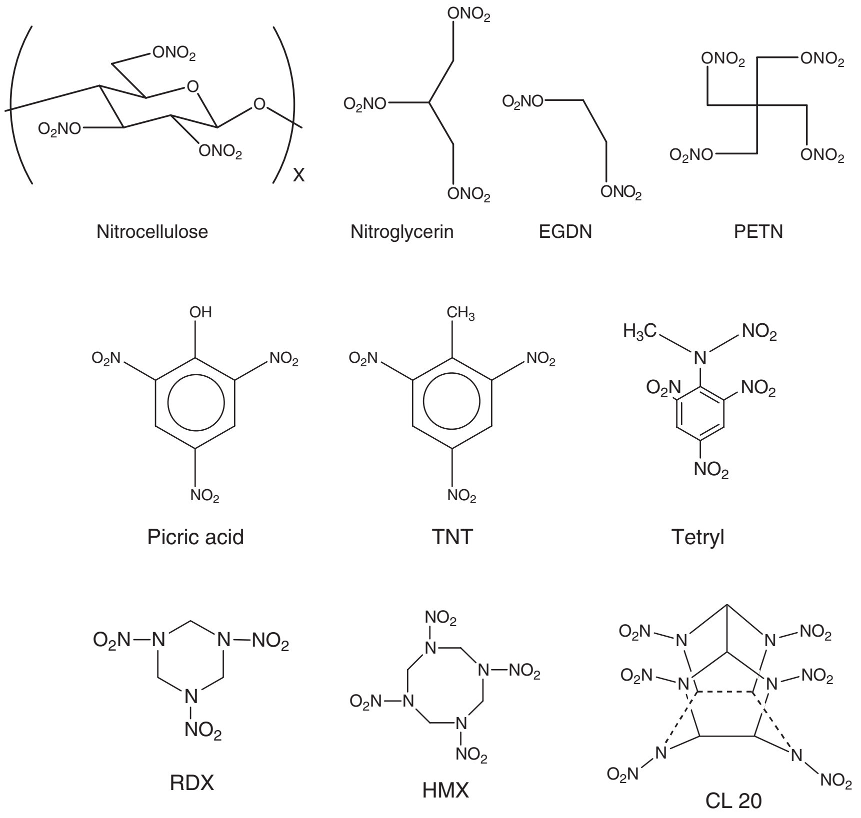


Figure 1 The common military explosives.

Apart from nitroglycerin (NG) and ethylene glycol dinitrate (EGDN), which are viscous liquids, the explosives shown in Figure 1 are powders, whose physical properties differ from other organic chemicals only by their exceptionally high density. Density is a major factor in determining the performance of an explosive (see Table 1). It determines the number of atoms per unit volume, which can be converted to gas. Density also determines how close the product gases find themselves to each other. The closer they are, the higher the repulsive forces between them and the faster they move away from each other.

Thus, as a general rule, military explosives have a density greater than $1.6\ g/cm^3$ and high oxygen and nitrogen content. Bulk detectors key on these properties. However, explosives can detonate at densities significantly lower than crystal density, and there are exceptions to the high oxygen (e.g., lead azide) or high nitrogen (e.g., TATP, see Figure 2) rule. Table 1 lists the chemical and detonation properties of some relevant explosives.

In addition to the requirements for rapid and substantial energy release, explosives must have a sufficiently large diameter to sustain detonation. Otherwise, rarefaction waves bouncing back from the charge edge reduce the pressure and temperature in the immediate area sufficiently that the total energy is not released. This minimum diameter is known as the "critical diameter" and is an important practical characteristic as well as another significant safety feature in the application of explosives. Thus, ammonium nitrate and fuel oil (ANFO) does not function well on the briefcase scale. Its use is reserved for large car or truck bombs. On the other hand, military explosives like C-4 (91% RDX) or Semtex H (85% RDX/pentaerythritol tetranitrate (PETN)) detonate in Gram-scale devices.

It is somewhat confusing that the term "critical diameter" is also used by those interested in the potential of an energetic material to undergo thermal runaway. Because, by definition, the energetic material releases heat when it decomposes, it has the potential to increase its local environmental temperature. Depending on the decomposition kinetics of the material, at some "critical dimension" the charge can self-heat to catastrophic reaction. This can be referred to in terms of the critical diameter or, more often, in terms of the initial environmental temperature that allows this scenario, the "critical temperature".

2.5. Chemistry of some common explosives

The chemical structures of some common military explosives are shown in Figure 1. These include the nitrate esters such as nitrocellulose (NC), NG, EGDN, and (PETN); nitroarenes such as trinitrotoluene (TNT, $CH_3—C_6H_2(NO_2)_3$), picric acid ($HO—C_6H_2(NO_2)_3$), and 2,4,6-trinitrophenylmethylnitramine (tetryl); and nitramines such as RDX ($C_3H_6N_6O_6$), HMX ($C_4H_8N_8O_8$), and hexanitrohexaazaisowurtzitane (CL—20). Of these, only CL—20 is "new", that is, less than 50 years old [3]. Mixtures of oxidizers and fuels, such as AN and FO (called ANFO), are also secondary explosives.

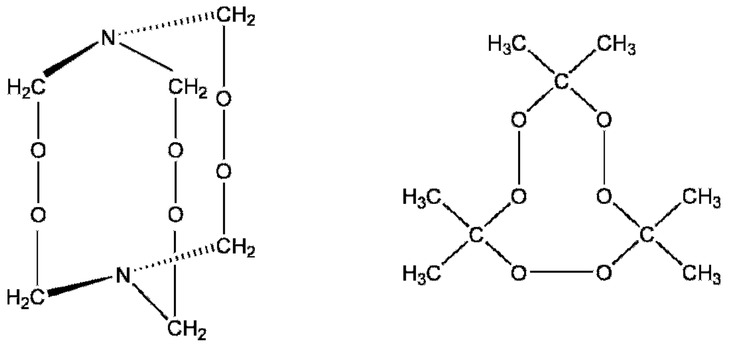
These differ from the secondary explosives shown in Figure 1, in that AN-based explosives are generally so insensitive that in addition to a "blasting cap", a strong booster is also required for initiation.

Table 1 Chemical and detonation properties of some explosives

Explosive	Density (g/cm^3)		Detonation velocity		% TNT Trauzl[†]	Nitrogen (%)	Oxygen (%)
	TMD	Bulk	$mm/\mu s^1$	g/cm^3			
Nitromethane	1.1	(liquid)	6.3	1.1	138	22.9	52.3
PETN	1.76		8.4	1.8	174	17.7	60.7
Tetryl	1.73		7.7	1.6	144	24.4	44.6
Picric acid	1.77		7.5	1.7	105	18.3	48.9
TNT	1.65		6.9	1.6	100	18.5	42.3
RDX	1.82		8.6	1.8	160	37.8	43.2
HMX	1.96		9.1	1.9	160	37.8	43.2
NG	1.6	(liquid)	7.7	1.6	185	18.5	63.4
AN	1.72	0.8	3.7	1.5	60	35.0	60.0
TATP	1.2		5.3	1.2	88	0	43.2
HMTD	1.6		5.1	1.1	60	13.5	46.1
UN	1.59		4.7	1.2	95	34.1	52.0

AN, ammonium nitrate; HMTD, hexamethylene triperoxide diamine; HMX, $C_4H_8N_8O_8$; NG, nitroglycerin; PETN, pentaerythritol tetranitrate; RDX, $C_3H_6N_6O_6$; TATP, triacetone triperoxide; TNT, trinitrotoluene; UN, urea nitrate; TMD, theoretical maximum density.

[†] TNT equivalence measured by the Trauzl (lead block expansion) test. Data compiled and adapted from Refs [1, 2].



HMTD TATP

Figure 2 Peroxide explosives.

2.6. Military explosives

Military explosives are required to meet stringent criteria because apart from a requirement for high performance, the military needs to be able to safely store them for decades, transport them anywhere from the poles to the equator, handle them under battlefield conditions, and still have them fully functional. In addition, availability of raw materials, ease of manufacture, and cost are important factors. Most candidate explosive compounds do not meet all these requirements.

Military explosives typically contain only the atoms of carbon (C), hydrogen (H), oxygen, (O), and nitrogen (N). The reason for this is found in the performance of these chemicals. This is usually achieved in military explosives by having oxygen carried by NO_2. That functionality may be attached to oxygen ($O—NO_2$) as in the nitrate esters (NC, NG, or PETN) or to carbon ($C—NO_2$) as in the nitroarenes (TNT, picric acid, or tetryl), or to nitrogen ($N—NO_2$) as in the nitramines (RDX, HMX, or CL—20). Although these explosives undergo thermal decomposition by several routes, most release some NO and NO_2, enough to be detected by chemiluminescence. Furthermore, nitrogen dioxide has various physiological consequences: nitrate esters are vasodilators and nitroarenes are toxic. However, the first concern of most explosive handlers is not toxicity but explosivity.

Today the most common military explosives are HMX, PETN, RDX, and TNT. In terms of performance, the ranking would be HMX > RDX > PETN > TNT. However, "good" explosive performance depends on the end objective. The military generally want to fragment or shatter metal. For that application, the pressure jump associated with the shock front is important; performance is measured in terms of detonation pressure or velocity (at a given packing density). For the mining industry, the objective is to move rock and dirt; heaving action is important, as(means jaise ki) is limited, controlled fragmentation. For that purpose, explosives with relatively slow detonation velocities, such as ANFO, are better than military explosives.

Ranking related to blast pressure of TNT is termed "TNT equivalence". This value cannot be uniquely defined because in a single shot the TNT equivalence calculated from overpressure and from impulse will differ and all values will vary with distance from the charge. Values shown in Table 1 probably vary by at least ±30% depending on the physical configuration of the test explosive. In general, materials with TNT equivalence less than 50% are not considered explosives; they may be stored or shipped in large quantities and without special security. However, it is worth considering that 5000 tons of a material with a TNT equivalence of 20% could still result in a blast on the order of 1 kiloton TNT.

2.7. Plastic explosives

Plastic explosives contain one or more of the explosives listed above, moulded in an inert, flexible binder. Because powders do not readily hold a shape and TNT is the only common melt-castable explosive, most of the explosive powders (RDX, HMX, PETN, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)) are plasticized to make a mouldable material, for example, C-4, Semtex H, PE4, sheet explosive. A variety of plasticizers are added, but the maximum level is usually 10–15% because most plasticizers are inert and would degrade explosive output. Plastic explosives were originally developed for convenient use in military demolitions but have since been widely used in terrorist bombs. For detection techniques that rely on vapour signatures, such as canine olfaction, it is worth considering that the plasticizer is much more volatile than the explosive component.

2.8. Commercial explosives

Dynamite is no longer a commonly used explosive in either North America or Western Europe. As first patented by Alfred Nobel in 1867, NG was adsorbed onto an inactive kieselguhr base; this is known as guhr dynamite. Later dynamites used wood meal, charcoal, sugar, and starch as inactive bases or active bases, such as nitrate salts or NC (collodion cotton); the latter type are known as gelignites or blasting gelatine. Early dynamites, which contained only NG, froze in winter weather. When they were frozen, they were less sensitive to initiation, but the intermediate state, half frozen/half thawed was quite sensitive. Furthermore, thawed explosives tended to exude NG, which is a danger with any old dynamite. A low-freezing dynamite was developed by nitrating a mixture of glycerine and ethylene glycol, but this was not widely used until the late 1920s when the production of ethylene glycol for anti-freeze made the precursor chemical relatively inexpensive. There have been many different formulations of dynamite, each tailored to a specific application. Table 2 gives a simplified version of some of these different varieties. Today the nitration is usually performed on a mixture of glycerine and ethylene glycol to yield NG and EGDN, but there is a version of dynamite containing no NG and only EGDN.

As of this writing, there is only one commercial manufacturer of dynamite in the United States, Dyno Nobel (Carthage, MO). For most commercial purposes, dynamites have now been replaced by AN-based formulations, which offer a better combination of performance, safety, and cost.

In addition to the main ingredients, dynamites may contain a variety of other ingrediients, usually at less than the 3% level: clear wheat, cob meal, balsa, starch,

Table 2 Example dynamite formulations

	Straight (%)	Ditching (%)	Extra (%)	Blasting gelatine (%)
NG/EGDN	40	40	20	90
NC	1	1	<1	7
AN (coarse and fine mix)	15	30	70	–
$NaNO_3$	30	20	–	–
Wood pulp	6	8	–	<1

AN, ammonium nitrate; NC, nitrocellulose

cork, guar gum, urea, and calcium stearate. Chalk is used in all formulations as an anti-acid, and if beads are added, they are phenolic rather than glass, which can cause friction problems. There is also "permissible" dynamite. Permissible explosives ("permitted explosives" in UK parlance) incorporate a chemical, often sodium chloride, to lower the flame temperature of the blast, thus, making it safer for use in underground coal mines where methane may be present in the atmosphere.

Modern commercial explosives are generally mixtures of AN and fuel. These mixtures do not have the high detonation velocity exhibited by military materials, but they do detonate satisfactorily. The key to their performance is an intimate mix of the oxidizer (AN) and fuel, such as in the formulation ANFO, where the fuel is allowed to soak into the AN. Often a dye is added as a safety marker to commercial ANFO, as otherwise there is no obvious visible difference between the explosive and neat AN. The latter is generally classed as an oxidizer and can be freely transported.

Owing to their intrinsic safety and inexpensive nature, AN/fuel formulations have almost completely replaced dynamites as the mining explosive. As a result, they are by far the most widely used explosive. AN formulations are sold as AN prill or solution, ANFO pre-mixed, AN water–gel (although this is becoming obsolete); AN emulsions, either in cartridges or as bulk material that is brought to the site and loaded directly from the truck to the borehole; and heavy ANFO (ANFO folded into an AN emulsion). AN formulations usually require the use of a high explosive booster, but powerful and cap-sensitive formulations can be prepared.

The makeup of the AN industry in the United States is rapidly changing, due in large part to the perceived security threat of AN. In 1996, there were 16 companies at 22 locations making solid AN. The annual production capacity was about 6 million tonnes. In 2005, there were only seven companies in 11 locations making solid AN. Of those, only two were making the high-density AN, which is used exclusively for agriculture. US use in 2005 was about 1 million tonnes of high-density AN and 2 million tonnes of low-density AN (for explosives), but the capacity has remained about the same as 1996.

2.9. Propellants

In contrast to high explosives that are intended to detonate, propellants are primarily intended to deflagrate. Under extreme conditions, however, some propellant compositions may undergo detonation. Although there is a wide range of propellant compositions, the commonest materials, and those that are likely to be encountered in improvised explosive devices, are the smokeless powders. These are widely used in gun propellants for small arms and shotguns. Such materials have been frequently used in pipe bombs and similar devices. The material is confined in a sealed container; after ignition, the hot gases produced cause an extreme buildup of pressure, leading to an explosion. Smokeless powders are based on NC, which may be combined with NG and various other ingredients, such as plasticisers, stabilisers, and burning rate modifiers. Nitrotoluenes may be incorporated as energetic plasticisers in some instances. Smokeless powders that have only NC as the energetic ingredient are referred to as "single-base" propellants, whereas those that also contain NG are known as "double-base" propellants. The polymeric nature and high molecular weight of NC lead to an extremely low vapour pressure. In general, it is a difficult material to detect other than by contact sampling, for example, swabbing of the exterior of containers contaminated with traces of the propellant. In practice, only smokeless powders containing a significant proportion of volatile constituents, such as NG or nitrotoluenes, are easily detected either by vapour detectors or by detection dogs.

2.10. Terrorist use of homemade explosives

During the period 1969–2000, Irish terrorists carried out many thousands of bombings. Initially, these involved commercial explosives or homemade materials based on sodium chlorate, nitrobenzene, or AN. In 1972, the UK and Irish governments introduced stringent controls on the sale of sodium chlorate, nitrobenzene, and pure AN throughout the island of Ireland. Indeed, pure AN fertilizer was replaced by an agriculturally acceptable, but safer material, adulterated with either calcium carbonate or more commonly dolomite, referred to as calcium ammonium nitrate. Nevertheless, large fertilizer-based bombs were used in the 1990s in attacks in Northern Ireland (e.g., at Omagh) and various other British citiesm including London, Manchester, and Birmingham. Approximately 500 kg was used at St Mary le Axe in April 1992 and about 1500 kg at Bishopsgate in April 1993. In the same period of time, the Spanish terrorist group ETA used homemade ammonal, a mixture of AN and aluminium powder, to devastating effect on a number of occasions.

In other countries, AN has been used less frequently in terrorist bombings; a notable exception was the bombing of the Murrah Federal building in Oklahoma City (April 1995). This event generated concern in the United States regarding the explosive nature of AN. Because AN explosives are easily prepared and the Oklahoma City bombing was so devastating, a number of research programmes aimed at desensitizing commercially available AN were developed. Sales restrictions were also considered. The restriction would have to be on either AN or other suitable oxidizer because any combustible non-explosive can be used as fuel: rosin, sulphur, charcoal, ground coal, flour, sugar, oil, or paraffin. To date, the terrorists have used FO (the commercial fuel), icing sugar (little associated odour), or aluminium (added heat release). When the combustible added to AN is explosive in its own right, for example, nitromethane or hydrazine, a more powerful material is obtained, for example, AN with hydrazine has a detonation velocity of 6800 m/s.

2.11. Peroxide explosives

The peroxide explosives TATP and hexamethylene triperoxide diamine (HMTD) have become popular with terrorists because they are easily prepared from readily obtainable ingredients, although the synthesis is fraught with danger (Figure 2).

Although they do not contain NO_2 groups, the O–O bond is a source of oxygen available for potentially rapid self-oxidation and explosion. Although neat hydrogen peroxide (H_2O_2) is detonable, most of the common industrial peroxides, which contain only one O–O functionality per molecule, have insufficient oxygen to gasify the majority of the C and H atoms in the molecule. These peroxides are not usually considered explosives, even though some have a reported "TNT equivalence". As TATP and HMTD contain three peroxide linkages per molecule, their explosive output is much higher than most organic peroxides. TATP is estimated as 88% and HMTD as 60% of TNT blast strength.

The unusual danger to public safety in the case of peroxide explosives is not their explosive performance but their ease of initiation and the ease with which terrorists have acquired and used the materials for their synthesis, although synthesis is actually quite hazardous. Both TATP and HMTD are classed as primary explosives. For example, Richard Reid, the would-be shoe bomber, used TATP as part of his firing train in the attempted bombing of a US airliner in December 2001, or the use of HMTD in the London bombings of 7 July 2005. HMTD was also one of the materials prepared and carried over the US/Canadian border in December 1999 by Ahmed Ressam as the ingredient for the initiators of his devices.

Hydrogen peroxide at the correct concentration is also detonable. It has been used extensively in propellant applications. Recent events suggest that terrorists are aware of its potential. It has been confiscated in an aborted terrorist bombing in Karachi (15 March 2004), thousands of gallons of it were confiscated in Jordan the same year, and it was allegedly involved in the abortive bomb attacks in London on 21 July 2005 [4]. Fortunately, the technology of such explosives is not quite as simple as it might first seem and attempts to use them by several terrorist groups have failed.

2.12. Exotic explosives

Terrorists do not have the same stringent requirements for safety and storage as military organizations or commercial enterprises. Their primary requirement is that the components be readily available. Exotic explosives include chemical explosives not suitable for use by the military or industry. The unsuitability is generally due to extreme sensitivity or lack of stability. This is the case for the peroxide explosives, which were examined and rejected by the US military in the early twentieth century. Exotics also include "improvised" explosives, detonable formulations malefactors can prepare. Recently discovered energetic materials would also fit in this category. They may have been synthesized in a government or academic laboratory specializing in explosive synthesis, but the achieved increase in performance or insensitivity is not sufficient to justify the investment in scale-up, formulation, safety testing, and manufacture [5–7].

Agrawal [8] has recently reviewed progress in the synthesis and formulation of new high-energy materials , concluding that the most promising in terms of enhanced thermal stability are TATB, tetranitro dibenzo-1,3a,4,4a-teraazapentalene, and 2,6-bis (picryl amino)-3,5-dintropyridine. Another new explosive that is currently under intensive study is 1,1-diamino-2,2-dinitroethylene (FOX-7) [9, 10] Although it is possible that some of these unusual explosives may be encountered in specialized commercial equipment, for example, oil-well perforators or advanced military munitions, they are not normally an issue for explosives detection systems.

2.13. Energetic salts

There are many oxidizer salts that potentially might be used to make composite explosives (Table 3) when mixed with suitable fuels. The classical example is of course the use of saltpetre, that, potassium nitrate, in black powder, although this is not a high explosive, but a low one, that is a propellant. Another example is the use of sodium chlorate and sugar to produce explosive mixtures. Potassium chlorate is one of the few, besides AN, that is readily available in bulk. Its use has long been recommended in the "do-it-yourself" literature for small, anti-personnel devices, but in Bali on 12 October 2002, terrorists demonstrated its potential in large devices. Chlorate, like other salts, has a very low vapour pressure, a detection problem for dogs as well as for any equipment relying on vapour. Some other potential oxidizers in Table 3 have not been demonstrated in detonable mixtures, but one suspects that with the appropriate fuel at a large enough charge and with sufficient booster, many of these salts might be detonable. At this point there is no easy way to prove or disprove their potential explosivity.

Urea nitrate (UN), more properly called uronium nitrate, is an energetic salt, and as such would not be expected to have much vapour pressure; however, it might be detectable due to evolved urea or nitrogen oxides. Detection of urea nitrate is essential because for over a decade it has been a frequent choice of terrorists. It was used in the bombing of the World Trade Center in New York City (February1993) and in many car bombings in Palestine. In 1992, the use of urea nitrate became so prevalent in bombings by the Shining Path that sales of urea were outlawed in Peru.

Table 3 Potential oxidizers for composite explosives

Nitrate	X NO_3	Nitrite	X NO_2	Permanganate	K MnO_4
Perchlorate	X ClO_4	Chlorate	X ClO_3	Hypochlorite	Ca $(OCl)_2$
Chromate	X CrO_4	Dichromate	X Cr_2O_7	Iodate	X IO_3

where X is a suitable cation, for example, ammonium, sodium, potassium, and calcium

2.14. Non-solid explosives

Determining the nature of a liquid in a sealed bottle remains a detection challenge. For this reason, use of liquid explosives might seem attractive to terrorists. Hydrogen peroxide has been seriously studied as a propellant and model explosive. Nitromethane (CH_3NO_2) is another compound in this category. Both of these liquids are produced on a very large scale for legitimate purposes. EGDN is readily synthesized from ethylene glycol. It is not usually used alone, but is often the principal ingredient of dynamite. Interestingly, EGDN, HMTD, and RDX were allegedly part of the millennium bomber's (Ahmed Ressam) intended device in 1999, and he apparently synthesized all three. Astrolite is an AN formulation fuelled with the energetic material hydrazine. This material was patented and sold for a time for commercial mining. Presumably handling issues became important, and it is no longer sold. Since the 1960s, both the US and Russian militaries have employed fuel-air explosives. These are made from common fuels and are extremely cost effective. The apparent simplicity of fuel-air explosives belies the very real difficulties in engineering such devices, which fortunately appears to have discouraged their use by terrorists.

3. IMPLICATIONS FOR DETECTION

The various properties of different explosives limit the circumstances in which they can be used, or at least reduce the likelihood of their use. This helps to reduce the range of threats that need to be addressed and to better focus detection efforts. For example, an explosive with a very large critical diameter is unlikely to be used in a small bomb.

Table 4 gives details of some relevant physical and thermal properties of a range of common explosives that have been encountered in terrorist bombs. It should be noted that DMNB (2,3-dimethyl-2,3-dinitrobutane) is one of the taggants added to plastic explosives under the Montreal Convention on marking of plastic explosives. Dinitrotoluenes are frequently added to blasting gelatine as a minor component and are also found in TNT as a significant impurity.

Most explosive detection equipments do not truly detect explosive vapour, rather they key on minute particles of the explosive [11]. The reason for this is that most explosives have very low vapour pressure, and low vapour pressures are rather difficult to measure. Methods based on mass loss or the direct measurement of tiny pressures are particularly prone to the influence of trace impurities of more volatile substances. Consequently, the values reported in the literature exhibit a high degree of scatter. To add to the confusion, different units of measurement are used. In general, measurements involving chemical determination of the amount of the specific compound in the vapour phase are to be preferred. If several different values are reported, and there is no better criterion for selection, it is probably best to take the lowest value.

Generally, vapour pressure measurements are fitted to a form of the Clausius–Clapeyron equation:

$$\mathrm{Log}_{10} P = \mathrm{A} + \mathrm{B}/T$$

Table 4 Physical and thermal properties of some explosives

	Molecular weight	Melting point (C)	Vapour pressure (Pa,25 C)	Exotherm C by DSC$^{\#}$
HMX	296	280°		277
RDX	222	204°	6.3×10^{-7}	253
Picric acid	229	122		319
PETN	316	141	1.9×10^{-6}	215
Tetryl	287	129		216
TNT	227	81	9.9×10^{-4}	320
AN	80	169	1.3×10^{-3}	328
NG	227	13	6.2×10^{-2}	209
DMNB	176	210–214	0.28	
2,4-DNT	182	69	0.7	368
EGDN	152	–23	6.4	>450
TATP	222	98	5.6	229
NM	61	–29	4.9×103	
UN	123	160	8.8×10^{-7}	172, 409

AN, ammonium nitrate; DMNB, 2,3-dimethyl-2,3-dinitrobutane; 2,4-DNT; EGDN, ethylene glycol dinitrate; HMX, $C_4H_8N_8O_8$; NG, nitroglycerin; NM; PETN, pentaerythritol tetranitrate; RDX, $C_3H_6N_6O_6$; TATP, triacetone triperoxide; TNT, trinitrotoluene; UN, urea nitrate; TMD, theoretical maximum density.

Notes: #At 20 per min; data compiled and adapted from Refs [1, 2, 11–17].

where P is pressure, A and B are constants, and T is temperature in Kelvin. At the higher pressures of interest to chemical engineers, for example, for distillation problems, the Antoine equation is used for greater accuracy, but this is unlikely to be relevant in explosives detection.

It is common to find vapour pressures quoted in millimetres (mm) mercury (Hg) in older papers, although sometimes the identical unit Torr is cited instead. In both cases, the conversion to the SI unit, the Pascal (Pa), is simply:

$$1\ \text{mm Hg} = 1\ \text{Torr} = 133\ \text{Pa}$$

In other cases, the vapour pressure is quoted as parts per million (ppm), parts per billion (ppb), or parts per trillion (ppt). When these terms are applied to gases and vapours they always refer to volumes,that is, 1 ppt is 1 volume of vapour in 10^{12} volumes of air. In the absence of other specific data about the ambient conditions, it is usual to simply take the atmospheric pressure to be the standard value of 101,325 Pa; hence, 1 ppt would be

$$1\ \text{ppt} = 101,325 \times 10^{-12} \approx 1.01 \times 10^{-7}\ \text{Pa}$$

TATP has such a high vapour pressure that it can probably be directly detected, whereas RDX has such a low vapour pressure that dogs alert on the bouquet of solvents used in its manufacture. Nitrate esters readily decompose to eliminate nitrogen dioxide (NO_2). This can be a clue for canines and certainly is for chemiluminescence.

Of the explosives listed in Table 4, only those such as NG with vapour pressures greater than 10^{-3} Pa at 25°C are good candidates for the direct detection of vapour by current instrumental techniques. However, vapour pressure rises markedly with temperature. In addition, consideration of the thermal stability data in Table 4 offers the possibility of heating samples containing traces of involatile explosives such as RDX or PETN to increase their vapour pressure and render them detectable. This is the basis of the common technique of combining a heated inlet system with a vapour-type detector, for example, the method of desorption from a swab on a heated stage often used with IMS or TEA systems. This approach has greatly broadened the scope of what were previously viewed as vapour-type detectors and is now standard practice; such instruments are now known as particle detectors.

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CHAPTER 3

DETECTION OF EXPLOSIVES BY DOGS

J.C. Oxley *and* L.P. Waggoner

Contents

1. INTRODUCTION

Probably the oldest need for trace detection was for the detection of poisons. Food tasters fulfilled that role, as did canaries when used by miners to warn of poisonous atmospheres underground. In more recent times, society has required detection of other chemicals. Often a dog meets the need, although research has been conducted on other species such as bees and rodents, and recently it has been suggested that the sensitivity of human olfaction is greater than generally appreciated, and that training of humans to enhance and apply their olfactory skills might pay dividends [1]. Nevertheless, such tasks generally rely on training of the dog or other species to use its highly developed sense of smell to detect materials or items of interest.

Detection dogs are very widely used and have many practical advantages. They have been successfully used for many functions, including detection of drugs, illegal food imports, explosives, arson and human remains. Dogs can be superbly sensitive and specific, and the technology is superficially easy as well as being portable, mobile and relatively inexpensive. The use of dogs is often a source of highly visible public reassurance and may well have a very practical deterrent effect on potential malefactors. However, quite often the user has no idea if the dog is actually working or not. Performance of the system depends a lot on the skill and

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enthusiasm of the dog handler to interpret responses and get good results. In general, detection dogs only alert to substances that have been included in their training and cannot communicate the identity of the threat that they have detected. Furthermore, many stories of the success of canines can be considered "lore" rather than scientific fact. Much research has been carried out in recent years to provide a sound scientific understanding of the ways in which detection dogs work, how they are best trained, the role of the human handler in the dog-handler team and the evaluation, maintenance and improvement of performance.

2. THE SCIENTIFIC BASIS OF EXPLOSIVES DETECTION BY DOGS

One of the most effective and available technologies employed for the detection of explosive materials is the explosive detection dog (EDD) and handler team. Dogs have a long history of use by law enforcement agencies for a variety of detection tasks [2], and are considered to be one of the most sensitive detection instruments available [3]; EDD teams are currently considered accurate, durable, flexible and are one of the most accessible technologies for conducting explosive detection tasks [4]. Many federal agencies, such as the Transportation Security Administration, the United States Secret Service and Department of Defense, as well as state and local agencies currently use EDD teams in their efforts to interdict explosives.

Despite significant advances in operational instrumentation for detecting explosives, the EDD team remains the most widely employed detection system. The popularity and, arguably, success of these programs obscure the considerable challenges that underlie utilizing the chemical detection capabilities of the dogs to attain efficient and effective olfactory detection performance. Although it is broadly and probably accurately assumed that dogs can be exceptionally capable explosive detectors, the vocations of training and handling EDD are predominantly craft rather than technological in nature due to a chasm between mature behavioral science and the practice of canine detection as well as a limited and sporadic history of research regarding canine detection. As for the first reason, unlike artisans of chemical detection instrumentation, the progenitors of canine detection did not ascend from academic scientific roots but rather of more immediately prescient demands of defending themselves and their colleagues from mortal threats. As for the second reason, one only need to examine the scant number of pages devoted to olfaction in a survey college textbook on sensation and perception as compared to vision and hearing; the two most plausible reasons for this discrepancy are the importance of seeing and hearing to human awareness and the complexity of studying a chemical sense as compared to that of vision and hearing.

Increased vigilance regarding security to protect against terrorist use of weapons of mass destruction, including especially explosive devices, as well as an increased interest in the comparison to the explosive detection capabilities of instrumental technologies, has led to increased scrutiny of canine explosive detection capabilities.

Despite recent increased interest in canine olfactory and applied EDD research, we still lack a complete and robust scientific model of the way dogs actually detect substances; however, considerable progress has been made [5]. In particular, it has proved helpful to apply similar concepts to the detection dog and handler system as would be applied to an instrumental detection system. For example:

- Specificity: how well is the target detected in the presence of potentially confusing non-targets?
- Dynamic range: what is the span between the smallest and largest amounts that can be detected?
- Robustness: does the detection system continue to operate correctly in adverse conditions?
- Duty cycle: how long can a dog work without deterioration in its detection performance under various environmental conditions?
- Sensitivity: what is the minimum amount that can be detected?
- Recovery: is performance fully restored after overload?

As with all research involving humans and other intelligent creatures, it is also essential to design the experiments to avoid the introduction of unintentional bias from over-helpful subjects. We should remember the example of geneticist Mendel and his overly helpful fellow monks, who quietly weeded the pea patch so that the results came out in line with Mendel's predictions. Thus, where appropriate, variants on the "double-blind" principle should be applied in experimental design, and statistically significant numbers of measurements need to be made to properly account for the inherent variability of living subjects.

2.1. What do dogs detect?

For explosives, there are three possible types of signature a dog can key on: (1) the explosive itself; (2) a contaminant or minor constituent of the explosive common to most batches of that explosive; and (3) a decomposition product of that explosive.

One theory advanced about the canine detection of explosive is that the dog actually identifies the specific explosive molecule. This line of reasoning concludes that training on a pure sample of a single explosive compound should enable a dog to detect any target containing that explosive, regardless of the presence of other materials in the vapor headspace. This does not appear to be the case.

Johnston, Waggoner and Williams designed an olfactory test chamber to explore dogs' reactions to various vapor concentrations of chemical compounds in air (see Figure 1). The start of a test is signaled to the dog by an audible tone. When air enters the chamber the dog has the choice of three paddles: (1) "fresh air"; (2) "non-target," that is smells of something other than the target; (3) "target." Pressing the correct paddle with its nose produces a reward for the dog. Such experiments are accompanied by chemical analysis of the actual headspace over the test samples.

Analysis of a group of smokeless powders of known composition showed that the main components of their headspace vapor were acetone, toluene and limonene; the concentration of nitroglycerin (NG) was relatively low. A series of

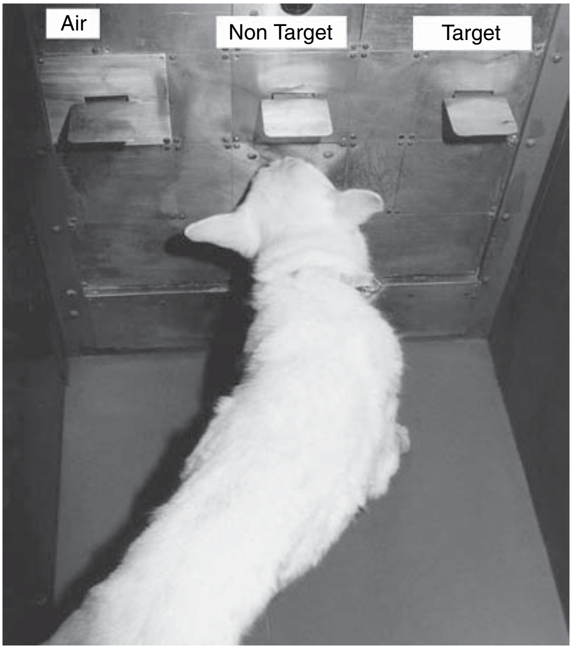

Figure 1 Auburn University olfactory test chamber.

experiments with a number of canines showed that the dogs identified a mixture of acetone, toluene and limonene as "smelling like smokeless powder." They responded less frequently to NG, or a mixture of acetone and toluene, or to any of the individual chemicals – acetone, toluene and limonene. Figure 2 shows the average responses from a large number of trials with a typical dog, canine 5174. There was a degree of variation in response among the dogs. It is likely that different canines took different approaches to finding the target [6, 7].

Analysis of the headspace of a group of TNT samples from different sources showed the principal vapor component to be 2,4-dinitrotoluene, with smaller amounts of the other dinitrotoluene isomers, and 1,3-dinitrobenzene [8]. Controlled tests in the olfaction chamber showed that most of the dogs principally responded to 2,4-dinitrotoluene as "smelling like TNT" and mostly ignored the other compounds [9].

The results cited above suggest that a canine actually respond to a mixture of the most abundant vapor constituents, which are most reliably related to reward in its training [10]. All other factors being equal, the dog's behavior is shaped to be controlled by the most advantageous (i.e., least cost or effort for reinforcement) strategy to obtain its anticipated reward. This performance in instrumental analogs would involve quite complex signal processing and pattern recognition. Such behavior may also help explain false detections where the dog identifies a target even though the target is not present. It may be that the odor from the false target actually contains some of the vapor components associated with the target; hence,

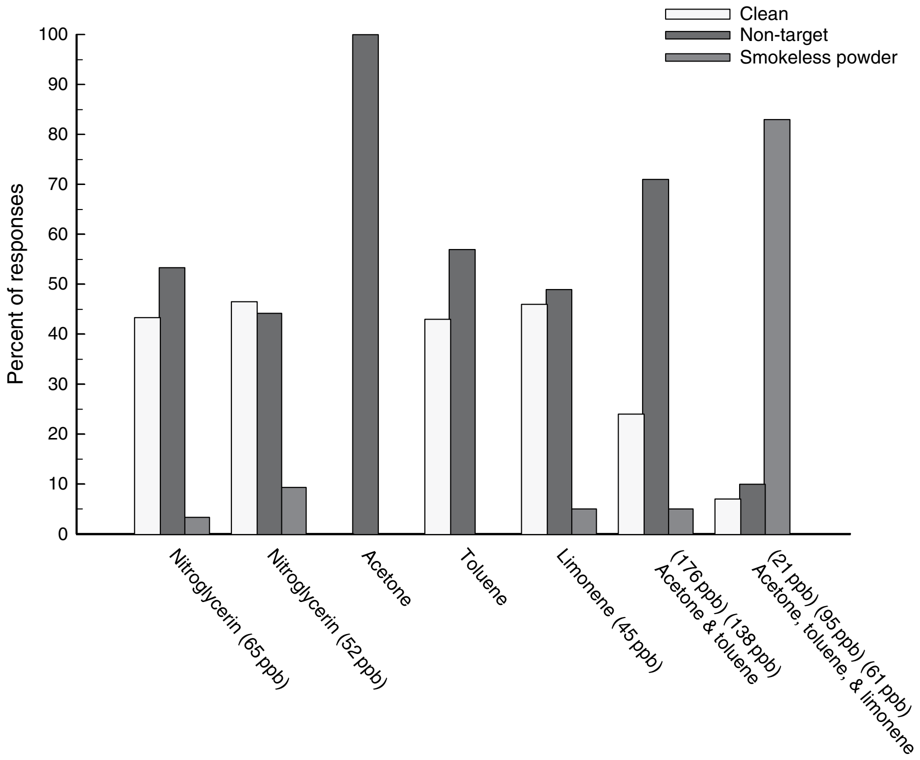

Figure 2 Example dog's response to vapor constituents.

from the dog's perspective such a response is correct. The complex bouquet of an explosive is an important consideration in recent efforts to design non-explosive or rendered-safe explosive canine training aids.

2.2. Sensitivity

It is generally recognized that dogs possess an acute sense of smell [11]. However, few quantitative studies have been published. One difficulty has been accurately measuring the amount of target compound in the vapor presented to the dog. Figure 3 summarizes results obtained using several dogs (six for each target compound) and an olfactory chamber offering only two choices for response: target compound "present" or "absent."

Depending on the target compound, the detection limit was in the 500 parts per trillion (ppt) range (2,4-DNT or the ICAO taggant dimethyl dinitrobutane) or in the 10 part per billion (ppb) range for NG, the cocaine stimulant methyl benzoate, or cyclohexanone (solvent used in the production of RDX and HMX). The curves are analogous to the sensitivity curves, which might be obtained from a physical detection instrument. The results demonstrate the very high sensitivity of the dog

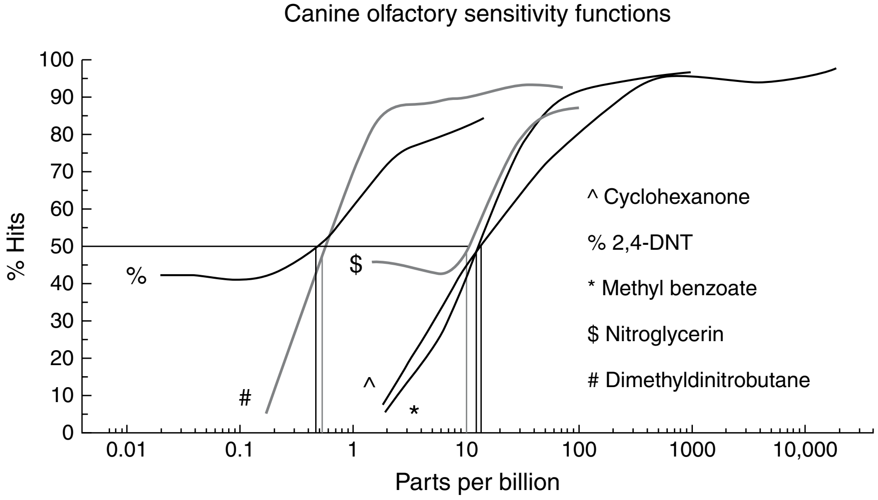

Figure 3 Dog detection sensitivity.

detection system [12]. Recently, olfactory detection thresholds of between 1 and 2 ppt have been demonstrated for *n*-amyl acetate in an intensive study of just two dogs [13], which is 30- to 20,000-fold lower than thresholds earlier reported for amyl acetate [14]. Assessments of canine olfactory sensitivity are largely dependent upon current instrumental capabilities for producing and controlling the delivery of, and measuring very low vapor concentrations, as well as experimental strategies to provide the dog with as unencumbered or naturalistic circumstance as possible in which to operate; thus, it is not surprising that olfactory sensitivity measurements have generally increased (i.e., lower thresholds) across years. Despite variability between sensitivity assessments, there is enough evidence to conservatively suggest that dogs clearly possess sufficient potential olfactory sensitivity for explosive detection tasks.

A more practical concern is *operational* sensitivity, and that depends strongly on how the dogs are trained [15]. Dogs trained to detect low concentrations of a target will detect low levels but may not recognize the signature of large quantities (Figure 4). Conversely, dogs trained on high concentrations of target will not necessarily detect low levels (Figure 5) [16]. Section 4.2 examines this issue in further detail.

2.3. Specificity

Whereas dogs demonstrate impressive sensitivity, their specificity is more impressive and possibly more important. Specificity addresses the degree to which a detection dog can discriminate between potentially confusing non-target substances or items, and the target it has been trained to seek. Both in experimental tests where trained dogs are exposed to a wide variety of confusing scents and in real-life operational experience, dogs display a high degree of selectivity [17, 18]. They can often do this more efficiently than physical detection instrumentation. Canine

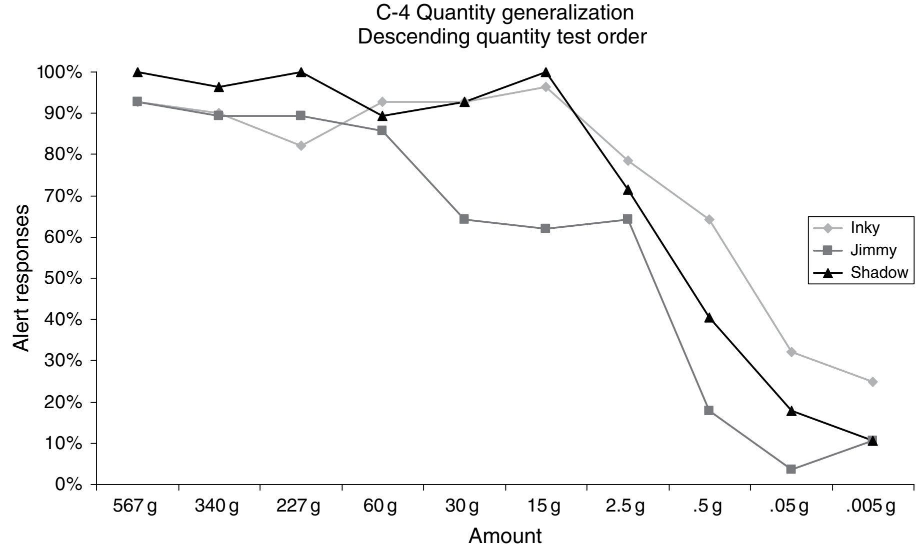

Figure 4 Responses to decreasing quantities of C-4 plastic explosive.

specificity can be seen clearly in Figure 2 where the dog discriminates between its target odor (the combined group of acetone, toluene and limonene) and individual components. However, a balance between specificity and generalization is necessary for optimum detection. The success of detector dogs lies not just in discriminating

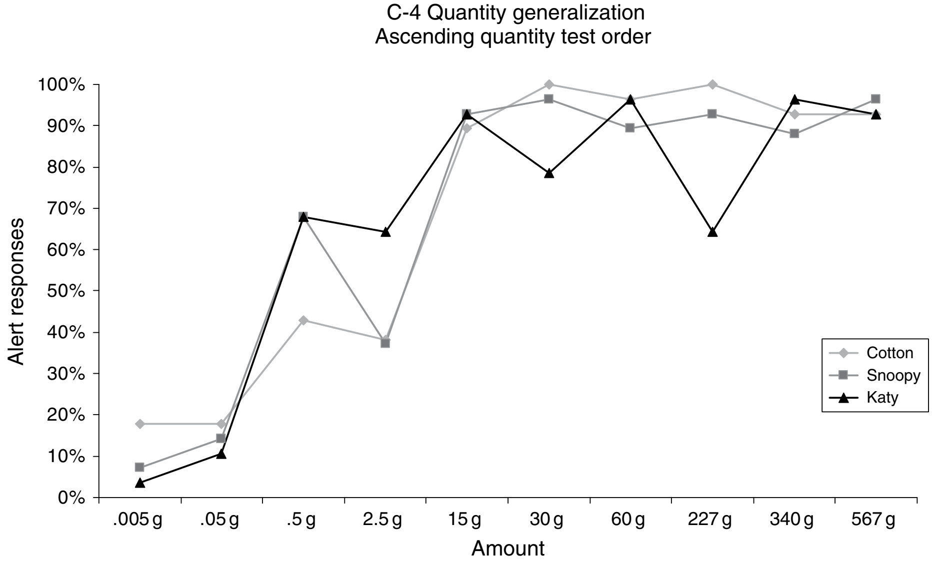

Figure 5 Responses to increasing quantities of C-4 plastic explosive.

a target, such as an explosive, from non-target substances, but in the complimentary process of generalizing from the specific target odor on which they have been trained to other target odors that are similar, but not exactly the same. Most explosive formulations exist in a variety of variants as a result of such factors as manufacturing location or process, the presence or absence of taggants, age, handling and storage.

2.4. Dynamic range

A long-standing issue in the operational training of detector dogs is often referred to in overarching terms as that of bulk versus trace detection. Can a dog trained on traces reliably detect the presence of very large amounts of the same substance and vice versa? It is important to consider that when a dog searches for target odors it will almost always first encounter a low concentration and track that odor to where it is most concentrated. This natural (i.e., untrained) "tracking-to-source" characteristic of species that are very odor-guided in their getting about in the world is perhaps the most important in their adaptation for detection tasks. This capability, which may be categorized under the heading of "dynamic range," has yet to be replicated in instrumental detection and it positions canine detection as the most capable detection tool available. Notwithstanding this tracking-to-source behavior, there remains the issue of the concentration range to which the dog will alert. This component of dynamic range is directly a product of training and is considered under the topic of generalization below.

2.5. Generalization

This is the ability of a dog trained to detect a specific target to also correctly detect similar but not identical targets. Table 1 shows that dogs trained on only one smokeless powder, Bullseye, have on average a 52% chance of detecting a powder from another manufacturer, IMR 4064.

If the dogs are trained on two different smokeless powders, Bullseye and Red Dot, which both happen to be Alliant products, the dogs' chances of detecting IMR increase to 61%. If they are trained on three smokeless powders, still all Alliant powders, their ability to generalize increases so that they have, on average, a 71%

Table 1 Generalization between different types of smokeless powder

Tested: Trained	Red dot	Unique	IMR 4064	Super-Lite
Bullseye	65 (25–91)	30 (4–62)	52 (27–94)	2 (0–6)
Bullseye Red dot		69 (31–98)	61 (33–94)	13 (0–29)
Bullseye Red dot Unique			71 (25–96)	5 (2–10)
Bullseye Red dot IMR 4064 Unique				8 (4–17)

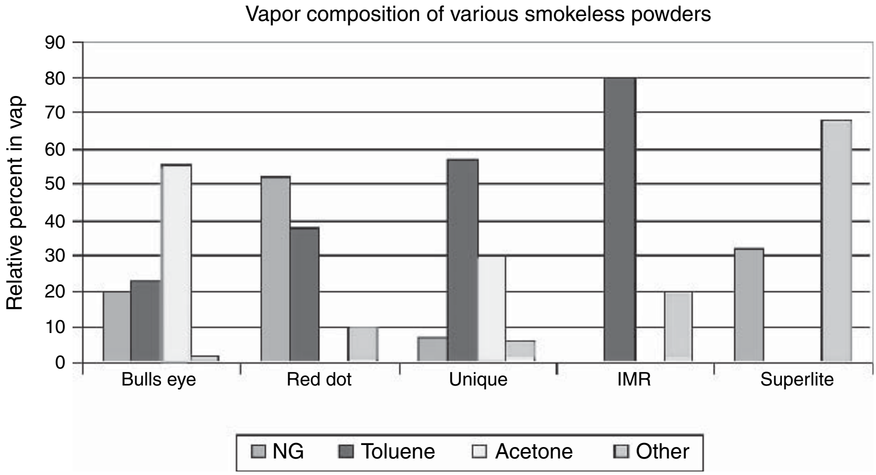

Figure 6 Analysis of vapor from some smokeless powders.

chance of identifying IMR. Figure 6 shows the differences in the vapor signature of these smokeless powders. The fact that dogs have difficulty generalizing to Superlite suggests, as does the study illustrated in Figure 2, that dogs do not use NG as the identifying signature of smokeless powder. The values in parentheses in Table 1 show the degree of variation among dogs. Thus, extreme caution should be used in assuming generalization across variants.

In considering the dog's ability to generalize, the amount of the target compound should be considered. If dogs are supposed to be able to detect trace amounts of a target, they should be trained on small amounts. For example, in the United States we stop at red, octagonal signs in the range of one-foot diameter. We probably would drive right by such a 20-foot diameter "stop" sign. For canine detection, the strategy should be to make the amount irrelevant by training with as varied a range of amounts as possible.

2.6. Duty cycle

In general, a detection dog is "on the job" 6.5 h a day and is actually "working" a total of 2.5 h during that time [19]. Experimental determination of duty cycle is of interest because it is the amount of time a dog will work without deterioration in its detection performance. Training has a large effect on willingness to search. Training factors such as the number of targets per time searched, target placement (high or low) and rate of reinforcement (extending search duration via reinforcement schedules) all affect the duty cycle. Tradition suggests 30 min before there is a decrease in willingness to search or accuracy in the search. Testing at Auburn's canine detection training center has shown an average duty time of 47 min, with a maximum between 90 and 120 min. Over that time frame, there was a slight increase in false alarm rate, but no noticeable decrease in search accuracy. The dog, itself, gave little indication of reaching its limits. Environmental temperature had the greatest impact on search accuracy. Also important were ambient humidity and the characteristics of site to be searched [20]. Remote air sampling for canine olfaction (RASCO) was pioneered by a South African team with the QMEDDS system in the early 1990s. RASCO systems remove environmental factors by keeping the canine in a comfortable, controlled environment and bringing air samples to him.

2.7. Robustness

The study, illustrated in Figure 7, was conducted at Auburn University where the dogs were initially trained on 10 targets and then tested periodically over 4 months with a variety of non-target compounds also present [21]. The odor memory demonstrated by these dogs is impressive. However, it may not be surprising because one of the things people often claim to remember is a smell from their youth. This study highlights an important concern because it suggests that training mistakes, such as the use of contaminated training aids, will result in long-term problems. The dog performance illustrated in Figure 7 was not a result of searching. The dogs walked around a circle with various stations and indicated whether the sample presented was the target material or not. Dogs used for actual searching probably need to practice with their handlers at least every week.

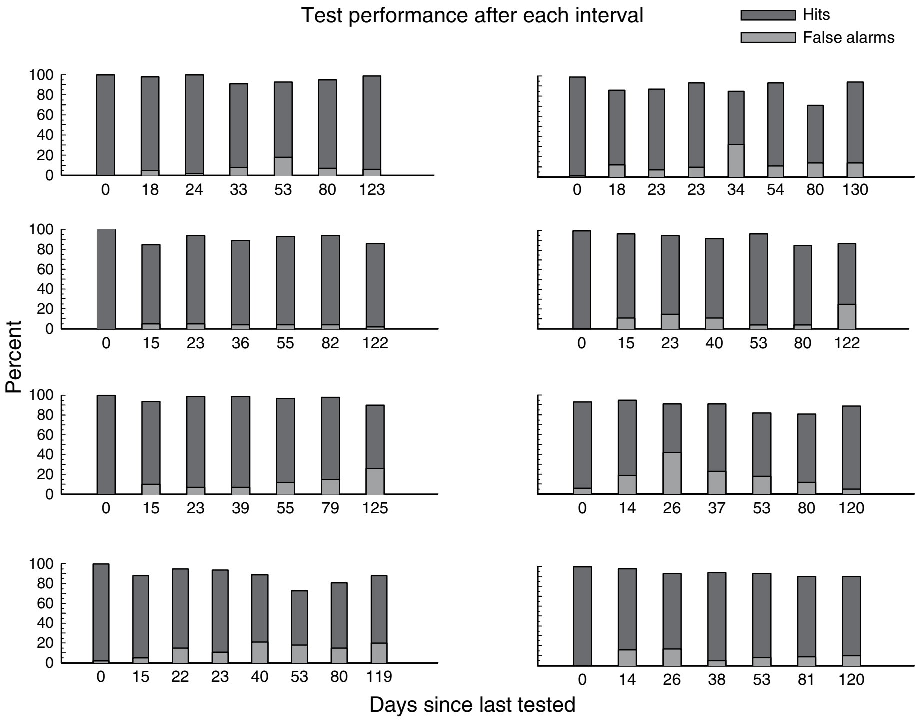

Figure 7 Performance of eight dogs over time.

3. TRAINING, EVALUATION AND MAINTENANCE

Training and evaluation of detection dogs still require much research. Despite the superficial simplicity and their relatively low initial capital cost, the use of detection dogs does, in fact, require a significant support infrastructure for training and care. These resource burdens are often overlooked but are in fact analogous to the requirements for training, maintenance and quality assurance for physical detection instruments and should be similarly evaluated in any operational analysis. The old saying "a man's best friend is his dog" is particularly relevant to the handler and detection dog partnership, and this can make objective performance assessment and quality assurance exceptionally difficult.

It should be clearly understood that there is a difference between a dog walking a line or wheel of samples and performing a search. In using a set of boxes, cans or blocks, which the canine is walked past, it is generally better to use a circular arrangement or wheel. Figure 8 shows a suitable example. If the dog is walked past a line of potential targets and non-targets, it will realize it should detect "something" before the end of the line. The use of a circular arrangement, where the dog is started at different positions in the circle, obviates the obvious alert at the last sample in line. This type of training is essential, especially during early training on a particular scent or reinforcement training. However, training in an operational setting, a search, is equally important as is training with its handler. There are a few publications dealing with canine scent training. Primarily, programs are run by experienced handlers.

Presently, US explosives detection dogs tend to be German or Belgian Shepherds, Malinois or Labradors, but there is more variation within a breed than between breeds [22]. Selecting a dog or breeding a dog with optimal olfactory capabilities has only recently been emphasized. Yet, for centuries animals have been bred to perform select tasks. Perhaps olfactory detection has lagged behind in this

Figure 8 A test circle with fixed positions for target, non-target, or no sample.

area because the characteristics of a potential detection canine have not been obvious. Recently, breeding programs aimed at scent recognition have used curiosity and playfulness as the desirable features.

Until recently an organized approach to detector dog training was completely lacking. Best-practice guidelines and performance standards were needed [23]. Even a database of detection dogs in various locales was not available. Part of the difficulty has been a somewhat acrimonious division among dog handlers on whether a dog finding the target compound should be rewarded with food or with play or praise. In the United States, the use of food reward was supported by the Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF). This system ensured the dog received some training every day because he only ate after finding the target(s). Play reward was supported by the US military dog training center at Lackland Air Force Base and the Transportation Security Agency. Of less contention was the type of alert to be given on target – a bark, sit or some passive response.

In the late 1990s the ATF issued guidelines for proficiency testing known as the National Odor Recognition Test (NORT) [24]. These tests require that the handler not know where the explosives samples are placed (a blind test) and that the dog recognize six explosives in 100 g quantities: black powder (free flowing or in safety fuse), double-base smokeless powder, dynamite (containing NG and EGDN), PETN, RDX and TNT. In addition, the canine must recognize four explosives from a list of improvised and ammonium nitrate-based explosives. The NORT document emphasizes the importance of proper storage of explosive and training aids so that the odor of the more volatile explosives does not contaminate other explosives. It also emphasizes the necessity of offering non-target samples (distracters) as well as blanks. In the early 1990s the Federal Bureau of Investigation began to set up scientific working groups on various topics. In 2004 Scientific Working Group on Dog and Orthogonal detector Guidelines (SWGDOG) was founded, and its 55-member committee is posting proposed training guidelines on the internet (http://www.swgdog.org).

4. CONCLUSIONS

Most substances targeted for detection emit a fairly complex mixture of chemical vapor constituents. Research indicates the most likely signature recognized by the canine is the group of compounds most abundant and consistently present in the vapor headspace. However, different dogs may not attend to exactly the same constituent(s). The signature may be a family of constituents most likely to control detection responses. Evidence suggests that the degree of response generalization between similar substances depends on the similarity of abundant vapor constituents in the training material and in variants of that material. To promote a reasonable degree of generalization, at least two variants should be used in training. This applies to variants in headspace composition (be it due to changes in manufacture or recrystallization) or variants in the amount of vapor-producing material.

Canines are a proven operational tool for substance detection, but as a practice, canine detection remains more of a "craft" than a technology. The quasi-technological state of detector dog technology fosters variability in detection capability and reliability, resulting in varying degrees of skepticism. Nevertheless, canine detection is used as the baseline capability to which instrumental devices are compared. Furthermore, despite all the unknowns and uncertainties, there are still many situations where detection dogs remain the best or, indeed, the only available option.

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CHAPTER 4

COLORIMETRIC DETECTION OF EXPLOSIVES

J. Almog *and* S. Zitrin

Contents

1. INTRODUCTION

Color reactions are chemical reactions that produce colored products. Identification of a compound, or more commonly a group of compounds, by color reactions is one of the oldest and simplest methods in analytical chemistry. It is based on the fact that a specific compound or a group of compounds, when treated by an appropriate reagent (often called "color reagent"), produce a color that is characteristic of this compound or group of compounds.

Color reactions have been extensively used in the field of explosives analysis [1–3]. Their application is easy and the equipment required is simple and inexpensive. Their sensitivities are often in the sub-microgram range. They enable rapid, on-site diagnostic detection of explosive materials, and are also used for preliminary laboratory tests of materials suspected of being explosive. Moreover, these tests can help in diagnosing impurities and degradation products of explosives.

The main drawback of the use of color reactions for the analysis of explosives lies in their often low specificity. Although their specificity varies according to the type of reactions – and some reactions are quite specific – it is generally not safe enough to establish an identification of an explosive in a forensic laboratory on color reactions alone. When the color is obtained, the key question is whether other compounds, which are not explosives, can produce the same color under identical experimental conditions. Unfortunately, the answer is usually, yes. Thus, in forensic analysis, where an erroneous identification may lead to a gross injustice, it is generally accepted that the identification of an explosive should not depend on color reactions alone.

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M. Marshall and J.C. Oxley (Editors)

In discussing their specificity, it is worthwhile to distinguish between two types of color reactions. In the first, the formation of a colored product involves only the transfer of electrons (oxidation/reduction); no atoms from the analyte become part of the colored product. An example of this type of reactions is the oxidation of diphenylamine (DPA) by nitrate ions (NO_3^-) to produce a deep blue color [3, 4]. The reaction is hardly specific for nitrate ions, as other ions or compounds are also capable of this oxidation, producing the same blue color. In the second type, atoms from the analyte are incorporated into the colored product. An example of this type of color reaction is the Griess reaction [4–6], which is discussed extensively later. Reactions of this type are usually more specific than those of the first type: in order to occur, the presence of certain atoms in the analyte is required (an exception is the color change of many acid–base indicators, where the atom attached to the analyte is a proton; in this case the specificity is rather low and is similar to the first type). In the Griess reaction, however, a nitrogen atom from the analyte – the nitrite ion – is incorporated into the colored product. Obviously, without its presence, no color is produced. Therefore the Griess reaction is quite specific to nitrite ions. As shown below, this does not mean that it is specific to explosives.

Reliable identification of explosives in a modern forensic laboratory is based on instrumental techniques, mainly spectrometric, often in conjunction with chromatographic methods. Gas chromatography–mass spectrometry (GC/MS) is considered to be an excellent and reliable method in forensic analysis, including the analysis of explosives.

Yet, color reactions have not become obsolete. Because of their simplicity and relatively low cost, they may be effectively used as initial diagnostic tests for explosive materials. Three examples for their application are discussed herewith:

1. Being part of an overall scheme for the analysis of explosives, color reactions can successfully and efficiently serve as preliminary laboratory tests. A typical example is an explosion in a bus, which produces hundreds of fragments. Obviously, it is impractical to apply GC/MS to each fragment; however, screening the fragments by color tests can help the analyst in choosing the exhibits for subsequent, more advanced, analytical testing methods.
2. Color reactions are used in the laboratory in conjunction with thin-layer chromatography (TLC) – a routine and highly popular method for the analysis of explosives (for a full review, see Ref. [1, chapter 5, pp. 59–85] and Ref. [2, chapter 2, pp. 33–41]). Spots on the TLC plates are visualized by spraying the plates with appropriate color reagents.
3. Color tests are the basis of many "field tests," which are carried out in the "field," i.e., outside the laboratory. A common situation is in border posts, where an unknown material is found on a person. A special kit (to be described later), based on color reactions, is employed to diagnose the unknown material. In case of a positive result, a sample of the material is sent to the laboratory for further analysis.

Another situation includes the detection of traces of explosives on suspects (often on their hands). Usually the suspects are apprehended after an explosion had occurred. A famous example of this scenario is tests that were carried out in the UK, in 1974, following the bombings of two pubs in Birmingham. The incident, which became known as the "Birmingham Six" case, is described in detail later.

Field tests based on color reactions are carried out on the hands of the apprehended persons as "elimination tests": swabs of the suspects' hands are sent to the laboratory for further analysis only in case of a positive result.

In conclusion, although color reactions have limited reliability and cannot be the sole basis for positive identification of explosives, they can still be efficient when employed in certain situations.

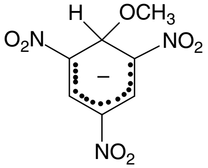
2. NITROAROMATIC EXPLOSIVES

It has been known for a long time that polynitroaromatic compounds produce colored products in contact with alkalis [1]. These color reactions have been extensively used for the identification of nitroaromatic explosives. In the Janowski reaction [7], a solution of the polynitroaromatic compound (di- or trinitroaromatic) in acetone is treated with concentrated aqueous KOH solution. 1,3,5-Trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT), treated with 30% aqueous KOH, produced violet-red and red colors, respectively. Many variations of the Janowski reaction were reported, using KOH or NaOH in aqueous or ethanolic solutions as reagents, and dissolving the explosives in acetone, ethanol or acetone–ethanol mixture [3, 8]. The reaction was used both for spot tests and for spraying TLC plates [9].

Polynitroaromatic compounds were reported to undergo color reactions with numerous bases, such as ammonia in methanol [3] and aqueous solution of tetramethylammonium hydroxide [10].

Ethylenediamine in dimethylsulfoxide solution [11] was a popular color reagent for nitroaromatic explosives in some military laboratories in the United States.

The structures of the colored products of the reactions between polynitroaromatic compounds and bases were first suggested by Meisenheimer [12]. They are usually described as resonance-stabilized complexes known as "Meisenheimer complexes." Thus, the red-colored product of a reaction between TNB and sodium methoxide was assigned the following formula (**1**):



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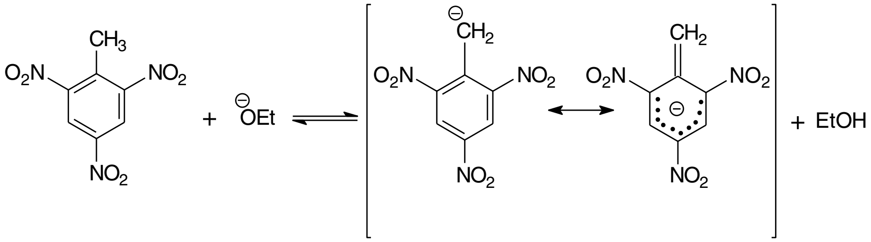
It seems that the color produced in a reaction between bases and polynitroaromatic compounds consists of more than one substance. It was observed that the initial brown color in the reaction between TNT and sodium ethoxide changed slowly to purple [13, 14]. It was also assumed that the initial brown color was most probably a Meisenheimer complex or a charge transfer complex (see later). The purple color produced when TNT was treated with sodium ethoxide was attributed to the TNT carbanion formed by proton abstraction from the methyl group of TNT (Eq. (1)):



(1)

It was also suggested that in some cases (e.g., the reaction between 1,3-dinitrobenzene in acetone and KOH) a carbanion from the basic solvent (e.g., $CH_3COCH_2^-$ from acetone) was incorporated into the nitroaromatic molecule [15].

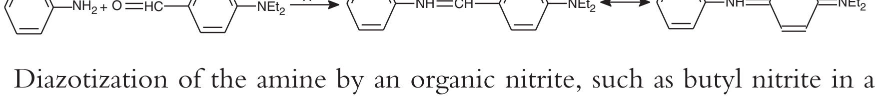
Another important mechanism, which is responsible for the formation of the colored products in the reaction between nitroaromatic compounds and some basic reagents such as aromatic amines, is the well-known charge transfer mechanism [16–19]. The aromatic amine acts as a π donor whereas the nitroaromatic compound serves as a π acceptor.

3,3′-Iminobispropylamine was used as a charge transfer color reagent in the TLC analysis of 29 nitroaromatic explosives and 5 nitromusks [20]. Nitromusks are synthetic compounds widely used in cosmetic products. Having a nitroaromatic structure, they can be mistaken for explosives by colorimetric field tests. Thus "Musk Ambrette" produces a purple color with alcoholic KOH [21]. Neither of the five nitromusks produces colored, charge transfer complexes with 3,3′-iminobispropylamine, so "false-positive" results are avoided.

Some polycyclic hydrocarbons, which are well-known π donors, also give colored products by a charge transfer mechanism [22].

Although most color tests for polynitroaromatic explosives are based on their reaction with bases, a completely different approach involves the reduction of nitroaromatic compound to the corresponding aromatic amine. Zn, $SnCl_2$, and $TiCl_3$ in acidic medium were used as reducing agents [23–26]. The aromatic amine is then identified by one of two methods:

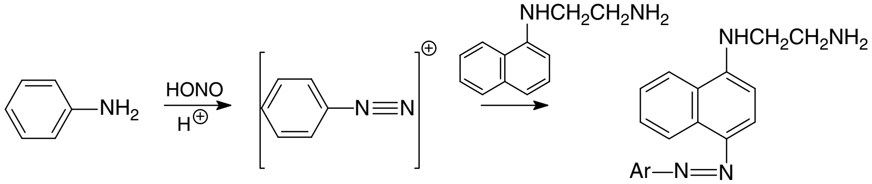
1. Reaction of the amine with *p*-dimethylaminobenzaldehyde (Ehrlich reagent) or *p*-diethylaminobenzaldehyde to produce a colored Schiff base [23–25]. The color formation is ascribed to a resonance hybrid between a protonated Schiff base and a quinoid system (Eq. (2)):



(2)

2. Diazotization of the amine by an organic nitrite, such as butyl nitrite in acidic medium, and subsequent coupling of the product with an active aromatic amine

such as *N*-1-naphthylethylenediamine (Bratton–Marshal reagent) [27] (Eq. (3)). A colored azo compound is produced [28, 29].



(3)

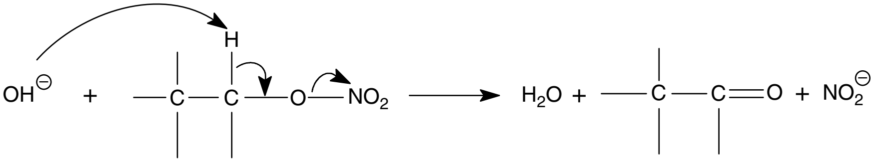
It is interesting to note that this method was used in an early analysis of the antibiotic compound chloramphenicol, whose structure includes a nitroaromatic group [30].

The major degradation products of nitroaromatic explosives are aromatic amines [2]. They were detected in groundwater in areas of former TNT plants, using TLC [26]. Visualization was carried out by direct reaction with *N*-1-naphthylethylenediamine, which produced red-violet spots.

3. NITRATE ESTERS AND NITRAMINES

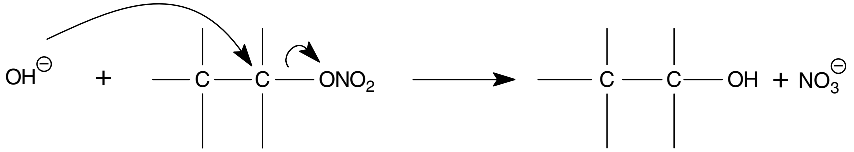
The most important color reaction for nitrate esters and nitramines is based on the formation of nitrite ions (NO_2^-), upon reaction of these compounds with alkalis [31, 32]. The nitrite ions are then detected by the classical Griess reaction [5, 6].

Several pathways are known to take place in the reaction between nitrate esters and alkalis. The mechanism that leads to the formation of nitrite ions is an "α-elimination": abstraction of an α-hydrogen atom, with the conversion of the nitrate ester to nitrite ion and the corresponding carbonyl compound [31] (Eq. (4)):



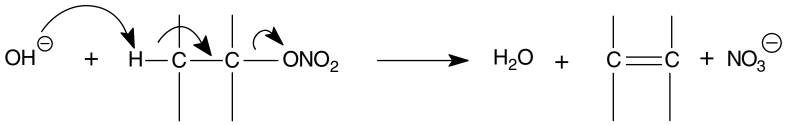
(4)

Other pathways in the reaction between nitrate esters and alkalis are simple hydrolysis and "β-elimination" – the abstraction of a β-hydrogen atom: simple hydrolysis (Eq. (5)):



(5)

The elimination of a β-hydrogen atom (Eq. (6)):



(6)

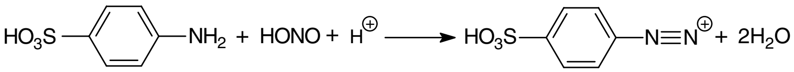
Both pathways lead to the formation of nitrate (NO_3^-) ions.

Nitrite ions can also be produced from nitrate esters by reducing the latter with zinc in acidic solutions [33] (Eq. (7)):

$$R{-}ONO_2 + Zn + 2H^{\oplus} \longrightarrow ROH + Zn^{2+} + HNO_2 \qquad (7)$$

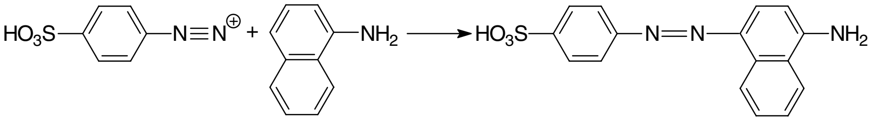
Alkaline hydrolysis of nitramines also leads to the formation of nitrite ions [1, 34].

The nitrite ions are detected by the Griess reaction, starting with their reaction with an aniline derivative, such as sulfanilic acid, or sulfanilamide. The reaction is carried out in an acidic medium (e.g., acetic acid) and leads to the formation of a diazonium ion (Eq. (8)):



(8)

The diazonium ion then reacts with a coupling reagent. This reagent is usually an aromatic compound with an electron-rich nucleus, rendering it susceptible to an electrophilic attack by the diazonium ion. A typical coupling reagent is 1-naphthylamine (α-naphthylamine). The following reaction takes place (Eq. (9)):



(9)

The product, an azo-type compound [4, 35], has a characteristic pink color.

The limit of detection of the nitrite ions by the Griess reaction, using the above-mentioned reagents, was reported [4] to be 0.05 μg (this value refers to the NO_2^- ions and not to the explosive which produces them).

In a typical procedure, the suspected explosive is first treated with ethanolic KOH. Under these conditions, nitrate esters, such as glycerine trinitrate (nitroglycerin, NG), cellulose nitrate (nitrocellulose, NC), ethylene glycol dinitrate (EGDN), and pentaerythritol tetranitrate (PETN), or nitramines, such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane), will produce nitrite ions. The Griess reagent consists of two separate solutions in acidic medium (usually acetic acid), which are applied subsequently: first the aniline derivative and then the coupling agent. The use of acetic acid solutions of sulfanilic acid and 1-naphthylamine is sometimes called the Ilosvay modification of the Griess reaction [1, 3, 36]. If the analyte is indeed a nitrate ester or a nitramine, a strong, characteristic pink color should appear.

Alkaline hydrolysis, followed by the use of sulfanilic acid and 1-naphtylamine, was the basis of a spot test for NG [37], as well as for several nitrate esters and nitramines, including NG, NC, tetryl, and RDX [38]. It is also a common spray for the detection of nitrate esters and nitramines on TLC plates [25, 29, 37, 39–41].

In the Franchimont test [42], nitramines are reduced to nitrite ions by zinc and acetic acid and then subjected to the Griess reaction. A modification of this test was used for the identification of nitramine impurities in RDX [43].

Other formulations of the Griess reagent included *N*,*N*-dimethyl-1-naphthylamine [33, 44] or *N*-1-naphthylethylenediamine [45, 46] as the coupling agent.

It was claimed that these reagents lead to more stable azo colors. In addition, 1-naphthylamine was reported to have possible carcinogenic properties [47].

Different combinations of nitrosated species and coupling reagents were studied by Fox [35].

In some, more recent formulations, phosphoric acid replaced acetic acid as the acidic medium [46, 48]. The use of hydrochloric acid as a solvent for the Griess reagents had also been reported [45].

After the "Birmingham Six" case, the Griess test has become highly controversial amongst the forensic community. Owing to its importance and impact on forensic science, this case is described herewith in detail.

On the night of 21 November 1974 two bombs exploded in two pubs in the city of Birmingham, in the United Kingdom. Twenty-one people were killed and 162 were wounded.

The police was under tremendous public pressure to find the perpetrators. Following the explosions, several people who later became known as the "Birmingham Six" were detained.

As part of a routine procedure, a local forensic scientist was summoned to swab the detainees' hands in an attempt to find explosives traces. He took etheral swabs from the suspects' hands. On these swabs, he applied a field test based on the Griess reaction. Two of the five tested positively on one of their hands. The suspects were then interrogated extensively and several of them signed a confession.

The trial of the "Birmingham Six" took place in June 1975. Except for the confessions and some (very little) circumstantial evidence, the prosecution based its case on forensic results. It was obvious that forensic evidence was extremely important: confessions could have been obtained by force, but what convincing explanation could one have for the presence of NG on his hands a few hours after an explosion?

In his court testimony, the chemist maintained that the results that he obtained (by the Griess-based procedure) gave evidence of the suspects' contact with NG.

At the end of the trial, the "Birmingham Six" were found guilty and sentenced to life imprisonment. Their first appeal was rejected (in March 1976). Since then, information had been accumulating (partly from IRA sources) raising the possibility that the "Birmingham Six" were innocent. A public campaign for the release of the "Birmingham Six" gathered momentum with the publication of Chris Mullin's (a Labour MP and a leader of this campaign) book, and the broadcasting, in

October 1985, of the Granada television program, "World in Action." The program dealt quite extensively with the forensic aspects of the case, emphasizing how crucial they were. In 1987 the case was sent back to the Appeals Court. It was then clarified to the court that the procedure used in 1974 could not be regarded as specific for NG, but despite the doubts (shared by the court) about this procedure the 1987 appeal was also dismissed.

However, the case would not fade away from the public agenda. A committee consisting of five forensic and explosives experts was appointed, and all forensic aspects were reviewed. This time the final appeal was successful and on 14 March 1991 the "Birmingham Six" were released after more than 16 years in prison.

As stated above, nitrate esters (such as NG or PETN) and nitramines (such as RDX or HMX), form nitrite ions under alkaline conditions and therefore can be detected by the Griess reaction. However, the Griess spot test by itself does not enable to distinguish between individual explosives within these groups.

Moreover, a nitrate ester such as NC, which is used in lacquers and paints, also produces the same pink color.

Another important source for "false-positive" results in the use of the Griess reaction for the identification of explosives is the possible presence of nitrate ions, together with some accidental reducing substances. In this situation, the nitrate ions (NO_3^-) could be reduced to nitrite ions (NO_2^-), giving a positive result in the Griess reaction.

The conclusion is that a positive Griess test on hands cannot constitute evidence of the hands having had contact with explosives. The Griess test should be a presumptive test, to be used only as a preliminary tool for the investigation. Its results should be confirmed in the laboratory before being presented in court.

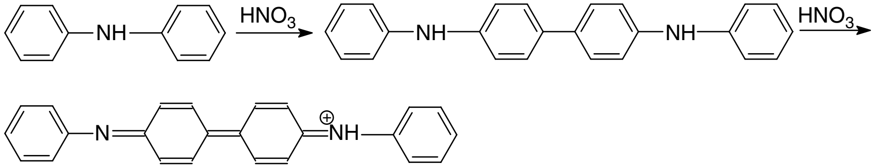
Following the "Birmingham Six" case, the Griess test has become somewhat discredited by the forensic community. It should be emphasized, however, that when properly used, it is an excellent tool which can serve as a basis for an efficient field test. An explosive detection kit (ETK (explosive testing kit)), partly based on the Griess test, was successfully used in Israel in several terror and non-terror investigations [49] (see below).

Recalling the above-mentioned classification of color reactions, it is clear that in the Griess reaction atoms from the analyte are incorporated into the colored product. This leads to a higher degree of specificity compared with oxidation/reduction reactions where only electrons (and no atoms) are transferred.

However, it cannot be overemphasized that the test is a preliminary, presumptive test, and its results can be presented in court only after they have been confirmed by generally accepted laboratory methods. The point is that when used properly, color tests could significantly assist the investigation and should not be discarded just because there are better, more accurate laboratory techniques.

The DPA test is another common spot test for nitrate esters and nitramines [1, 3, 4, 50–55]. The reagent (1% DPA in concentrated sulfuric acid) is oxidized in the presence of these explosives, producing a deep blue color.

The oxidizing agents are nitrate and nitrite ions, formed by the action of sulfuric acid on explosives. This reaction, a classical test for nitrate ions [4], is not specific: it involves only oxidation/reduction and no atoms from the analyte are incorporated into the colored product. Therefore, the blue color may also be obtained with other oxidizing agents (Eq. (10)):



(10)

Diphenylbenzidine [38, 44, 50, 56, 57] and nitrodiphenylamine [50] react in a similar way to DPA.

A solution of the alkaloid brucine in concentrated sulfuric acid was reported [4, 38, 50] to give orange-red colors with nitrate esters and nitramines, probably by oxidation of brucine.

Several color reactions were reported for heterocyclic nitramines RDX and HMX [43, 44, 53, 58]. These nitramines release formaldehyde when treated with concentrated sulfuric acid. Therefore, the use of 1,8-dihhydroxynaphthalene-3,6-disulfonic acid (chromotropic acid) in concentrated sulfuric acid – a known reagent for the detection of formaldehyde [4] – produced the expected violet-pink color. The reaction is hardly specific: other compounds that release formaldehyde under similar conditions will react in the same way.

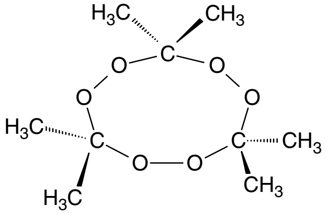
Another non-specific color reagent for RDX and HMX is a solution of thymol in concentrated sulfuric acid [3, 56, 59]. It produces a typical red color. Positive results are also obtained with non-explosive compounds such as sugars and aldehydes.

4. IMPROVISED EXPLOSIVES NOT CONTAINING NITRO GROUPS

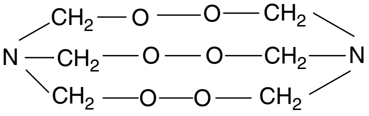
Improvised explosives that did not contain nitro groups started showing up in terrorist and criminal activities in the late 1970s. Of particular importance are compounds that contain organic peroxide functionality. Another improvised material that does not contain nitro group is urea nitrate. The ordinary color tests that are suitable for identifying common explosives containing nitro groups are irrelevant for these compounds. Therefore, special color tests had to be developed for them.

5. PEROXIDE-BASED EXPLOSIVES

For over 20 years two improvised explosives containing the peroxide group have been of constant concern to legal authorities. Both triacetonetriperoxide (TATP) (**2**) and hexamethylenetriperoxide diamine (HMTD) (**3**) are easily prepared from readily available starting materials. Both compounds have been encountered for the first time by the Israel Police in the late 1970s and early 1980s [60], but incidents involving TATP occurred since then also in the United States as well as in Europe [61–63].



2. TATP



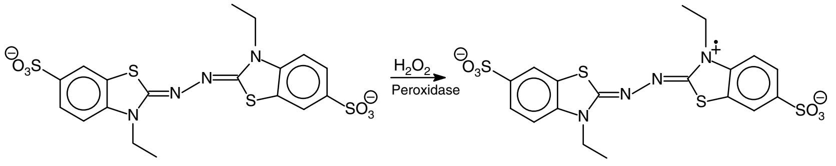
3. HMTD

Because of their ease of preparation and extreme sensitivity, the two peroxides have become a great threat to law-enforcement agencies. To assist the development of optimal defensive measures, they have been studied by several research groups and their analytical properties, physical characteristics, and explosive properties have been thoroughly explored [64–84].

The first identification of terror-related organic peroxide took place in 1979. White powder extracted from a detonator was brought for identification to the analytical laboratory of the Israel Police. The detonator, which was made of plastic instead of metal, was found on a woman crossing a bridge over the Jordan River. Normal TLC procedures failed to detect nitro-containing compounds. The IR spectrum had no absorption bands corresponding to nitro groups, and there were no bands relating to aromatic compounds. Mass spectrometry corroborated by re-examination of the IR spectrum led to the identification of the powder as an organic peroxide with the structure (**3**) [60]. TATP (**2**) was encountered for the first time in 1980, also in Israel. White powder from unexploded bomb was brought to the laboratory for analysis. As with (**3**), no color reactions typical of common explosives could be observed. The IR spectrum indicated neither a nitro group nor an aromatic structure. The compound was eventually identified by mass spectrometry and NMR spectrometry to possess the structure (**2**) [60].

Because the two peroxides have an unsuspicious appearance – being white powders with no specific characteristics – there was an urgent need to develop a rapid and simple color test for their detection. In 1999, Keinan and Itzhaky registered a patent on Peroxide Explosive Tester (PET™) [85], which enables rapid on-site detection of TATP. The peroxide explosive is first hydrolyzed in an acidic medium to hydrogen peroxide, which oxidizes a colorless substrate to a colored product. The latter reaction takes place in the presence of an enzyme known to catalyze oxidation reactions by hydrogen peroxide. In presence of organic peroxides, the outcome is a green-blue color and the detection limit is in the sub-microgram level. The inventors packed their device in the form of an easy-to-operate pen, composed of three refills, each one containing one of the chemical components necessary for the color reaction: acidic medium, substrate, and enzyme. The device is currently being miniaturized to enable easier application (E. Keinan, Personal communication, February 2006). Another field test based on the same idea, was reported a few years later by Schulte-Ladbeck, Kolla, and Karst.

Their scheme contains a preliminary stage, in which unknown samples are first treated with a catalase solution to remove hydrogen peroxide traces, to provide selectivity toward peroxide-based bleaching powders that are contained in commercial laundry detergents [86]. Instead of acidic decomposition, as in Keinan's “PET™” [85], the residue in the latter technique is decomposed to hydrogen peroxide by UV irradiation. The colorless substrate in their scheme is 2,2-azino-*bis*(3-ethylbenzothiazoline)-6-sulfonate (ABTS) (**4**), (Eq. (11)), which is oxidized to the green radical cation of ABTS (**5**). Oxidation of ABTS by hydrogen peroxide in presence of peroxidase [87] is as follows:

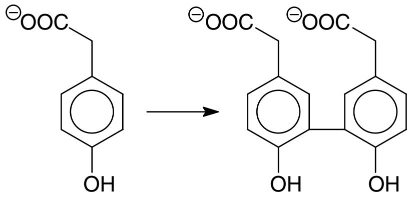


(11)

4. ABTS

5. ABTS$^{\cdot+}$
Green radical cation

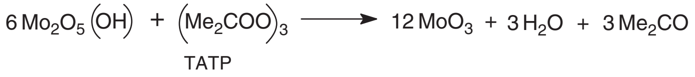
The authors report detection limits of 8×10^{-6} mol/dm^3 for TATP and 8×10^{-7} mol/dm^3 for HMTD. When *p*-hydroxyphenylacetic acid (*p*-HPAA) (**6**) was used as the oxidation substrate instead of ABTS, a highly fluorescent dimer (**7**) was formed. This dimer could be detected spectrophotometrically, although the sensitivity dropped (Eq. (12)). Both methods also enabled a semi-quantitative estimation of TATP and HMTD concentrations [86]. Dimerization of *p*-hydroxyphenylacetic acid (*p*-HPAA) by hydrogen peroxide in presence of peroxidase [86] is as follows:



(12)

6. *p*-HPAA **7.** Fluorescent dimer

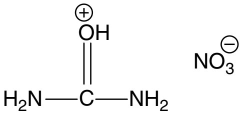
A non-enzymatic color reaction for TATP and other organic peroxides was reported recently by Apblett et al. [87, 88]. The dark blue color of molybdenum hydrogen bronze suspension is changed to yellow upon oxidation with TATP. The same reagent can also be used for quick neutralization of the sensitive explosive: a lasting final blue color indicates complete neutralization. The reaction with TATP is depicted in Eq. (13).



$$6\,Mo_2O_5(OH) + \underset{\text{TATP}}{(Me_2COO)_3} \longrightarrow 12\,MoO_3 + 3\,H_2O + 3\,Me_2CO \qquad (13)$$

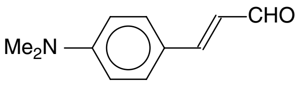
6. UREA NITRATE

Urea nitrate (**8**) is a powerful, improvised explosive, frequently made and used by terrorists. It can be prepared quickly and easily by adding nitric acid to a cooled aqueous solution of urea. The white precipitate thus formed is filtered, washed with cold water, and dried in air. Even unskilled workers can prepare large amounts of this material in "backyard" facilities [89]. Urea nitrate, in its pure form, is a white, crystalline powder, which, just by looking at it, can hardly be distinguished from "innocent powders" (e.g., sugar). It is assumed that about half a ton of this material was used in the first World Trade Center bombing, in February 1993 [89]. In Israel, urea nitrate is believed to be one of the most widespread explosives used by Palestinian terrorists, responsible for the loss of many lives. Quantitative data on the explosive performance of urea nitrate have been reported by a joint group of researchers from the Defense Evaluation and Research Agency (DERA, UK) and the FBI [90].

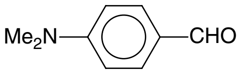


8. Urea nitrate (uronium nitrate)

A simple, fast and specific color test for urea nitrate was reported recently by Almog et al. It is based on the reaction between urea nitrate and ethanolic solution of *p*-dimethylaminocinnamaldehyde (*p*-DMAC) (**9**) under neutral conditions [91]. A red pigment is formed within 1 min from contact. Its structure has also been determined by the same group, by X-ray crystallography [92]. It appears to be a resonance hybrid between a protonated Schiff base (**10**) and a quinoid system (**10a**) (Eq. (14)). The limit of detection on filter paper is $\sim$0.1 mg/cm^2. Urea itself, which is the starting material for urea nitrate, does not react with *p*-DMAC under the same conditions. Other potential sources of false-positive response such as common fertilizers, medications containing the urea moiety and various amines, do not produce the red pigment with *p*-DMAC.

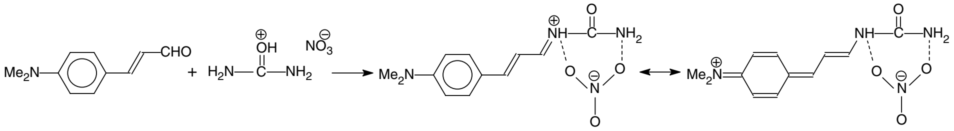


9. *p*-DMAC



11. *p*-DMAB

p-Dimethylaminobenzaldehyde (*p*-DMAB) (**11**), which is one vinyl shorter than *p*-DMAC, also reacts with urea nitrate under similar conditions, to produce a typical yellow pigment of analogous structure [91, 92]. The essence of the proposed technique lies in the fact that urea nitrate, as opposed to urea, is strongly acidic (pH 1–2) because of the presence of the nitric acid moiety in its molecule (**8**). Thus, although neutral urea does not react with *p*-DMAC, urea nitrate does, as it provides the necessary acidity for the reaction to occur. Actually, *p*-DMAC does not detect urea, but uronium ion[1] (**8**). Another color test for urea nitrate, which is less specific but is simple and quick, was developed in Israel by A. Bornstein. It is based on the fact that urea nitrate is highly acidic; thus, the pH indicator bromophenol blue changes its color from blue to yellow upon reaction with trace amounts of urea nitrate [95]. Red pigment formation in the reaction between *p*-DMAC and urea nitrate [91, 92] is as follows:



9. p-DMAC **8.** Urea nitrate (Uronium nitrate) **10.** Red pigment (Schiff base form) **10a.** Red pigment (quinoid form)

(14)

7. FIELD TESTS

Field tests are analytical tests that are normally carried out outside the laboratory (in the "field"). Field tests for explosives are usually performed when a rapid, on-site diagnostic detection of explosive materials is required. Thus, they are often carried out on suspects' hands and belongings, in post-explosion sites, or in border stations, seaports, and airports. It should be emphasized that they constitute only preliminary examinations, and positive results should not be presented to court unless confirmed by reliable laboratory methods. Because field tests are usually carried out by individuals with no scientific background, their application must be easy, involving simple equipment and methodology.

In forensic laboratories, chemical spot tests based on color reactions, have been replaced over the years by modern, more accurate instrumental methods. However, analytical techniques based on color formation are still commonly employed in field tests for explosives. Being inexpensive, simple, easy-to-operate and often quite sensitive (see above), they are most suitable for use outside the laboratory as presumptive field tests for the presence of explosives.

Several kits for explosives detection, which are based on color reactions, were reported or introduced commercially. Some of those that have been surveyed by the chemical literature are described in this chapter. This is by no means an exhaustive list. Many other kits, some of which are commercially available, but have not appeared in peer-reviewed journals, can be found by searching the web.

A kit for detecting explosives on suspects' hands or clothing – "Explosives Handling Detection Kit" – was developed by Newhouser and Dougherty in 1972 [96]. It was designed to detect three types of explosives, defined by the authors as "TNT-based explosives," "RDX-based explosives," and "NG-

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[1] "Uronium" like "ammonium" is the correct term for the positive ion that is derived from urea by the addition of a proton or another positive ion [91–94]. Hence, the correct name for urea nitrate would be uronium nitrate.

dynamites." A special polyester tape was used to collect particles of the first two groups from hands or clothing. For NG, vapors from the suspected items were collected into polyethylene bags and then passed through glass beads pretreated with the color reagent. The color reagents were ethanolic NaOH for the nitroaromatic ("TNT-based") explosives, thymol in concentrated H_2SO_4 for RDX, and *N*,*N′*-diphenylbenzidine for NG. This work [96] included practical suggestions indicating which areas on the suspect's body should be tested (e.g., under fingernails, under rings, in pockets), as well as studies on the persistence of the explosives on hands or clothing.

An "ETK" (Explosives Testing Kit) was developed in Israel and its first version was published in 1986. In its original version [49] it could detect traces of nitro-based organic explosives (nitroaromatic, nitrate esters, and nitramines) as well as improvised explosives based on inorganic fertilizers. The application for the organic explosives is carried out in two steps. The first step is a modification of the Janowski reaction [7]: A solution of KOH in ethanol/dimethylsulfoxide (instead of the common aqueous or alcoholic solutions) is applied to the sample. If a polynitroaromatic compound is present, a typical color (e.g., violet with TNT) is obtained. Under the same conditions, nitrate esters or nitramines produce nitrite ions (see above). In the second step, the NO_2^- ions are detected by the Griess reaction, using *N*-1-naphthylethylenediamine and sulfanilamide as reagents. As the action of the alkaline solution on nitrate esters leads also to nitrate (NO_3^-) ions, which do not contribute to the color reaction (see above), the formulation contains a reducing agent such as ascorbic acid. Thus, nitrate ions are reduced to nitrite ions, and the overall sensitivity is increased. Sensitivities were reported to be on the order of 10^{-7} g for TNT and 10^{-8} g for NG.

The original ETK has been modified for improved sensitivity and stability [97]. Another version applying the same reagents from spray cans instead of dropping-bottles (Expray^{TM}) is also commercially available [98].

A field test for the detection of TNT in contaminated soils (e.g., near ammunition plants) was based on the color reaction between TNT and alkalis (the Janowski reaction [7]) [26]. A few milligrams of the suspected soil are placed on filter paper and sprayed with 1 M NaOH:acetone (1:1). A red color indicates the possible presence of TNT. Detection limits were reported to be 2–50 mg of TNT per 1 kg of soil, depending on the type of soil. The same group [55] used the oxidation of DPA in concentrated H_2SO_4 as the basis of a field test for nitrate esters and nitramines in soil.

Another field technique for screening soils for the presence of TNT, 2,4-dinitrotoluene (2,4-DNT) and RDX was reported [99]. The color reagents were KOH for TNT (red color) and sodium sulfite for 2,4-DNT (blue-purple color). In screening soil for the presence of RDX, the first step would be to remove any potential contaminants – nitrite and nitrate ions – from the soil, using an ion exchange resin. The RDX is then reduced by zinc powder and the resulting NO_2^- ions are detected by the Griess reaction. Detection limits were estimated to be 1 mg of TNT or RDX and 2 mg of 2,4-DNT per 1 kg of soil.

A novel concept for colorimetric field detection of polynitroaromatic explosives was described by Arbuthnot et al. It is based on colorimetric changes that occur when the polynitroaromatic compounds react with poly(vinyl chloride) membrane containing a thin film of Jeffamine T-403. The technique was tested for detection of TNT and DNT vapors that yielded different absorption spectra [100].

A portable and automated field screening, for assessing contamination by TNT in military sites, was reported by Pamula in 2004. Microliter droplets of TNT in dimethylsulfoxide and KOH in water are reacted on a chip in a programmed way, to form the typical color. The reported detection of TNT is linear in the range of 12.5–50 μg/ml [101].

Perhaps the latest addition to this arsenal is the Lawrence Livermore National Laboratory "ELITE™" explosives detection device. Similarly to the aforementioned ETK, it can detect traces of military, as well as homemade explosives, by applying the common Meisenheimer and Griess reagents. Because of the addition of a heating device and efficient swiping for sample collection, the reported sensitivity of ELITE™ is 2–50 times higher than that of other commercial field tests [102]. For example, ELITE™ detection limits for TNT, 2,4-DNT, and tetryl were found to be 50, 100, and 50 ng, respectively. Lower thresholds (25–50 ng) were reported for PETN, RDX, HMX, and NC [102].

Colorimetric field tests for TATP and HMTD were described in Section 5 dealing with peroxide-based explosives. This group contains Keinan's "PET™" [85] (E. Keinan, Personal Communication, February 2006) and the kit developed by Schulte-Ladbeck et al., which involves also a preliminary stage to avoid false-positive responses by non-explosive peroxides [86]. The color change of molybdenum hydrogen bronze suspension upon reaction with TATP was recommended also as a field test. Exposure of filter paper strips which were soaked in butanol suspension of the molybdenum compound to TATP or hydrogen peroxide vapors rapidly bleaches the blue color [87, 88].

The colorimetric reaction of urea nitrate with *p*-DMAC [91] was also adopted as a field test, "UN-1™." The reagent (0.4% in ethanolic solution) is sprayed on the sample, or on the suspected area, and the appearance of a red color within 1 min indicates the presence of urea nitrate [103].

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CHAPTER 5

NUCLEAR TECHNOLOGIES

P.J. Griffin

Contents

1. BASIS FOR DETECTION

X-ray-based material interrogation methods typically use X-ray interactions with the electrons in a material to determine the material density and sometimes the average atomic number. Nuclear-based interrogation methods involve probing the nucleus of an atom rather than the electron cloud and open the possibility of using the isotope-specific nuclear cross sections, the probability of an interaction, to determine the elemental constituents in a material. Nuclear-based interrogation approaches include, but are not restricted to, an interrogation with neutrons as the probing radiation. An interaction with an atom in the test material is typically signaled to the detector as either a reduction in the transmission of the probing radiation or by the detection of a

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secondary radiation associated with the nuclear interaction. A number of nuclear-based interrogation approaches have been investigated with respect to their potential for explosive detection. Some nuclear-based explosive detection algorithms use a combination of detection algorithms to improve the accuracy of the material identification.

The following sections present a summary of the physics that underlies the nuclear detection technologies, a survey of neutron-based detection approaches, and an overview of non-neutron-based nuclear detection technologies.

2. PHYSICS UNDERLYING NUCLEAR DETECTION METHODS

2.1. Detection principles

The following subsections present background material on the physics and nomenclature used to address the nuclear detection technologies. The subsections are divided into neutron- and non-neutron-based nuclear detection methods.

2.1.1. Neutron-based detection

Neutrons are uncharged particles, so when they irradiate materials they interact by way of nuclear interactions with the neutrons and protons in the nucleus of the atoms of the target material. For most target materials, the neutron cross section, or probability of interaction, is much smaller than that for a photon with the electron cloud surrounding an atom. Thus, the neutrons have a greater penetration range. Because of this ability to penetrate deep into dense materials, neutron interrogation has been proposed for explosive detection in small items, such as passenger bags, as well as for large cargo containers. When neutrons interact with materials, they are sensitive to the structure of the nucleus. Thus, neutrons probe not only to the elemental content of the target material, but also the isotopic mixture.

Figure 1 shows the energy dependence of the neutron cross section for representative materials/reactions. Some reactions are seen to exhibit a threshold

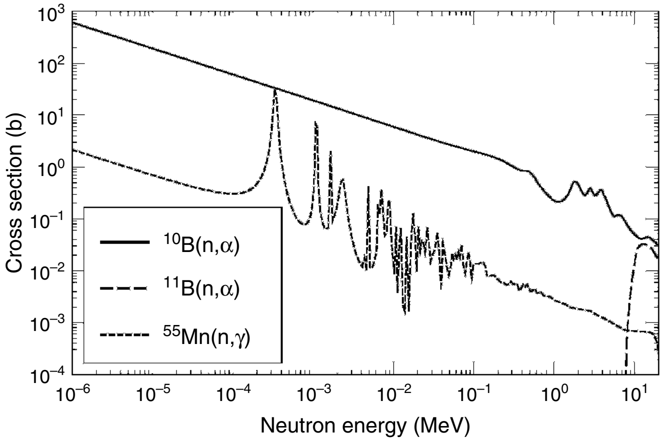

Figure 1 Variability of the neutron cross sections for different isotopes.

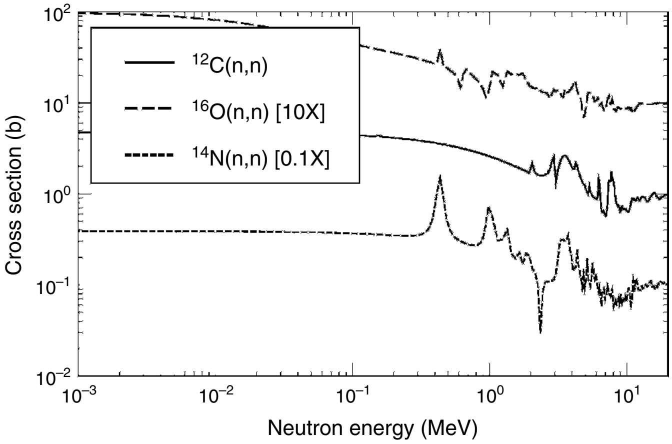

Figure 2 High-energy resonance behavior for some neutron cross sections.

energy, e.g., $^{11}B(n,\alpha)$. Neutrons with an energy less than the threshold energy are not capable of inducing the specified reaction. Two of the curves in Figure 1 [$^{10}B(n,\alpha)$ versus $^{11}B(n,\alpha)$ cross section] demonstrate the variability of the neutron cross section even for the same reaction within isotopes of a given element. Whereas photon cross sections are proportional to a power of the atomic number of the target atom,[1] the neutron cross sections vary between materials but do not have any clearly identifiable rules. Some rules for the magnitude of the cross section for specific reaction channels have been deduced, but these rules are energy-specific and are based on information on the nuclear structure of the target atoms. The nuclear reaction cross section with the lowest threshold energy in every element has a $1/v$, or $1/\sqrt{E}$, energy dependence for the low-energy portion of the cross section, where v is the velocity of the incident neutron. There is typically a complex resonance structure in the epithermal energy range (ev to keV) for (n,γ) reactions, e.g., $^{55}Mn(n,\gamma)$. Figure 2 shows that the high-energy elastic cross sections for some materials can also exhibit a resonance structure. The curves in Figure 2 have been offset to avoid an overlap of resonance structures.

Neutrons interactions include scattering (elastic and inelastic) as well as transmutation reactions, e.g., (n,α) or (n,p). The target atom is typically denoted as $_{Z}X^{A}$ where X is the symbol for the target element, Z is the atomic number (the number of electrons/protons in the target atom), and A is the atomic mass (the sum of the neutrons and protons in the nucleus). The scattering may be elastic, where the incident neutron energy is transferred to the kinetic energy of the outgoing neutron and to the target atom in such a manner that both energy and momentum are conserved, or inelastic, where the target atom is excited and left in a higher energy state. In an inelastic reaction, the excited target atom radiates the energy through

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[1] For 100 keV photons, the photoelectric cross section is proportional to $\sim Z^4$, where Z is the atomic number of the atom. For 3 MeV photons, the photoelectric cross section is proportional to $\sim Z^{4.6}$. The Compton photon cross sections are proportional to Z.

emitted gammas and returns to the stable ground state or to a metastable energy state that may subsequently decay with a specified half-life. An inelastic scattering reaction is represented as

$$\mathrm{n} + {}_{z}\mathrm{X}^{A} \rightarrow \mathrm{n} + {}_{z}\mathrm{X}^{A^{*}} \tag{1}$$

where the * in the outgoing residual atom indicates that the atom is in an excited state. In an elastic reaction, the conservation of energy and momentum imply that the average neutron energy after an elastic collision is given by

$$\overline{E_{\text{out}}} = E_{\text{in}} \times \frac{1}{2}\left[1 + \frac{(A-1)^2}{(A+1)^2}\right] \tag{2}$$

Thus, for hydrogen with $A = 1$, the incident neutron loses, on average, half of its energy. For a high atomic number target, such as lead (${}_{82}\mathrm{Pb}^{208}$ and other isotopes of Pb), the incident neutron loses, on average, only ~1% of its energy. So, whereas high atomic number materials attenuate photons, the neutrons lose very little energy through scattering by high atomic number materials. It is low atomic number hydrogenous materials that rapidly downscatter the neutron energy.

In a transmutation reaction, the incident neutron is absorbed, forming a compound nucleus that decays so that the residual nucleus is different from the target nucleus and the outgoing channel typically includes two particles. A transmutation reaction can be written as

$$\mathrm{n} + {}_{Z}\mathrm{T}^{A} \rightarrow {}_{0+z}\mathrm{r}^{1+\mathrm{a}} + {}_{Z-z}\mathrm{R}^{A-\mathrm{a}} \tag{3}$$

In this reaction, a neutron is incident on a target atom with the elemental symbol T (atomic number Z and atomic weight A). The outgoing channel has a light and a heavy particle. The light particle, indicated by an elemental symbol "r", is typically a proton, ${}_{1}\mathrm{H}^{1}$; a deuteron, ${}_{1}\mathrm{H}^{2}$; or an alpha particle, ${}_{2}\mathrm{He}^{4}$. The heavy residual atom, denoted by the elemental symbol "R," represents the target atom changed by whatever neutrons and/or protons that were transferred/picked up from the incident neutron. This reaction is often denoted as ${}_{Z}\mathrm{T}^{A}(n,{}_{z}\mathrm{r}^{1+\mathrm{a}})_{Z-z}\mathrm{R}^{A-\mathrm{a}}$ or in a shorthand notation as $(n,{}_{z}\mathrm{r}^{1+\mathrm{a}})$. Sometimes the incident neutron is absorbed. This reaction is called an (n,γ) reaction and is denoted as ${}_{Z}\mathrm{T}^{A}(\mathrm{n},\gamma)_{Z}\mathrm{T}^{A+1}$. (n,p) and (n,α) reactions, where α represents an alpha particle, ${}_{2}\mathrm{He}^{4}$, are typically threshold reactions. The (n,γ) reaction does not, typically, have a threshold energy. Thus, the lowest energy reaction is typically a (n,γ) reaction where the incident neutron is absorbed and the target atom is left in a metastable excited state that subsequently decays. The decay is typically accompanied by the emission of prompt gammas. Some elements, such as ${}_{48}\mathrm{Cd}^{\mathrm{nat}}$ or ${}_{64}\mathrm{Gd}^{\mathrm{nat}}$, have a very large thermal neutron absorption (n,γ) cross section.[2] These materials are often used for neutron shielding. For some target isotopes, e.g., ${}_{5}\mathrm{B}^{10}$ and ${}_{3}\mathrm{Li}^{6}$, there is a very large thermal neutron (n,α) cross section that extends to higher neutron energies than do typical (n,γ) reactions. These materials (boron and lithium) also play a critical role in neutron shielding. As there are no materials that exhibit a large

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[2] The superscript "nat" indicates a material with a ratio of isotopes identical to the isotopic ratio for the naturally occurring element.

capture cross section at high neutron energies, high-energy neutron shielding is often accomplished by using an hydrogenous material to downscatter the neutron and boron, lithium, cadmium, or gadolinium to absorb the low-energy downscattered neutrons.

Some reactions have a threshold energy, i.e., an energy below which the reaction cannot occur because of energetic considerations. Because there can be an exchange of energy between the particle's kinetic energy and the rest mass energy of the atoms, the energy in the outgoing reaction channel can be greater or less than the kinetic energy in the entrance reaction channel. We notate the kinetic energy of a particle as *K* and use a subscript to indicate the particle naming convention introduced in Eq. (3). The difference between the binding energy of the particles in the exit channel and that in the entrance channel is called the reaction *Q*-value. The *Q*-value is the kinetic energy released in the reaction. For a case where the target atom, T, is at rest, and the incident neutron has an energy E_{n}, the *Q*-value for the (n, ${}_{z}\mathrm{r}^{1+\mathrm{a}}$) reaction is given by

$$Q\left(\mathrm{n},{}_{z}\mathrm{r}^{1+a}\right)=B_{\mathrm{R}}+B_{\mathrm{r}}-B_{\mathrm{T}} \tag{4}$$

2.1.2. Non-neutron-based detection

Non-neutron-based detection can be based on probing the atom with other particles, such as photons, protons, muons, or by electromagnetic interrogation. At high energies, typically greater than 8 MeV, an incident photon can induce a photonuclear reaction where a neutron or proton is emitted from the target material. At higher energies, multiple nucleons (neutrons or protons) can be emitted. A compendium of photonuclear cross sections can be found in Refs [1, 2]. Modeling of photonuclear processes is implemented in some of the recent radiation transport codes, such as MCNP5, MCNPX, PICA, and FLUKA. The incident photons used to excite photonuclear reactions are typically a broad energy spectrum generated by bremsstrahlung radiation from high-energy electrons produced by linear accelerators and impacting high-*Z* targets.

Each nucleus has a unique set of excited states. The energy widths of these excited states are very narrow (<<1 eV) and they have a small lifetime (<1 ns). However, when a nucleus is excited into a state above the ground state, it isotropically emits characteristic radiation as it de-excites. Although the decay is isotropic for any given photon emission, angular correlations can exist between the multiple emitted photons in a given decay path. A technique, referred to as nuclear resonance fluorescence (NRF), uses a broad energy photon source (typically a bremsstrahlung source) to excite a target material. The isotropically emitted radiation is then detected by very sensitive high resolution gamma detectors in backward directions that are shielded from the bremsstrahlung source photons.

A giant dipolar resonance (GDR) exists in the majority of photoabsorption and photonuclear reactions. This resonance energy corresponds to the fundamental frequency for absorption of electric dipole radiation by the nucleus acting as a whole. It can be envisioned as an oscillation of neutrons against the protons in a nucleus. The GDR occurs at energies of 20–24 MeV in light material and of 13–15 MeV in heavy nuclei. A compendium of the GDR parameters is found in Ref. [3].

Protons can also exhibit very strong nuclear resonance reactions in materials. One example is the $^{13}C(p,\gamma)^{14}N^*$ reaction for a proton energy of 1.747 MeV. This reaction has a very narrow width, about 122 eV. The resonance reaction produces a photon with a very narrow spread in the emitted energy. In the case of ^{13}C, the photon is emitted with an energy of 9.17 MeV. The inverse reaction, using a monoenergetic 9.17 MeV photon, can also be used to detect the presence of ^{14}N in the target material. Nuclear resonance absorption (NRA) or gamma resonance absorption (GRA) are names given to the use of this inverse process for explosive detection purposes. The use of the forward proton-induced reaction has been proposed as a source of monoenergetic photons to be used for the interrogation of nitrogen in a target whereas the inverse absorption reaction is proposed as a material-sensitive detector of the transmitted (unscattered) photons after traversal through the test object. The energy/angle relationship for the photon resonant emission is

$$\cos\theta_R = \frac{E/Mc^2}{v/c} = \frac{p_\gamma}{p} \tag{5}$$

The resonance angle is 80.7° for the $^{14}N(\gamma,p)^{13}C$ reaction. The photon energy in the outgoing channel of the production (inverse) reaction can be affected by Doppler shifting of the emitted photons due to the recoil of the residual nucleus. Owing to this Doppler broadening, only gamma rays emitted in a 0.7° wide beam are at the resonance energy.

Alternative resonance reactions with emitted photons resonant with absorption on the constituents of explosives include the following:

- $^{15}N(p,\alpha\gamma)^{12}C$ that produces 4.44 MeV photons for 2.6 MeV incident protons
- $^{19}F(p,\alpha\gamma)^{16}O$ that produces 6.92 and 7.11 MeV photons for 1.03 MeV incident protons.

For the detection of some materials, even cosmic ray muons have been investigated as a probing radiation. Because cosmic ray muons scatter from heavier elements at larger angles than from those off of lighter elements, the trajectories of the cosmic rays has been proposed as a means of determining the location of heavyweight nuclei. Los Alamos researchers have used the background cosmic ray radiation to acquire images of uranium surrounded by lower atomic number materials.

There are other properties of the nucleus that can be probed by means other than interrogating with an incident neutron. Some nuclei, such as $_7N^{14}$, $_{17}Cl^{35}$, $_{17}Cl^{37}$, and $_8O^{17}$, have a nonspherical electric charge distribution and possess a nuclear quadrupole moment. This quadrupole moment is affected by the electronic binding of the atom within the chemical compound. When an atom with a quadrupole moment is within an electric field gradient, the quadrupole experiences a torque and precesses at a given frequency. The nucleus' precessional frequency is determined by the local quadrupole moment and by the electric field surrounding the atom. A radio frequency (RF) pulse tuned to the quadrupole precessional frequency can be used to disturb the preferred orientation. As the atoms return to the preferred orientation, they release an electromagnetic signal (at one or more frequencies) that can be analyzed. The signal is a decaying voltage picked up in the receiver coil. The signal is Fourier transformed to get a frequency spectrum. The emitted signature is unique to the atom and the local molecular environment. The relaxation time for the excited nucleus is also an important parameter in the nuclear quadrupole resonance (NQR) process. It can depend on the atom, the compound, and the ambient temperature. No external magnetic field is required for this technique, the field gradient is provided by the molecular composition of the material being interrogated [4, 5].

2.2. Neutron sources

The most difficult part of neutron-based explosive detection methods is efficiently generating the required neutrons while protecting the public from radiation exposure. Some approaches desire monoenergetic neutrons whereas other approaches require a broad energy neutron spectrum. It is very desirable to have a source that can be turned off when the detection process is not in operation. Shielding of neutrons is very difficult, requiring either large volumes for spherical divergence of the neutrons or bulky shielding (typically borated or lithiated polyethylene) for neutron downscattering and absorption.

2.2.1. Isotopic

Some materials have a spontaneous decay process that emits neutrons. Some short-lived fission products are in this class and are responsible for the delayed neutron emission from fission events. Another material in this class is ^{252}Cf that has a spontaneous fission decay mode. ^{252}Cf is probably the most useful material to use as a source of neutrons with a broad energy spectrum.

^{252}Cf spontaneous fissions have a "fast" neutron energy spectrum, shown in Figure 3, with an average energy of ~2.2 MeV. On average, 3.76 neutrons are emitted per spontaneous fission. The neutron emission rate is 2.34×10^{12} n/(s-g)

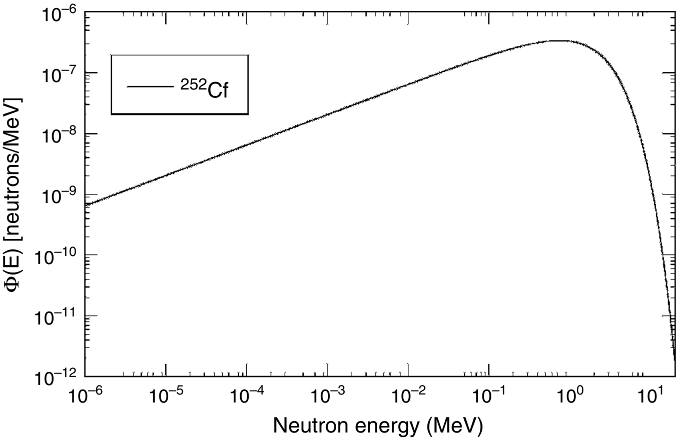

Figure 3 ^{252}Cf fission spectrum.

or 4.1×10^9 n/(s-Ci) for ^{252}Cf that has a specific activity of 5.4E2 Ci/g. ^{252}Cf has an alpha decay mode as well as the spontaneous fission decay mode.

2.2.2. (α,n) Reactions

There are many isotopes that decay by alpha emission. When these isotopes are placed in intimate contact with another material, such as beryllium, the resulting (α,n) reaction can be used as a neutron source. Beryllium is the target material with the highest neutron yield. Other targets include ^{7}Li, ^{11}B, ^{19}F, and ^{18}O. Table 1 shows the characteristics of some typical (α,n) sources.

2.2.3. (γ,n) Reactions

Photoneutron reactions or (γ,n) reactions can also be used to produce neutrons. Most materials have a high binding energy and require incident gamma rays with an energy >10 MeV to get photo-disintegration. Beryllium and deuterium are two exceptions. With these two materials, photoneutron emission occurs for incident gammas with energies of 1.666 and 2.226 MeV, respectively. Ra–Be and Sb–Be are two examples of (γ,n) sources based on the decay gammas from activated nuclei rather than photons produced from an accelerator-driven photon reaction. These decay gamma sources have a very large gamma background that is difficult to shield.

2.2.4. Accelerator-based

Accelerators can be used to create monoenergetic neutron sources using the reactions: ^{7}Li(p,n)^{7}Be, ^{3}H(p,n)^{3}He, ^{12}C(d,n)^{13}N, ^{2}H(d,n)^{3}He, and ^{3}He(d,n)^{4}He. These reactions are only truly monoenergetic (for a given scattering angle) in specific energy regions [6]. For example, the ^{7}Li(p,n) reaction has a threshold energy of 1.881 MeV for the incident proton to produce the (p,n) reaction, but when the incident proton energy exceeds 2.372 MeV, the reaction can result in the residual ^{7}Be being in an excited metastable state. At 3.697 MeV a three body breakup channel, ^{7}Li(p,n^{3}He)^{4}He, occurs. In these last two cases with a high incident energy proton, the energy partitioning of the outgoing particles results in the emission of some neutrons (at a given angle) with a lower energy than that for the neutron emission associated with the ^{7}Be residual nucleus being left in the ground state.

The range of monoenergetic neutrons that can be produced from these accelerator-driven reactions varies with the specific reaction and the energy of the incident particle. The range of commonly available outgoing monoenergetic neutron energies includes a region that goes from near 0 to 7.7 MeV in addition to the

Table 1 Isotropic neutron sources

Metric	^{241}Am–Be	^{239}Pu–Be	^{210}Po–Be
Yield (n/(s-Ci)	2.2×10^6	1.7×10^6	2.5×10^6
Alpha half-life	458 years	24,360 years	138 days
Specific activity (Ci/g)	3.4	6.2E−2	4.5E3
Average neutron energy (MeV)	4.5	3.2	4.2

energy region from 11.7 to 20.4 MeV. Outside of these two energy regions in accelerator-produced neutron sources, there will be some contamination of the outgoing neutron spectrum with lower energy neutrons.

Electron accelerators can also be used to produce high-energy electrons that impact a high-Z target to produce high-energy bremsstrahlung radiation. The bremsstrahlung radiation can then be used as a source of neutron production through (γ,n) reactions on materials such as beryllium.

2.2.5. Reactor-based

Fast fission ^{235}U metal assemblies or water-moderated reactors with enriched uranium oxide fuel are easy sources of high-intensity neutrons [$>10^{11}$ n/(cm^2-s)]. The major problem with a reactor as a neutron source is that it is not small, portable, nor easily protected in the environment desired for application as part of a typical explosive inspection system.

2.3. Detectors

Nuclear explosive detection approaches typically use particles to probe the nucleus of the target material. The interrogation procedure involves the measurement of transmitted/emitted neutron or gamma radiation. The selection of an appropriate radiation detector can be a very important part of a detection technique. Trade-offs in the detector selection involve the sensitivity of the detector, interferent reactions, cost of the detector material, logistic issues such as the need for cryogenic cooling, and possibility of radiation damage to the detector during the measurement process from other types of radiation in the operational environment.

2.3.1. Neutron detectors

Neutron detectors are often separated into two types; low-energy neutron and fast neutron detectors. Low-energy neutrons are typically detected through the use of a material/reaction with a large thermal neutron cross section, such as the $^{10}B(n,\alpha)$, $^{6}Li(n,\alpha)$, $^{3}He(n,p)$, or $^{235}U(n,f)$. The (n,f) notation indicates a fission reaction where the exit channel has a light and a heavy fission product. Figure 4 shows the cross sections for these high cross section low-energy reactions. The energy deposition of the charged particle in the exit channel is used to register a detection of a low-energy neutron interaction. In a neutron pulse-type detector, the ionization of the charged particle is measured. Signal/detector thresholding techniques are used to remove ionization events resulting from gamma interactions.

An example of a low-energy neutron detector is a BF_3 chamber. In this detector, boron trifloride is the gas in a proportional counter and serves as a target for the neutron. When a reaction occurs, the recoiling alpha and lithium particles produce ionization in the proportional chamber gas. For small (less than the range of the alpha particle or $\sim$1 cm) BF_3 chambers, the charged particle can impact the wall before it has deposited all of its recoil energy. This results in a small detected pulse and a “wall effect”. In mixed neutron/gamma fields with a high gamma flux,

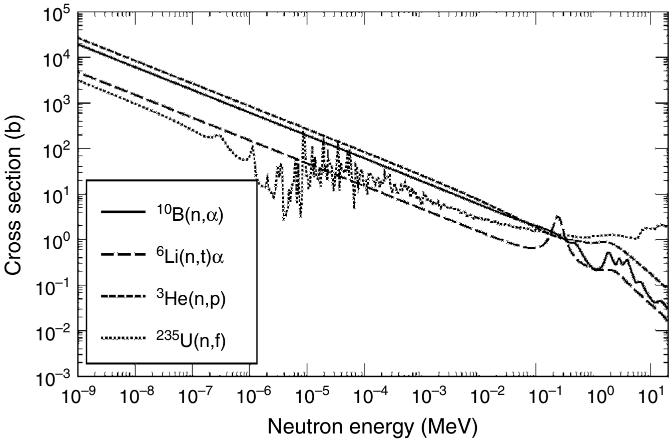

Figure 4 High cross section low-energy reactions.

pulse pileup can result in apparent gamma peaks that have the composite energy from several separate gamma-ray interactions.

An alternate approach to this use of gaseous boron as a detecting material is a boron-lined ionization chamber. Here a common proportional counting chamber is lined with boron. A proportional counter uses a fill gas that does not exhibit a significant electron attachment coefficient, such as a noble gas. In a proportional counter, the signal is based on the secondary ionization created by collisions between electrons and the neutral fill gas. Polyatomic gases, such as methane, are often added to preferentially suppress the effect of photon interactions by absorbing the photons in a mode that does not lead to further ionization. One common fill gas is a mixture of 90% argon and 10% methane referred to as P-10 gas.

Boron-loaded scintillators are yet a third way of using this high neutron cross section material in a detector. A scintillator converts the kinetic energy of the charged particles into detectable light in such a way that there is a linear relationship between the light yield and the deposited energy. The decay of the luminescence should also be fast so that a distinct light pulse can be generated. A wide range of organic plastic and liquid materials (e.g., stilbene, Eljen EJ-212, and Bicron BC-400), as well as inorganic materials (e.g., sodium-activated cesium iodide, bismuth germanate, and yttrium aluminum perovskite) can be used as scintillating materials. These materials are typically loaded with boron in this type of a detector. The scintillator is typically thin (1–2 mm) so that it is relatively transparent to its own scintillation light. Scintillators are typically less effective than ionization chambers in discriminating against gamma-ray interactions.

A fission chamber is another variation in a ionization chamber designed to detect neutron interactions. Fission chambers have the advantage of a large ionization signal (~160 MeV from the kinetic energy of the fission fragments) that permits discrimination of low neutron fluxes in the presence of a high gamma background.

Self-powered neutron detectors (SPNDs) use a material such as cadmium that has a high cross section for low-energy neutrons and produces copious gammas or betas in the decay of the excited residual nuclei. If the decay particles are gammas, a material surrounding the detector material is used to convert the gammas into electrons through photoelectric or Compton interactions. The gamma-induced electrons or beta particles produce a current that is then collected and measured directly without any externally supplied bias voltage. SPNDs are always operated in current mode rather than pulsed mode. Some SPNDs have a prompt response (e.g., Cd-based) whereas others have a delayed response due to the half-life of the beta decay reactions.

Fast neutron detection sometimes uses a hydrogenous moderator to slow down the neutrons and then employs a low-energy neutron detector as described above. One common fast neutron detector is a Bonner sphere. In this detector, a scintillator is placed in the center of a polyethylene sphere. Radiation transport calculations are used to produce efficiency curves that depend on the energy of the incident neutron. Another common fast neutron detector is a “long counter.” This detector uses a slow neutron detector (originally a BF_3 chamber) at the center of a cylindrical moderator designed so that the detector is only sensitive to neutrons incident from one side.

For neutrons with an energy greater than $\sim 1\,\mathrm{keV}$, the recoil resulting from elastic interactions can be used as a basis for the detection of ionization from a neutron interaction. Hydrogen is the most common target material for fast neutron detection using the elastic recoil energy. These detectors are often referred to as proton recoil detectors. Whereas low-energy neutron detection typically just measures the occurrence of an event or neutron interaction, high-energy detectors ($E_n > 10\,\mathrm{keV}$) often provide information on the energy of the incident neutron. For non-relativistic neutrons with incoming energy, E_n, scattering with an angle of Θ in the center of mass coordinate system (θ for the recoil nucleus in the lab coordinate system) from a target atom with atomic number A, the energy of the recoiling nucleus is given by

$$E_R = \frac{2A}{(1+\mathrm{A})^2}(1-\cos\Theta)E_n = \frac{4A}{(1+A)^2}\left(\cos\,\theta^2\right)E_n \tag{6}$$

The proton recoil is often measured by hydrogen-containing scintillators. Complications with the use of this type of detector relate to the mixed neutron/gamma response of the scintillating material, nonlinear light output of the scintillator with the deposited energy, loss of energy for events near the edge of the scintillator material because of the range of the proton, multiple scattering effects, pulse shape discrimination against gamma rays, and complications in the deconvolution or unfolding of the energy dependence of the detector response.

2.3.2. Gamma detectors

A wide range of methods exist for detecting gamma rays. Methods include a cryogenically cooled high-purity germanium (HPGe) detector, ionization chamber, scintillation materials, semiconductor diodes, and photoconductive detectors (PCDs). A reference such as Ref. [7] should be consulted to get specific information on the various detection approaches. HPGe detectors have excellent energy

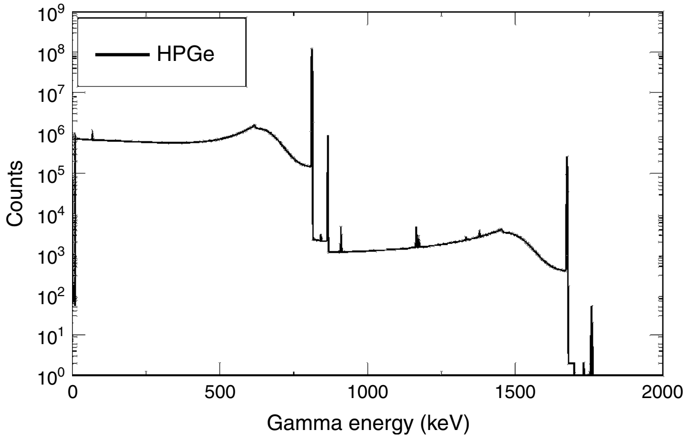

Figure 5 HPGe response to activated nickel.

resolution (~0.1%) but they are expensive and require cryogenic cooling that can present logistic difficulties. HPGe detectors are also easily damaged in neutron environments. HPGe detectors have a signal efficiency about 10× less than a NaI detector. A NaI scintillator has significantly less energy resolution. Figures 5 and 6 show simulations of the HPGe and NaI detector signal from a nickel sample activated in a water moderated reactor. Bismuth germanate ($Bi_4Ge_3O_{12}$, often denoted as BGO) and cadmium–zinc telluride ($Cd_{1-x}Zn_xTe$, often denoted as CZT) are two other common gamma detectors. The high atomic number results in a CZT detector that has a high photoelectric absorption cross section and a high efficiency for low-energy photons. This detector also has a large bandgap so it can be operated at room temperature. The BGO inorganic scintillator detector has a high density and a high atomic number giving it a good efficiency. BGO is also a

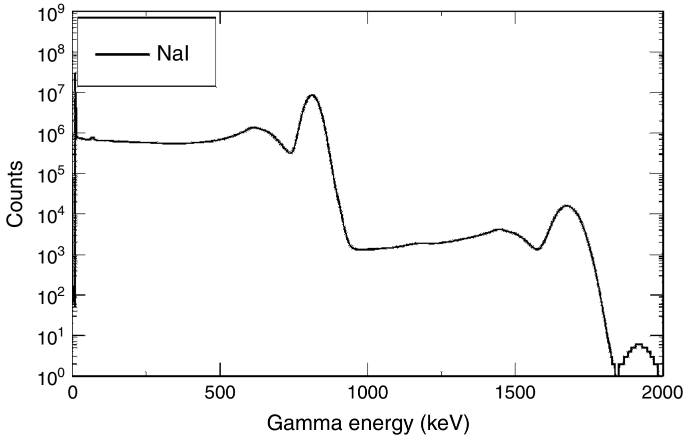

Figure 6 NaI response to activated nickel.

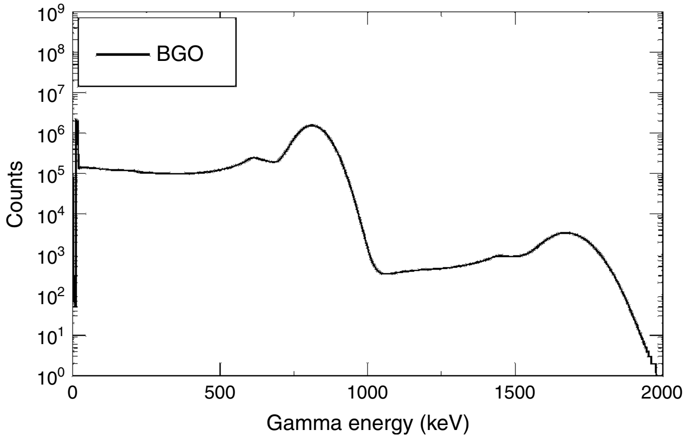

Figure 7 BGO response to activated nickel.

fairly rugged detector but it has a low light output. It is often used when high gamma count rates are more important than energy resolution. The same activated nickel gamma spectrum used in Figures 5 and 6 is used to simulate the gamma response of the BGO and CZT detectors in Figures 7 and 8.

Ionization chambers are very sensitive detectors, but they only report a dose, i.e., rad(material), metric rather than providing an energy-dependent spectrum. P-i-N diodes are less sensitive, typically measure silicon dose [rad(Si)] in the active area of the detector, but are easily damaged in a radiation environment showing increased leakage current after being exposed to a high level of neutrons. Diamond PCDs have a small signal (are less sensitive) but exhibit a very fast response (less than nanoseconds) and they can be predamaged to stabilize their response in the presence of a high neutron fluence.

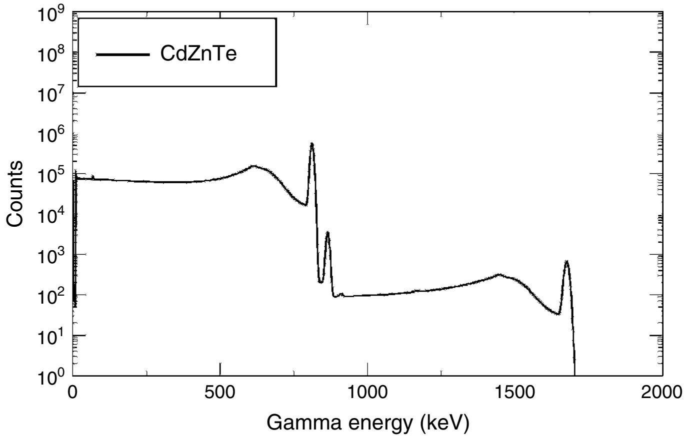

Figure 8 CZT response to activated nickel.

3. SURVEY OF NEUTRON-BASED DETECTION APPROACHES

As neutron-based technologies have evolved, the newer approaches are often refinements or extensions of the older approaches. The following survey of approaches is structured to show how the neutron-based detection technologies have evolved.

3.1. Thermal neutron activation

One of the first nuclear technologies [8] proposed for explosive detection was thermal neutron activation (TNA). This is also one of the most thoroughly investigated nuclear explosive detection technologies [9, 10]. This technology employs a thermal energy neutron source to interrogate a sample, e.g., an airport passenger bag. Because high-energy neutrons are easier to generate than thermal energy neutrons, implementations of this technology often employ a fast neutron source and a scattering material to degrade the source neutron energy before it is directed onto the sample. When the thermal neutron passes through the material in the sample, there can be capture/absorption reactions with the elements in the sample. Nitrogen has a large thermal capture cross section (~75 mb) relative to the capture cross section for other elements found in explosives. The nitrogen capture reaction also emits a very distinctive 10.8292 MeV gamma (along with other gamma rays). The thermal capture and emission of the 10.8292 MeV gamma is delayed by the neutron thermalization time, which makes it easier to detect in the presence of many other inelastically scattered gammas. Gamma detectors measure the 10.8292 MeV capture gamma and produce a measure of the nitrogen content in the section of the sample being interrogated by the neutron beam. In practice, the neutron beam is collimated and scanned over the bag. The resulting nitrogen map is used to determine the possible presence of explosives.

Various neutron sources have been proposed for use with this detection technology [9]. The TNA approach uses a thermal capture reaction, so it does not require an accelerator to produce a monoenergetic neutron source. Spontaneous fission neutrons from a ^{252}Cf source are the most commonly proposed source [11, 9] and was employed in a pre-production prototype of TNA. This prototype used a 150 μg 80 mCi source. One implementation of TNA weighted 28,000 lb, required a 41 m^2 area, cost $1.4M for fabrication, and had an estimated $0.705M annual operation cost [12]. Early thermal neutron work [13] proposed the use of antimony–beryllium, radium–beryllium, and polonium–beryllium sources that used an (α,n) reaction to produce the broad-spectrum neutrons. These sources proved to have too small a neutron yield for practical development and attention was turned to accelerator sources. Neutrons from the accelerator-based ^{2}H(d,n)^{3}He and ^{9}Be(d,n)^{3}He sources have been proposed for more recent implementations of TNA [14, 15]. The advantages of the accelerator sources for TNA relate to a higher neutron yield and the ability to turn off the neutron production.

The major advantage of the TNA technology is that it can produce a nitrogen map and many important explosives have a high nitrogen content. The neutrons employed by this technology will also easily penetrate metal screens that may shield conventional X-ray methods. The most important problem with this approach is that nitrogen content, by itself, is not distinctive enough to prevent a large false alarm rate. Because of this, attempts have been made to combine the TNA nitrogen map with the density map from conventional X-ray methods. One example of this combined technology is the XENIX system [14]. The detection probability and false alarm rate of this combined technology did not meet the Federal Aviation Administration (FAA) explosive detection system (EDS) certification specifications in effect at that time.

Other disadvantages of this system include its large weight, high cost, and the presence of a radioactive source. The fielding of TNA prototypes demonstrated that none of these issues preclude the application of the technology, they just suggest that other technologies are preferable. Shielding and collimation of the thermalized neutron beam are significant challenges to this technology. Refinements to the TNA prototype have been proposed, which address decreases in the size and weight.

Pre-production TNA prototypes exist, but there is no obvious path for the development of a stand-alone TNA system that meets the FAA/TSA EDS certification requirements for large checked baggage. The TNA technology development resulted in advances in several areas and highlighted the importance of including bag clutter in determining detection performance [16]. A comparison of the potential of the TNA technology for checked baggage with the detection performance demonstrated by current tomographic X-ray systems suggests that a neutron- or accelerator-based technology that can only detect nitrogen is not a good candidate for deployment. Further development of neutron- or accelerator-based explosive detection technologies has been concentrated on methods that can also provide quantitative metrics on the presence of other elements, in addition to nitrogen, that are in explosives and in typical checked bags. The better detection potential that comes from having quantitative information on the presence of other elements in typical bags, such as carbon, oxygen, and hydrogen, is required to offset the weight, volume, and operating cost disadvantages of neutron- or accelerator-based approaches.

3.2. Fast neutron activation

The fast neutron activation (FNA) technology was an outgrowth of attempts to get more information than nitrogen content from neutron interrogation approaches. In FNA, high-energy neutrons, rather than thermalized neutrons, are used to scan the contents of a container. Gammas from neutrons inelastically scattered on oxygen (6.13 MeV gammas from ^{16}O), carbon (4.44 MeV gammas from ^{12}C), and nitrogen (5.11, 2.31, 1.63 MeV gammas from ^{14}N) atoms in the container are measured by detectors that surround the container. High-energy neutrons are required to excite these inelastic reactions. A monoenergetic neutron source simplifies the analysis of the inelastic gamma signatures. Most FNA implementations use a deuterium–tritium ^{3}H(d,n)^{4}He reaction (DT) to produce a monoenergetic $\sim$14 MeV neutron source. The DT reaction is one of the easiest reactions (low incident particle energy, typically ~150 keV deuteron, onto a tritiated target, high cross section) to produce monoenergetic neutrons. Another reaction used is the deuterium–deuterium $^{2}H(d,n)^{3}He$ reaction (DD) that can produce monoenergetic neutrons with energies between 2.45 and 7.71 MeV [17] (depending on the energy of the incident deuteron).

The inelastic scattered gammas from nitrogen are very weak and hard to detect in the detector pulse continuum. With low-energy resolution gamma detectors (such as NaI) the 5.11 MeV gamma coalesces with escape peaks from the ^{16}O inelastic lines. Various detector options can be employed to improve the detection of the nitrogen gamma signature, such as the use of high-energy resolution HPGe or the use of anti-Compton shields with NaI detectors. These detector options raise other considerations such as the detector time resolution and the cost of the detectors. In response to this difficulty in using FNA to measure the nitrogen content, variants of the FNA approach use a microsecond (μs) or faster pulsed neutron source and a time-dependent detection of the neutron capture signatures from nitrogen. A later section will discuss this variant in more detail. The neutrons that are thermalized in a target being analyzed are used to measure the nitrogen content with the same capture reaction that was used in TNA. In a typical airport passenger checked bag, the small amount of material and small neutron interaction cross sections result in only a small percentage (~1%) of the fast (14 MeV) neutrons being thermalized within the bag material itself and the neutron thermalization time in a hydrocarbon, such as plastic, is about 0.2 ms.

One FNA approach is referred to as pulsed interrogation neutron and gamma (PING) [18]. In this approach, an accelerator is used to produce 14 MeV neutrons from the DT reaction. The accelerator is pulsed at about 8 kHz with a 7 μs wide deuteron pulse. In addition to nitrogen, sulfur (5.42 MeV gammas from ^{32}S) and chlorine (6.111 MeV gammas from ^{35}Cl) have been detected with PING using the thermal capture gamma signature. Chlorine detection may be important in the detection of some non-nitrogen-based explosives and in the detection of some drugs, such as cocaine. Sulfur can be important in the detection of some chemical warfare agents.

Significant weight, volume, and operating costs are commonly associated with the installation and operation of an accelerator to produce neutrons in an airport environment. However, small inexpensive sealed tube neutron DT kHz-pulsed accelerators are available [19]. The issues with these sealed tube neutron generators is their relatively low neutron yield (typically about 10^{10} n/s) [20, 19] and short tube lifetime (typically less than 2000 h at high flux operation). Sealed tube neutron generators can also exhibit stability problems during operation [21]. Recent advances in sealed tube sources is addressing some of these limitations.

Even though the accelerator portion of a DT system is small, the 14 MeV neutron shielding requirements are very stressing and can make insignificant any savings in the total system weight and volume. The 14 MeV neutrons are emitted in a nearly isotropic angular distribution and take more shielding (on a per neutron basis) than do the fission spectrum neutrons (~2 MeV) from a ^{252}Cf source. Some neutron production reactions (e.g., $^{9}Be(d,n)^{10}B$ as used for pulsed fast neutron transmission spectroscopy (PFNTS) discussed in Section 3.4) use a higher incident energy particle and produce a more forward-peaked neutron emission that is much more efficiently collimated and focused on the target region of a sample [21].

FNA systems only produce a 2D view with no depth profile. The systems usually have large a pixel size and subsequently a poor image. The pixel size is related to the size of the collimated incident neutron beam and the spread of the neutron beam while traversing the thickness of the container.

The 2D view produced by this system is a critical limitation. Several approaches have been suggested to address this limitation. One such approach, discussed in the next section, is to use the associated particle method to determine the direction and timing of the source neutrons. Others have suggested the application of imaging processing techniques that can vary the location of a focal plane to provide a 3D image while using an isotropic uncollimated and continuous neutron source. The most popular refinement to FNA is the use of a pulsed neutron source. The pulsed fast neutron analysis (PFNA) method, addressed in Section 3.5, can provide the needed 3D information.

3.3. Fast neutron-associated particle

This technology is a refinement of the sealed tube DT neutron source FNA approach. In fast neutron-associated particle (FNAP), the detection of the associated alpha particle recoil is used to specify the time and direction of the neutron emission. The DT neutron source uses the ^{3}H(d,n)^{4}He reaction. The reaction product consists of a 14 MeV neutron and a 3.5 MeV alpha particle. In associated particle imaging (API) [22], the alpha particle is detected by a position-sensitive alpha detector. The site of the alpha particle can be combined with simple kinematic considerations to determine the direction of the emitted neutron. The timing between the alpha detection and any subsequent gamma from neutron inelastic scattering can be combined with the geometry, the velocity of the neutron, and the velocity of the photons, to estimate the depth in the sample where the inelastic reaction took place. Thus, with associated particle detection, the inexpensive sealed tube DT application of the FNA approach can be used to produce a 3D image.

One implementation of this approach is referred to as associated particle sealed tube neutron generator (APSTNG) [20]. Some proposals [23] have been made to combine the APSTNG time-correlated 3D image information with the “not time-correlated” and “not image-related” slow neutron capture gammas. These approaches incorporate an array of neutron detectors so that neutron transmission spectroscopy can be performed. Unfortunately, implementation details have not been developed on how these detection approaches can be applied with any degree of synergy or data fusion, rather than in a strictly additive sense.

Because the neutron direction is known, the FNAP approach does not require the use of collimators to focus the incident beam and there is no need to pulse the source. However, as the neutrons are emitted in an essentially isotropic distribution, many neutrons still fail to impact the target bag and neutron shielding is needed in all directions surrounding the source and bag regions. In addition, the scattering of the neutrons in the shielded material along with the resulting inelastic and capture gammas produces a significant background that may interfere with the detection of the prompt gammas from the inelastic events produced in the target material.

The time resolution of the alpha and gamma correlated detection in FNAP is limited to about 1 ns. This results in a spatial depth resolution for the inelastic reaction of about 5 cm. The edge smearing from the deuteron spot size and neutron scattering within the bag similarly limit the resolution in the x and y directions. Thus, this approach typically has used a detection voxel of ~5 cm × 5 cm × 5 cm.

Dead time considerations in the alpha particle detection limit the count rate, and hence limit the neutron flux that can be used with this approach. This means that large scan times will probably be required with most implementations of this approach.

The incorporation of associated alpha particle detection in a sealed tube neutron generator (STNG) appears to severely aggravate the concerns over the limited neutron flux and tube lifetime previously detailed for STNG FNA approaches. A mean time to failure of some APSTNGs at a neutron flux of 10^7 n/s is about 200 h [24]. Work is continuing to improve this mean time to failure.

Signal-to-noise considerations make most neutron-based explosive detection approaches very difficult to implement. The basis for combining multiple detection approaches (FNA, along with thermal gamma detection and neutron transmission spectroscopy) in a FNAP application that preserves the small volume advantage of a APSTNG remains to be established. There are distinct advantages associated with the API approach, but the concomitant reductions in available neutron flux, issues of tube lifetime, and the intrinsic poor spatial resolution must be taken into consideration for potential applications.

3.4. Pulsed fast neutron transmission spectroscopy

In the PFNTS method, a collimated broad energy (0.5–8 MeV) or "white neutron" neutron beam is passed through the material being examined. The energy-dependent neutron transmission is measured. By comparing the energy-dependent attenuation of the source neutron spectrum, the ratios of hydrogen, oxygen, carbon, and nitrogen in the bag volume elements can be determined [25]. A fictitious element "X" with a smooth energy-dependent cross section is often considered [26] to help normalize the transmitted number density. This element "X" is intended to represent a smooth neutron attenuation that can be attributed to elements not specifically represented in the hydrogen/oxygen/carbon/nitrogen decomposition. For every pixel in the target, the energy dependence in the transmitted neutron spectrum is used to unfold the relative amounts of these five elements (hydrogen, oxygen, carbon, nitrogen, and element "X"). Figures 9 and 10 show how projections in these dimensions can be used to distinguish the presence of explosive and, often (~72% of the time [27]) even to identify the type of explosive. A set of 38,000 normalized elemental measurements were made by the University of Oregon on a set of actual airline suitcases [28]. The contours in Figures 9 and 10 are drawn to enclose approximately 95% of the points that fell in the indicated categories, that is, in benign non-threat suitcases and in suitcases where threat-level quantities of the indicated explosive catagories were

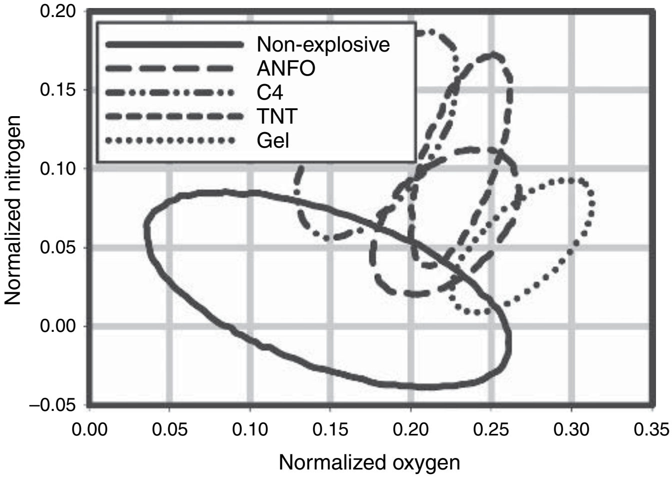

Figure 9 Nitrogen/oxygen distribution in explosive and non-explosive paths in cluttered bags.

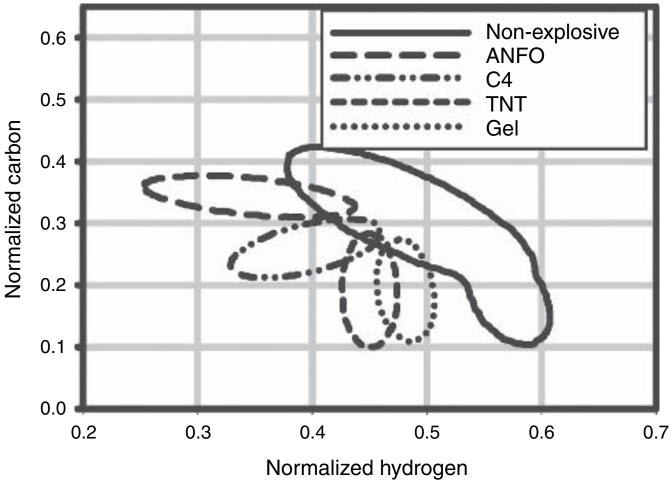

Figure 10 Carbon/hydrogen distribution in explosive and non-explosive paths in cluttered bags.

concealed. The overlap in the contours for explosive and non-explosive paths in Figure 9 indicates why projected-path nitrogen-only detection schemes have a very difficult task if one requires a very low false alarm rate (<5%) from non-threat suitcases. In addition to the obvious overlap in the threat and non-explosive contours seen in the figures, one must also keep in mind that these contours only represent the 95% envelope. Because the non-explosive contour was also drawn to encompass about 95% of the benign non-threat points, there is a wide dispersion of the remaining 5% of the non-threat points over the nitrogen/oxygen mapping space, including the area enclosed by the contours for the various explosive threat categories. The outliers in the distribution of "nonexplosive" points in the raw data [28] show how difficult it is to eliminate the possibility of a false alarm without significantly impacting the probability of detecting the explosive.

In some applications of the PFNTS method, a 5D representation of the elemental composition and the spatial distributions of "potentially explosive" adjacent pixels are used to support the detection algorithm. Various algorithms can be used to reduce this 5D elemental information into an "explosive potential" for a single pixel. Variations in the detection algorithm can increase the basis set beyond the nominal five elements. The Tensor algorithm considers another element Y, which is changed from element to element within a specified set of cross sections during a regression calculation until a best fit is obtained. Different spatial correlation algorithms can be used to further reduce the map of "explosive potential" metrics into a yes/no decision on the presence of an explosive in the test article. The University of Oregon refers to their detection algorithm as a "B-matrix" and bases their "explosive potential" metric on comparison with the explosive/non-explosive probability seen in a simulation database. Separate "B-matrices" are maintained for each explosive class that the algorithm is designed to detect. The Tensor work uses a neural network trained on a set of explosive and non-explosive bags.

The PFNTS approach requires the use of a tightly bunched, pulsed neutron source. Time of flight is used to determine the energy of the transmitted neutrons. This width of the initial neutron pulse and the time resolution of the time-of-flight measurement limits the energy resolution of the transmitted spectrum. Flight paths of 4–10 m are commonly used. The narrow peaks in the interaction cross sections will not be seen in a typical PFNTS measurement, but will be smeared out by the energy resolution of the detectors [29]. Thus, the element identification in this approach depends upon the broad energy-dependent structures in the cross sections, not the narrow resonances.

Because this method examines the energy-dependent neutron attenuation, it is critical that a broad energy neutron source be employed. This rules out $^{2}H(^{2}H,n)^{3}He$ (DD reaction) and $^{2}H(^{3}H,n)^{4}He$ (DT reaction) sources that also have a restricted energy spectrum. To get a reasonable neutron flux for high-energy neutrons (up to 8 MeV is strongly desired for elemental identification), accelerators are generally required. $^{9}Be(d,n)^{10}B$ or $^{9}Be(p,n)^{9}B$ reactions are candidate neutron sources [30]. The accelerators required to exploit these neutron-producing reactions need a high current ($\sim$10 mA peak current, ns pulse width, and ms repetition frequency) and a fairly high-energy incident source particle ($>$4 MeV in the case of the deuteron-initiated reaction). Most researchers in laboratory PFNTS experiments have utilized a deuteron accelerator and the $^{9}Be(d,n)^{10}B$ reaction.

3.5. Pulsed fast neutron analysis

One of the most popular refinements of FNA involves the use of a pulsed neutron source. There are many options for the neutron accelerators used for PFNA. One representative approach is the use of a 300 μA $^{2}H^{-}$ injector with a 6 MeV deuteron accelerator as a DD source for neutrons [31, 32]. All of the PFNA approaches require a very tightly bunched neutron pulse, usually a beam with a 1–2 ns full-width at half-maximum (FWHM) [18, 33, 21]. This nanosecond pulse width represents the current state of the art for accelerators, and, when coupled with the neutron time of flight, determines the minimum spatial resolution within the depth of the bag. For a 6 MeV neutron and a 1 ns neutron pulse, the spatial resolution within the depth of the test object is limited to about $1.4 \times 10^6 \sqrt{E_n}\,\Delta t = 3.43$ cm.

The literature reports PFNA conceptual designs that use an accelerator pulse repetition rate of 5–15 MHz with DD sources and 8 kHz with DT sources. These high current short pulse width and high repetition rate accelerators are large and heavy. A pulsed tandem cascade accelerator is typically about 5 ft in diameter, 25 ft long, and 6 ft high. A deuteron Pelletron Van de Graff weighs about 4500 kg. The size and weight are the principal issues in the airport integration of this technology. Approaches have been suggested to significantly reduce the size and weight of the required accelerators and to ease the airport integration issues. Work on advanced accelerator designs is continuing.

A proposal has been made for a PFNA-based system designed to detect illicit materials for air cargo inspection (ACI). This system is referred to as PFNA ACI. The PFNA ACI is a proprietary design that utilizes a tandem Van de Graff accelerator to accelerate deuterons. The neutron beam is collimated in a scan arm and focused on the front surface of the container. Testing has been conducted on aircraft LD3 container as well as truck cargo trailers.

There is considerable momentum behind an investigation of the potential of a PFNA system. A prototype of a PFNA system has been tested at the Ysleta Port of Entry (located near El Paso, Texas) on truck cargo containers. Projects on ongoing to have a PFNA system tested in an airport environment.

The first step in the detection algorithm is to use the detected gammas to produce “image files” containing the basic scan carbon, oxygen, and nitrogen density in each voxel. The radiographic neutron attenuation and the elemental density images are then used to derive a hydrogen image file. All elements that scatter but do not absorb neutrons are grouped into the hydrogen image file. The image files are then optimized using smoothing, contrasting, and artifact removal. As the volume-dependent cargo composition is approximated by the radiographic measurements, this information is fed back into the algorithm to refine the estimates for the elemental densities in the voxels. A typical scan produces a large quantity of data. The PFNA prototype systems have used a discriminant analysis, a neural net algorithm, and the input elemental density images to determine if each voxel might constitute an alarm area. Each voxel can be tagged as either “benign,” “explosive,” or “opaque.” The parameters in the discriminant analysis include various elemental densities as well as more complicated features represented by sums, products, and ratios of elemental densities. Thresholds for the discriminants (densities, density ratios, and estimated statistical significance) are considered in the analysis algorithms. The analysis algorithms also contain a “connectivity” algorithm that can place connectivity requirements based on the similarity of elemental features in adjacent voxels. Pixel connectivity is used to relate the potential threat to the minimum threat quantities being considered for a specific threat material. The material density, elemental ratios, and pixel connectivity features are combined before an algorithm-based region alarm is raised. The "connectivity" algorithm includes features (threshold and discriminants) that are averaged over the connected pixels.

Filters are sometimes derived from test cargo calibration runs to optimize the explosive detection. The PFNA detection algorithm can be totally automated but previous demonstrations (prior to the 2005 Ysleta Port of Entry testing) have used operator intervention to evaluate the basic scan alarm regions before a directed scan is made of the selected basic scan alarm regions.

4. SURVEY OF NON-NEUTRON-BASED NUCLEAR DETECTION METHODS

The following sections detail some of the nuclear detection technologies that are not based on the explicit use of neutrons. Most of these detection technologies are based on material interrogation using electromagnetic radiation that interacts with atoms and gives off a signature according to the properties of the target nuclei.

4.1. Nuclear resonance absorption

The NRA explosive detection approach is quite different from the neutron-based detection technologies discussed in the previous sections. The NRA method uses a high-energy photon to interrogate the nitrogen content in the target material (cargo) through the $^{14}N(\gamma,p)^{13}C$ reaction. Because this approach uses an incident gamma it is sometimes referred to the GRA method. NRA has been considered for the detection of explosives in cargo because the high-energy photon has the penetration needed for container inspection systems. The original application of NRA to explosive detection was done by Triumph [34]. Work on NRA has been conducted by Soreq [35] and Los Alamos National Laboratory [36]. Grumman has also been involved in NRA development activities. The Grumman work emphasized the advances in the accelerator design (high target current, target cooling) required for the application of NRA to cargo. Between 1978 and 1996 the FAA spent about \$12.1M [37] on the development of an NRA system for explosive detection.

The NRA detection method is based on the 122 eV wide giant resonance in the $^{14}N(\gamma,p)^{13}C$ reaction at an incident photon energy of 9.17 MeV. This resonance reaction has a peak resonance differential cross section of ~200 mb and an angle- and energy-integrated resonance cross section of ~4 b. Even at the resonance energy, the 9.17 MeV photons are very penetrating (7 cm of liquid nitrogen provides only 10% beam attenuation). The generation of the high-intensity incident 9.17 MeV photon beam is one of the principal challenges associated with this NRA approach. One approach is to use a filtered bremsstrahlung source, but this option has major signal-to-noise issues. The approach used in all previous demonstrations of NRA for explosive detection is to use the $^{13}C(p,\gamma)^{14}N$ inverse reaction to produce the photons. Due to the doppler shift of the recoiling ^{14}N, only the gamma rays emitted in an 0.7° wide beam at 80.7° are at the resonance energy. The accelerator concepts proposed for this inverse reaction with a 1.745 MeV incident proton include a radio frequency quadrupole (RFQ) pulsed linac and an electrostatic continuous wave (CW) accelerator [38, 39]. A representative proposal for cargo explosive detection is for a very high current, 10 mA, accelerator with a 1 cm beam spot, a 25 keV beam spread, a 600 μs pulse width, and a 10 Hz pulse repetition frequency. NRA prototypes have used a 0.5 mA beam current. The major challenges for the design of this accelerator are the proton heating of the target, the associated potential target degradation, and detector interference from gammas produced in the accelerator target materials.

Bismuth germanate (BGO) scintillator detectors (temperature stabilized and with a 15% average energy resolution) have been used in NRA detection systems [40] but interference from other proton-induced gamma rays provides a high background signal. To exploit the selective absorption of the 9.17 MeV photons in the nitrogen contained in explosives in cargo containers, one would like a gamma detector that is particularly sensitive to the transmitted 9.17 MeV photons. Soreq [41] has developed a nitrogen-rich (31% by weight) ^{14}N-based ionization detector liquid scintillator based on di-methyl-tetrazole that is resonance sensitive (24% efficient for resonant photons) and is well suited for the explosive detection application.

In addition to the 9.17 MeV photon transmission, the NRA approach needs a background gamma measurement to assist in compensating for the mass-dependent attenuation (non-resonant absorption) of the photons in the cargo. Prototype NRA systems have used gammas from the ^{19}F(p,$\alpha\gamma$)^{16}O reaction produced in the target for this purpose.

One serious disadvantage of the NRA method is its limitation to detecting just nitrogen. The work with TNA has suggested that a nitrogen-only detection method is not a good candidate for explosive detection at the FAA requirement levels (high P_{d}, low P_{fa}, small explosive quantity). Other resonance reactions on ^{12}C and ^{16}O have been suggested but they have not been demonstrated to be feasible for the explosive detection due to the narrow width of the proposed resonances and the inability to exploit the inverse reaction for efficient production of the required resonance energy photons because of the three-body breakup inverse reaction that has no defined resonance angle.

Another disadvantage with NRA is the requirement for very advanced high current accelerator. This accelerator will have all of the disadvantages (large size, large weight, radiation shielding) associated with the neutron-based accelerators.

4.2. Nuclear quadrupole resonance

NQR is an electromagnetic interrogation technique that probes with radiation in the MHz frequency range. Unlike nuclear magnetic resonance (NMR) techniques that require a large static magnetic field to orient the nuclei in the target material, NQR does not require an external magnetic field. This technique makes use of the splitting of the nuclear spin states by the electromagnetic radiation interaction with the nuclear charge density in the interrogated material. The coupling between existing nuclear quadrupole moments and the gradient of the electric field determines the NQR signal. NQR provides a chemical specificity as the signal is related to the particular molecular configuration of the nuclei possessing the quadrupole moment. The NQR detection is restricted to crystalline solids; amorphous materials, and liquids are not detected. The physics behind this detection technique was addressed in Section 2.1.

In NQR, the electromagnetic radiation flips the spin of a nucleus with a quadrupole moment. As the nucleus relaxes, it emits a unique signal. This approach has been investigated for use in the detection of land mines and for small explosive masses in mail [42]. The chemical specificity of this approach and its ability to detect small threat quantities of some explosives, such as RDX are attributes that make it useful in some explosive detection scenarios. The relaxation time for the material determines how rapidly the electromagnetic pulse sequence can be repeated. Some materials, such as PETN, have a long relaxation time making multiple pulse interrogation approaches more time consuming. There is a temperature sensitivity to the relaxation time. Thus the interrogation process typically uses pulse sequences parameters that are effective over the probable temperature range for the inspected materials [43].

The major drawbacks of the NQR approach are (1) not all explosives have a NQR signal (either nitrogen and chlorine are not present, or they are not in a position where there is a gradient in the electric field); (2) material can be shielded from the radiofrequency interrogation by thin metallic containers; and (3) there can be interference from AM band radiofrequency signals. Another important limiting consideration for this interrogation is the thermally generated internal noise. This noise can increase the time required to acquire the signal. When metallic shielding is present, this presence is clearly indicated and a shield alarm can be raised rather than a false positive or false negative. The presence of piezoelectric and ferromagnetic materials in an inspected container can also give rise to spurious signals that can mask the true NQR signals. The effect of these spurious responses can be reduced by using specially designed pulse sequences. Because of the first two limitations of this approach (metal shielding and limited scope of explosive detection materials), NQR will probably have a restricted role as a stand-alone explosive detection approach. But, because of its very good chemical specificity and sensitivity, it can play a significant role in (1) in "systems approaches" where sensor fusion is used and (2) in the alarm resolution of detections from other explosive detection systems.

4.3. Nuclear resonance fluorescence

The physics foundations for NRF were presented in Section 2.1. This technique uses photons to excite the nucleus that then emits characteristic gamma radiation as it de-excited. The de-excitation structure is unique to the target nucleus so this technique provides very good elemental/isotopic identification. However, the detection of the high-energy (2–10 MeV) narrow line gamma emissions will require a high-resolution detector, such as an HPGe detector, that is expensive and probably[3] requires cryogenic cooling. The source of the incident photons is typically bremsstrahlung radiation. This is a very inefficient photon source and presents significant radiation shielding issues.

The NRF explosive detection technology is much more immature than are the NRA, PFNA, and NQR approaches. Whereas PFNA and NQR have prototype systems and are examining engineering trade-offs for specific applications, NRF is at the stage where basic physics experiments are being performed in science laboratories.

5. PROBLEMS WITH THE USE OF NUCLEAR TECHNIQUES FOR EXPLOSIVE DETECTION

The previous sections detailed the performance of nuclear detection technologies. The reader will see that these technologies have some important advantages, including their potential for elemental identification and ability to penetrate deep into cargo containers. Unfortunately, nuclear technologies also have some important disadvantages. The following sections briefly describe some of these disadvantages.

5.1. Field deployment of neutron sources

Nuclear detection approaches that use radioactive isotopic sources (e.g., ^{252}Cf for spontaneous fission and asociated neutron emission or ^{60}Co for gamma emission) will have to obtain state and federal licenses to field the equipment and abide by applicable health and safety regulations. The licensing process takes some time to put into place and may restrict the easy movement of the detection equipment to new locations. This impacts the ability to rapidly re-locate equipment based up intelligence estimates of the behavior of smugglers. The use of fixed pre-licensed sites can help to some extent.

The presence of nuclear material at a site increases the threat from terrorists who may attempt to steal the material or to explosively disperse it. In the post-September 11 environment, the requirements for the protection of radioactive material are being significantly increased. This results in increased security costs and risks.

5.2. Health hazards because of radiation

The regulations associated with the use of radioactive source material will typically require that access to the source material be restricted from untrained individuals. This is usually accomplished by postings, interlocks, and physical barriers. In addition, the operations and maintenance personnel that may come into close proximity to the radioactive source material may be required to use personal dosimeters to

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[3] HPGe detectors can be operated at temperatures higher than that of liquid nitrogen, 77 K, but with a decrease in the energy resolution.

monitor their yearly exposure to radiation. This monitoring has logistic issues and added costs.

5.3. Material activation

When neutrons are involved in the detection process, neutron activation of the inspected materials will occur. The logistics of the operation of the detection system must be designed to ensure that no irradiated material can be activated to a degree that it requires material control measures or presents a hazard to the owner of the material. Bounding analysis of existing TNA and PFNA systems have shown that these systems can easily meet these requirements without impacting the operations protocol. Other neutron detection technologies will have to be assessed with respect to their activation potential, but this is not expected to be a significant issue for currently envisioned applications of neutron-based explosive detection systems.

5.4. Neutron shielding

Shielding of the scattered neutrons is a significant issue, but one that is confidently modeled and easily verified by measurement. Neutrons are not easily shielded. They tend to scatter without attenuation from high atomic number materials and only lose part of their energy when they scatter off low atomic number materials. The neutron fluence drops off as the square of the distance from a point source. Shielding is typically accomplished by a combination of distance and by using borated hydrogenous material. Implementation of shielding techniques will probably require that the explosive detection system be operated in a separate building and requires a significant footprint within an inspection facility (e.g., an airport or port of entry).

5.5. Public perception of radiation

The most significant issue with the fielding of a neutron-based explosive detection technology is public perception. Most people have difficulty putting into perspective low probability high consequence events. This has resulted in the word "nuclear" being associated with health risks and environmental issues even when detailed analysis shows that there is no issue.

6. SUMMARY

This paper has detailed the physical principles underlying the use of nuclear technologies that have been proposed for the detection of explosives. It has also recapitulated the current stage of development for nuclear-based explosive detection systems. Nuclear technologies are shown to have some strong advantages, but they also come with some distinct logistic issues. The future of nuclear detection technologies will depend upon the details of the threat detection requirements (set of materials and threat quantity) for a particular application. Nuclear technologies have a high penetration capability and a material specificity that makes them very promising options for small threat quantities in dense cargo containers.

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CHAPTER 6

X-RAY TECHNOLOGIES

R.F. Eilbert

Contents

1. INTRODUCTION

X-ray systems are an attractive choice for inspecting baggage and containers to identify concealed weapons and illicit substances. This inspection technology has matured over a 110-year period. Wilhelm Roentgen [1, 2] discovered X-rays in 1895 from experiments conducted with cathode ray tubes. The imaging properties of X-rays were appreciated within a matter of months. Continuous advances in X-ray generation, detection, and data acquisition have resulted in today's X-ray inspection technologies, which range from reliable industry standards to cutting-edge techniques.

Aspects of Explosives Detection
M. Marshall and J.C. Oxley (Editors)

X-ray systems provide a unique ability to detail images of the contents inside parcels. An experienced operator of such systems gleans a wealth of information from X-ray images and recognizes a wide variety of objects, both dangerous and innocuous, from the projected image. This is especially true for metallic objects that stand out clearly from the background contents. Owing to their organic makeup, many explosives do not have a distinctive appearance when imaged and might be easily overlooked. The last 15 years has seen the application of automated, computerized analysis of X-ray images for improved security.

This chapter focuses on systems in which X-rays originate from a single, fixed source position or a limited number of fixed source positions. This stands in contrast to tomographic techniques, which provide cross-sectional images or, in some cases, rendered 3-D images of the inspected item. Huge progress has been made in applying tomographic X-ray techniques for security applications. These techniques are discussed in Chapter 7 and are only mentioned here briefly. Gamma rays and X-rays are both high-energy photons and are distinguished by their process of origination rather than any difference in intrinsic quality. Gamma rays originate within the nucleus of atoms or from the disintegration subatomic particles, whereas X-rays are formed from interactions within the electron shell surrounding atomic nuclei. As such, gamma rays are generally more energetic then X-rays, but in reality there is a considerable overlap. Inspection techniques employing gamma rays can be found in Chapter 5.

2. X-RAY PHYSICS

2.1. Production of X-rays

X-ray tubes, energized by application of high voltage, are the most common and economical means for generating X-rays. The basic design of this tube has changed little since the introduction of the Coolidge tube in 1913. Figure 1 illustrates an X-ray tube schematically. A large electric potential is established between a heated filament (cathode) and a heavy metal target (anode) typically tungsten, rhenium, or molybdenum brazed into a copper base.

A high-voltage AC transformer is commonly used to create the electric potential. A bridge rectifies the voltage before it is applied to the X-ray tube. The simplest such system uses a two-phase AC primary, but the resulting tube voltage is quite variable. Capacitive filtering and/or high-frequency phasing is employed for a more constant tube potential. The heating of the filament overcomes the inherent work function of the filament metal allowing release of electrons into the vacuum surrounding the filament. The electrons rapidly accelerate toward the anode. For baggage inspection, typical voltages of roughly 150 kVp provide a sufficiently penetrating beam. Palette systems employ voltages up to 450 kVp that is effectively the upper limit for producing X-rays in this fashion.

Shaping of the cathode and hooded anode to minimize focal spot size is a specialized art. Apparent focal spots of 1 mm^2 (as viewed from the detectors) are typical for baggage systems. Tube currents are commonly in the range of

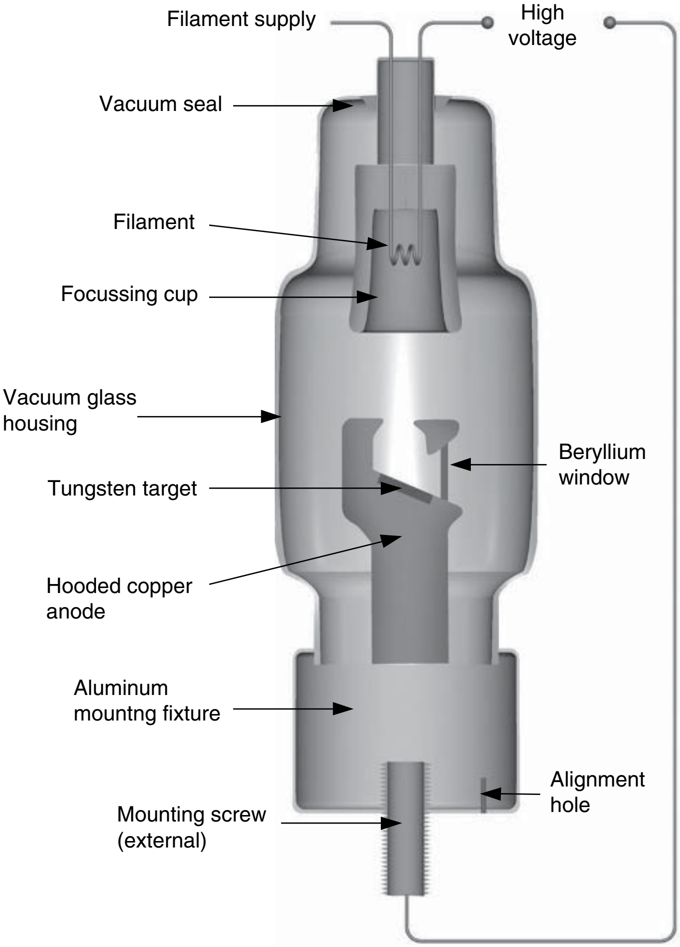

Figure 1 Schematic illustration of X-ray tube.

0.5–2.0 mA, resulting in a total dissipated power of roughly 75–300 W, which can be handled by air cooling. By comparison, medical computed tomography (CT) tubes may run at currents up to 100 mA with power levels reaching 15,000 W. These require high-speed rotating anodes, but such tubes are not employed for conventional cabinet X-ray systems.

Most of the electric power within the tube is dissipated as heat with only a few percent being transformed into useful X-rays. Higher voltage operation is more efficient as X-ray production rises roughly as the cube of applied voltage. Figure 2 shows typical spectra produced off a tungsten target. X-rays are emitted by two basic mechanisms when high-energy electrons impact onto a metal anode.

Scattering events produce a continuous spectrum of X-ray energies, but the flux tapers off to zero as X-ray energies approach the applied voltage, $E_{\max}/e$, where e is

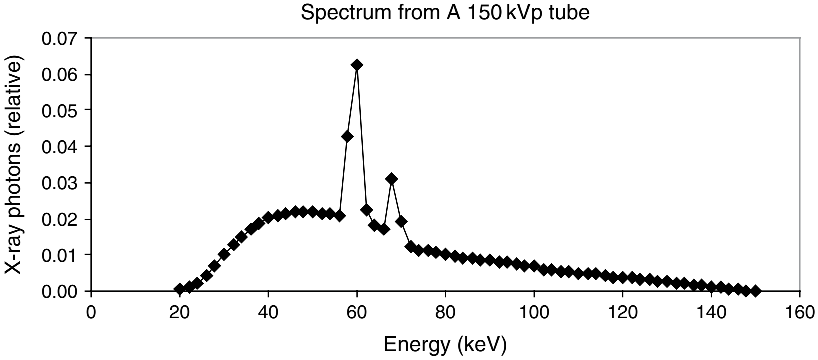

Figure 2 Typical spectrum from an X-ray tube with a tungsten anode operated at 150 kVp. Fluorescence peaks occur at 57.98, 59.32, 67.24, and 69.08 keV.

the electron's charge. For thin targets, the flux of X-rays of energy E was shown in 1923 to vary in proportion to $(E_{\mathrm{max}} - E)$ by Kramers [3]. Low-energy radiation is reduced by inherent filtration from the tube glass and anode itself, and is effectively eliminated below 20 keV. The continuous portion of the spectrum is known as bremsstrahlung (German word for braking radiation). In addition, there are X-ray emissions at specific energies called characteristic radiation or fluorescence. These X-rays are produced by electron transitions typically filling the innermost atomic shell or K-shell, after this shell has been vacated by a knockout interaction. Fluorescence production varies roughly as the square of the term $(E_{\mathrm{max}} - E_{\mathrm{char}})$. A number of workers have modeled the spectral distribution of X-rays through direct measurement and semi-empirical formulas [4–9].

X-ray energy, E, is related to the frequency, ν, of the radiation by the well-known Planck equation

$$E = h\nu \tag{1}$$

where h is Planck's constant. Spectra are usually presented in terms of X-ray fluence (X-rays/cm^2) or flux, Φ, (X-rays/cm^2/s). In contrast, detectors typically respond to X-ray intensity (keV/cm^2/s), which includes a weighting for the X-ray energy:

$$I = E\Phi \tag{2}$$

X-ray dose measures deposited X-ray energy per unit mass at a given locale in a target. It is usually measured in units of mR (milliRad) or μSv (microSievert), with 1 mR = 10 μSv. Figure 3 shows the relationship between fluence and dose. Note the peaking behavior near 60 keV.

2.2. Attenuation of X-rays

X-rays are removed from a collimated beam either by scattering out of the beam or by being absorbed. The process is quantized and probabilistic in nature. An X-ray beam can be considered as a flow of discrete photon particles each having a specific

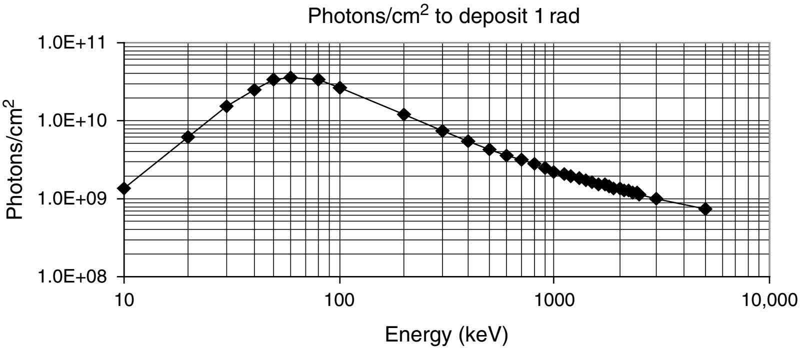

Figure 3 X-ray fluence required to deposit 1000 mR dose in air as a function of photon energy.

energy or frequency and traveling at the speed of light. The intensity of a directed monoenergetic beam passing perpendicularly through a material of thickness x is well described by the Beer–Lambert law [10].

$$\frac{I}{I_0} = \exp[-\mu(E, Z, \rho)x] \tag{3}$$

where I is the outgoing intensity, I_0 is the incoming intensity, and μ is the material's linear attenuation coefficient, which depends strongly on the X-ray energy and the atomic number Z of the target and is directly proportional to the material's physical density, ρ.

This leads naturally to the concept of X-ray attenuation, defined as the natural logarithm of the transmitted intensity fraction:

$$A \equiv \mathrm{LOG}\left(\frac{-I}{I_0}\right) = \left(\frac{\mu}{\rho}\right)t \tag{4}$$

where μ/ρ is the mass attenuation coefficient, and t the areal density (=density × thickness). This formulation is convenient in that μ/ρ varies with E and Z, but the density dependence has been subsumed. The mass attenuation coefficient is directly proportional to the atomic interaction cross section, σ, divided by the atomic weight, M. The relationship between mass attenuation coefficient and atomic cross section is given by

$$\left(\frac{\mu}{\rho}\right) = \frac{N_0\sigma}{M} \tag{5}$$

where N_0 is Avogadro's constant.

For X-rays from a continuous energy spectrum, $p(E)$, passing through a series of materials indexed by i, the formula for attenuation generalizes to

$$A = \mathrm{LOG}\left\{\int \mathrm{d}E\, p(E) \times \mathrm{EXP}\left[-\sum \left(\frac{\mu}{\rho}\right)_i t_i\right]\right\} \tag{6}$$

Note that the order in which the series of materials occurs is immaterial; the contribution of each is weighted according to its areal density and mass attenuation coefficient.

X-ray attenuation occurs via four basic modes of interaction, shown schematically in Figure 4. Coherent X-ray scatter (CXRS) is an energy preserving interaction between an X-ray photon and an entire atom or crystalline matrix. Incoherent or Compton scatter represents a direct interaction between an X-ray and an

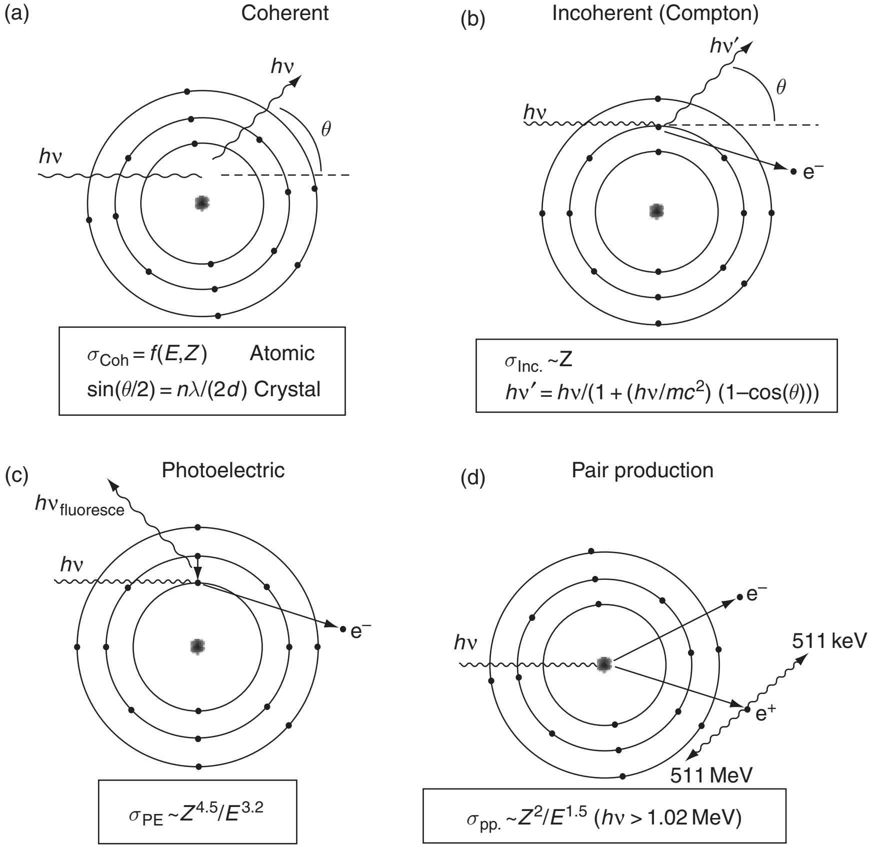

Figure 4 Schematic representation of four basic modes of X-ray attenuation. Coherent scatter (a) is an elastic interaction with the whole atom. Incoherent scatter (b) occurs off individual electrons and energy loss depends on the scatter angle. In photoelectric absorption (c), an electron is ionized and a fluorescent X-ray is subsequently emitted at a well-defined energy. Pair production (d) occurs in the MeV range stimulated by the strong electric field near the atomic nucleus; the X-ray energy creates an electron and positron pair. Triplet production (not shown) is driven by the electric field around an individual electron and creates an electron/positron pair and ejects the interacting orbital electron. Significant relationships describing the interactions are given. The atomic cross section σ, generally varies with Z by one power higher than the mass absorption coefficient (μ/ρ).

electron, which approximately may be considered free of its atomic environment. A simple formula was first advanced by Arthur Compton [11] to relate photon scatter angle and energy. The cross section for photons scattering off electrons was first worked out by Thomson and was later generalized to include relativistic effects as the Klein–Nishina equation. Photoelectric absorption is an inelastic interaction in which X-ray energy is expended to ionize an electron from an inner atomic shell. Though another X-ray is generated in the process, its energy is much lower and seldom escapes from the target material, so that total absorption of the original X-ray energy is the rule. Finally, pair production (and triplet production) is a process in which an X-ray of energy beyond 1022 keV reacts to create an electron/positron pair resulting in the local deposition of at least 511 keV of energy. For a more extensive treatment of these interactions, refer to Johns and Cunningham [12]. Numerous tabulations of X-ray attenuation coefficients have been compiled [13–18].

The general behavior of these competing modes of X-ray attenuations is shown for aluminum in Figure 5 as a function of X-ray energy. For the lowest X-ray energies (1–10 keV) the photoelectric attenuation predominates. The Compton process overtakes the photoelectric mode as energies rise higher. Finally, in the MeV range, pair production becomes the dominant attenuation mode. Figure 6 shows the total mass attenuation coefficient versus atomic number, *Z*, at 50, 500, and 5000 keV. Figure 7 is similar but only includes the coefficient for the predominating mass attenuation mode, namely, photoelectric for 50 keV, Compton for 500 keV and pair production at 5000 keV.

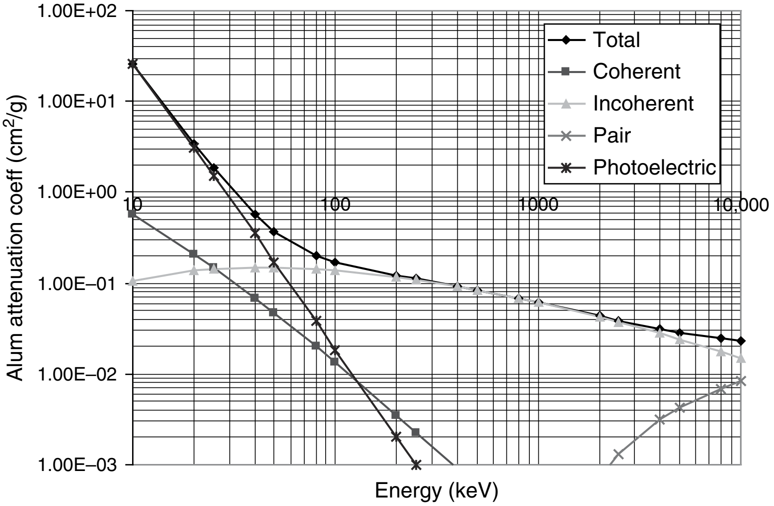

Figure 5 X-ray mass attenuation coefficients for aluminum as a function of photon energy. At low energies, photoelectric absorption predominates. At higher energy, incoherent (Compton) scatter becomes almost the exclusive contributing mode. Eventually, pair production dominates at very high energies (above 10 MeV).

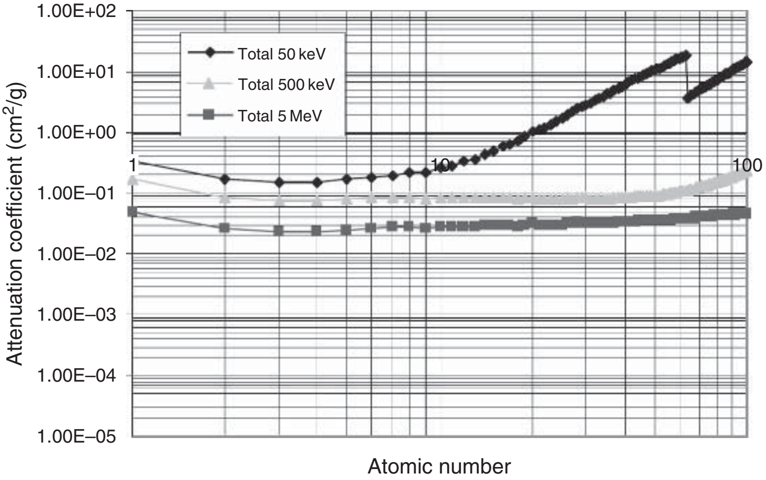

Figure 6 The atomic number dependence of the total mass attenuation coefficient in different energy domains (50, 500, and 5000 keV). The strongest *Z* dependence is seen for X-ray energies in the low-energy range.

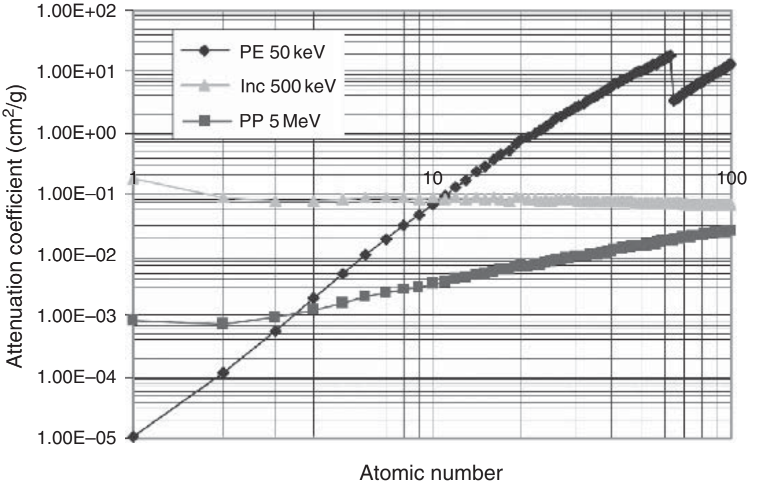

Figure 7 The atomic number dependence of attenuation in different energy domains. This is illustrated by how the mass attenuation coefficient of the predominating mode (photoelectric (PE) at 50 keV, incoherent (Inc) at 500 keVand pair production (PP) at 5 MeV) varies with *Z*.

2.3. X-ray detectors

Detectors are used to convert X-ray flux into an electrical signal, which can then be digitized and stored. For imaging cabinet X-ray systems, the detectors usually consist of a folded linear array of scintillators optically coupled to photodiodes. Typically, 500–1000 such detector elements are present for single-energy imaging and twice this number may be employed for dual-energy systems. These detectors are read out every few milliseconds, allowing a raster-scanned image to be formed with pixel size on the order of a millimeter. Linear arrays take advantage of fan beam collimation, which is much less susceptible to scattering artifacts than with cone beams.

The most common scintillation materials are CsI(Tl) (thallium-activated cesium iodide), CWO (pure cadmium tungstate), and rare-earth phosphors in the form of strips of medical intensifying screen, although thicker (and pricier) ceramic versions of these phosphors are also available. CsI(Tl) has the highest X-ray to light conversion efficiency, but suffers from the problem of appreciable afterglow on the timescales of 20–2000 ms, which can leads to undesirable artifacts. CWO shows effectively no afterglow in this time domain, and is almost twice as attenuating as CsI(Tl), but produces only about 40% of the photodiode current that CsI(Tl) generates. These crystals are transparent to their own scintillation light, so it is necessary to bundle small crystals into linear arrays with light reflective material on all sides except the face coupled to the photodiode. The phosphor on intensifying screens is thin ($<\sim 0.3$ mm) and semi-opaque to its own radiation, so no special measures are necessary to suppress lateral spreading of light. The properties of these and other inorganic scintillators have been presented in number of reviews [19–25]. Photodiode current passes through a high gain transconductance amplifier and then may be further shaped and amplified. A/D conversion may be performed on a voltage, derived via sample-and-hold circuitry or via true integrator/reset electronics.

Other detection methods have been used for scanning systems. The original airport digital scanners used a "flying-spot" pencil beam and read-out was purely serial. A single large detector in the form of a cylinder of scintillator was used and light was collected at the ends of the cylinders by photomultiplier tubes. Similarly, large area detectors coupled to photomultipliers are used for detection of scattered radiation. Some experimental systems have made use of CZT (cadmium zinc telluride) [26]. This is a high-Z semiconductor that offers conversion efficiency superior to scintillator, but is expensive, is difficult to make in bulk and requires a large bias voltage for charge collection. Occasionally, pressurized xenon gas ionization detectors have been utilized, but these have never attained popularity for security screening applications due to maintenance issues and detector thickness considerations.

2.4. Dual-energy X-ray

Figure 8 shows the X-ray mass attenuation coefficient as a function of atomic number for 50 and 100 keV X-rays. Attenuation coefficients rise roughly two orders of magnitude over the full Z range. Transmitted X-ray beam intensity for a given thickness (say 1 g/cm^2) will vary over a wide range (eight orders of magnitude) depending on Z. Note that the attenuation coefficients generally increase with Z except for an anomaly at the first element whose k-edge energy exceeds the X-ray energy ($Z = 64$ for 50 keV and $Z = 87$ for 100 keV).

Figure 9 shows the ratio of the attenuation coefficient at 100 keV to that at 50 keV. These energies roughly represent the HI and LO energy spectra produced

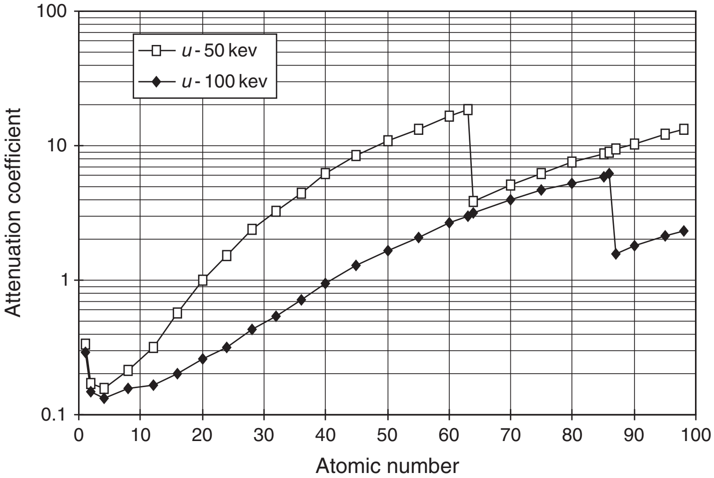

Figure 8 X-ray mass attenuation coefficient as a function of atomic number for monoenergetic X-rays of 50 and 100 keV. Sharp declines occur when the energy for k-edge absorption just exceeds the X-ray energy.

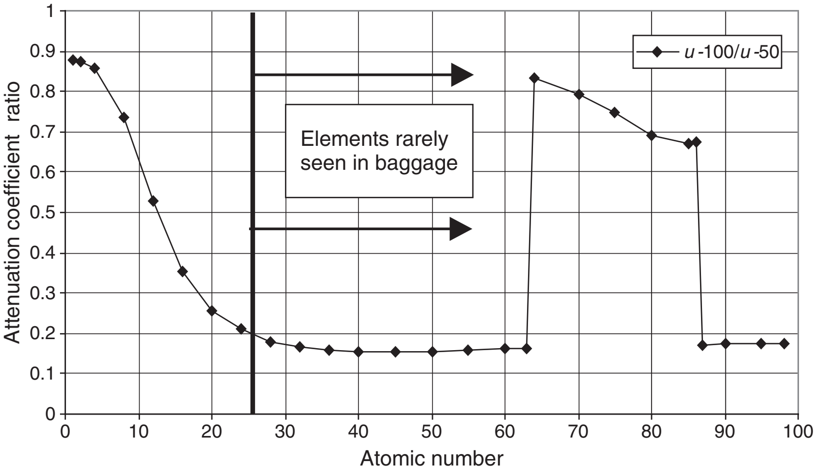

Figure 9 The ratio of HI energy (100 keV) to LO energy (50 keV) attenuation coefficients. This ratio is a sensitive indicator of atomic number for *Z* below roughly 26 (iron).

in dual-energy X-ray systems. The ratio is seen to decrease smoothly as a function of atomic number apart from some anomalous, k-edge-induced behavior in the high-*Z* region. In particular, the HI-to-LO attenuation ratio can be used to determine *Z* with good sensitivity below approximately *Z* of 26 (iron).

In the mid-1970s, Alvarez and Macovski [27, 28] made a significant finding that had been overlooked for many years. For purposes of computing X-ray attenuations, any target can be closely represented as a unique mixture of two basis materials, regardless of the incident spectrum. The approximation is valid in the range of energies most useful to medical diagnostics, that is 20–200 keV, excluding targets of high atomic number (roughly $>Z=50$). Moreover, the representation is linear, so that, for example, a doubling of target thickness results in a doubling in the thickness of the basis components. This stands in contrast to attenuation, which varies non-linearly with target thickness because of beam hardening. Measurement of attenuation using two different energy spectra (the so-called HI and LO attenuations) is sufficient to determine the thickness values of the selected basis materials. This decomposition plays a key role in processing data from dual-energy X-ray systems.

In practice, two means for generating dual-energy data are commonly used. With "true dual-energy," the HI and LO attenuations are derived from measurements taken at two different X-ray tube high voltages. Alternatively, "pseudo-dual-energy" uses only a single X-ray source, which is sensed by two separate detector arrays responsive to different portions of the X-ray spectrum. The difference in response is because of differences in scintillator material, thickness and/or beam filtration. In the front/back arrangement, the HI detector is positioned directly behind the LO detector and thus is sensing a hardened beam.

To illustrate how these systems work, Figure 10 shows the relative response to 2.47 g/cm^2 of nitrogen ($Z=7$) and 0.627 g/cm^2 of copper ($Z=29$). N is typical of an organic target, while Cu is representative of metals. Figure 10(a) shows the effect on the HI beam, selected to be 150 kVp and pre-filtered through brass. The incident X-ray intensity spectrum on the target is shown as the upper spectrum. The intensity spectra deposited in a thick detector after passing through the N and Cu targets, respectively, are shown as the curves below the HI-AIR spectrum. The thicknesses of N and Cu targets are selected so that these curves nearly coincide. For the LO beam, taken as 80 kVp, the analogous X-ray intensity spectra are shown in Figure 10(b). Note the clearly suppressed intensity with the Cu target, caused by the greater spectral absorption by Cu. Figure 10(c) shows the fraction of total incident beam intensity deposited in the detectors for the various beam and target scenarios above.

Analogous curves, from a pseudo-dual-energy system utilizing front/back detectors, are shown in Figure 10(d–f). The LO-AIR curve shows the beam intensity spectrum of a 150 kVp beam that is deposited in a thin scintillator. Figure 10e shows the X-ray intensity deposited in a thin scintillator after the beam has passed through N and Cu targets, respectively, are shown. The HI-AIR spectrum in Figure 10(d) is the remaining beam after passing through the LO detector and then a brass filter. The effects of absorption by the N and Cu targets are also plotted in Figure 10(d). Figure 10(f) shows the fraction of total incident beam intensity deposited in the detectors for the various beam and target scenarios with this pseudo-dual-energy system.

These figures demonstrate that the true dual-energy system produces a noticeably larger differential response between the two targets. This translates into greater sensitivity in discriminating materials having different Z values with the true dual-energy approach. This superiority in sensitivity is offset by practical considerations,

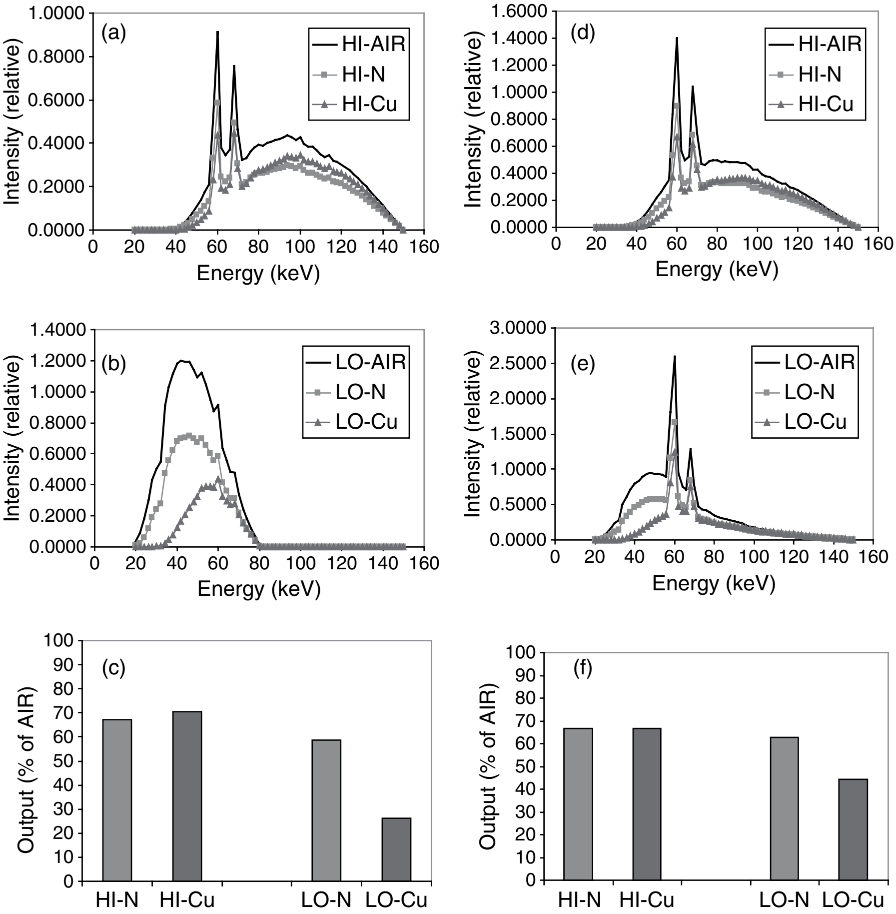

Figure 10 Relative detector response to 2.47 g/cm^2 of nitrogen versus 0.647 g/cm^2 of copper with for true dual-energy systems (a–c) and pseudo-dual-energy systems (d–f). The top level shows the original HI spectrum and how it would be reduced after exiting each of the absorbers. The middle level is the same for the LO spectrum. The absorber thicknesses were chosen so that the HI beam output would be reduced to about 68% of its AIR value. The LO output for copper is more dramatically reduced with the true dual-energy system, yielding better sensitivity in *Z* discrimination.

such as system cost and data bandwidth, which confer advantages to the pseudo-dual-energy approach.

2.5. Effective atomic number

Most common materials consist of a mix of elements. Yet a uniform material will attenuate X-rays as if it were composed of a single effective atomic number, Z_{eff}, which may assume a non-integer value. Remarkably, Z_{eff} depends solely on the elemental composition and is essentially independent of X-ray energy.

Tri-color X-ray images assign coded colors as “organic,” “inorganic,” or “metallic” on the basis of Z_{eff}. Typically, the organic range includes material having $Z_{\text{eff}} < 10$, inorganic having $10 \leq Z_{\text{eff}} < 18$, and metallic having $Z_{\text{eff}} \geq 18$. Of course, these assignments are based on the composite of all material traversed in the luggage by X-rays for each image pixel.

Assume a material is a uniform compound consisting of N elements, having an atomic number Z_i and contributing mass m_i $(i = 1, \ldots, N)$. In chemistry, the concept of average atomic number, is defined as

$$Z_{\text{avg}} = \frac{\sum m_i Z_i}{\sum m_i} \tag{7}$$

Z_{avg} can differ significantly from Z_{eff}, which more strongly weights the higher Z elements in the compound. The formula for Z_{eff} is given by the following equation (Johns and Cunningham, 1983):

$$Z_{\text{eff}} = \left(\frac{\sum a_i Z_i^{\;3.5}}{\sum a_i} \right)^{1/3.5} \tag{8}$$

Here, $a_i = m_i Z_i / A_i$, where A_i is the atomic weight. Strictly speaking, a_i is proportional to each element’s bulk electron density, which to a good approximation is proportional to the element’s bulk density. The choice of the exponent value (=3.5) is empirical and other authors have presented similar formulas with somewhat different choices for the exponent.

For a material consisting of a single element, Z_{eff} is identical with that element’s atomic number Z. Compounds will have a Z_{eff} intermediate between the lightest and heaviest component atom. For example, pure silica (SiO_2) is a compound of silicon ($Z = 14$) and oxygen ($Z = 8$) and has a Z_{eff} of 11.75. Its Z_{avg} is 10.80, almost 1 atomic unit less. Note that silica attenuates X-rays similarly to magnesium ($Z = 12$), which is consistent with its appearance as an inorganic material on three-color X-ray imaging systems.

To a good approximation, Z_{eff} is independent of the X-ray spectrum and is not a function of X-ray energy. This is true to the extent that X-ray attenuation is dominated by the photoelectric and Compton interactions and that no component element’s k-edge lies within the active part of the X-ray spectrum. Coherent scatter is relatively small provided the X-ray energy is above 35 keV and atomic number is below 20. Coherent scatter effects are taken into account empirically through the choice of exponent in the Z_{eff} formula. The photoelectric and Compton interactions remain the dominant modes up to 2000 keV, beyond which pair production becomes significant. Because X-ray tube spectra typically cut off below 25 keV, the Z_{eff} concept is viable for materials composed of elements with k-edge lying below this value, i.e., with Z below 47 (silver). This includes virtually all items that might commonly be found in luggage.

3. HISTORY OF X-RAY SCREENING TECHNOLOGY

Many criminal and terrorist events have occurred over the last 50 years, which have spurred development of X-ray screening. Air flights have been targets of particular concern. Measure has been met with countermeasure as the threats have escalated. Governmental agreements and regulations have fostered the advancement of commercial X-ray screening technology. Table 1 gives a timeline of major developments in X-ray security inspection.

Table 1 Timeline of major events in the history of X-ray security screening – criminal incidents are indicated in dark shading, commercial developments in light shading, and governmental actions without shading

Year	Event
1930	First recorded skyjacking, Pan Am mail plane, Lima, Peru
1955	First successful bombing of civilian US aircraft (Jack Graham)
1960	First suicide bomber, National Airlines; demands for baggage inspection
1961	First skyjacking to Cuba
1963	Tokyo Convention: agreement on handling hijack incidents
1965	Introduction of fluoroscopic system for baggage scanning
1968–1972	Epidemic of skyjackings (364 listed by DoT)
1969	FAA creates Task Force on the Deterrence of Air Piracy
1970	Hague Convention: extradition or prosecution of hijackers
1971	Montreal Convention: extends Hague convention to others aviation crimes
1972	FAA issues emergency rule for mandatory inspection of carry-on baggage and scanning of all passengers by airlines
1973	US–Cuba Hijacking Agreement
1974	Anti-hijacking or Air Transportation Security Act of 1974, validates 1972 emergency rules and authorizes FAA R&D effort for airport security
1974	Anti-hijacking or Air Transportation Security Act of 1974
1974	AS&E "flying spot" system, first digital baggage scanner
1977	Dual-energy CT X-ray used to characterize explosives
1979	Linear array of detectors introduced as X-ray screening systems by Picker and ScanRay
1985	TWA Flight 847 hijacked from Athens, Greece, 17 day standoff in Beirut
1985	Air India Flight 182 explodes en route from Montreal to London
1985	Terrorists attack Rome's Leonardo da Vinci Airport
1985	International Security and Development Act of 1985, provides for air marshals and expands FAA R&D for airport security
1986	First cargo scanners using an RFQ Linac X-ray source
1986	X-ray backscatter imaging introduced in baggage inspection (AS&E 101Z)
1987	Korean Airlines Flight 858 blown up over Indian Ocean
1987	Dual-energy X-ray: EG&G Astrophysics ESCAN offer color-coded images

Table 1 (*Continued*)

Year	Event
1988	Array Systems: automated recognition of weapons
1988	Pan Am Flight 103 downed over Lockerbie, Scotland
1989	UTA Flight 772 destroyed by bomb over Chad
1989	Avianca Flight 203 explodes over Colombia
1990	Vivid H-1: first practical automated detection of explosives via X-rays
1990	Magal AISYS-370: automatic detection of blasting caps
1990	Aviation Security Improvement Act of 1990, authorizes screening of checked bags for explosives, expedites FAA R&D programs
1991	XENIS system: EG&G Linescan X-ray system pre-screener for TNA
1991	DARPA cargo system test facilities at Houston, TX and Tacoma, WA
1991	Vivid demonstrates automated detection of contraband and currency
1991	1st FAA international symposium on explosives detection
1991	Low-dose personnel screeners: AS&E BodySearch and AGS Secure1000
1991	Stereoscopic X-ray imaging system prototype
1992	Automated detection of blasting caps: Vivid H-1
1992	Invision CTX 5000: automated detection of explosives via CT analysis
1992	EG&G Z-Scan: dual-energy, dual-view X-ray system
1992	Schlumberger Sycoscan: 2.5 MeV dual-energy cargo scanner
1992	Prototype coherent X-ray scatter used for explosives detection
1992	FAA proposes SPEARS (Screener Proficiency Evaluation and Reporting System)
1993	BAA initiates 100% checked bag screening using Vivid VDS systems
1993	FAA establishes EDS certification standard
1994	Philippines Airlines Flight 434 downed over Pacific Ocean
1994	First EDS device to pass FAA certification (Invision CTX 5000)
1996	Vivid/Gilardoni APS: real-time explosive detection for carry-on systems
1996	EuropScan Xcaliber: multi-energy (35–140 keV) X-ray scanner
1996	AS&E MobileSearch: cargo scan using a mobile truck
1996	US Customs evaluates automated detection for narcotics
1998	L-3 eXaminer 3DX6000, first commercial full 3-D CT for EDS
1998	Vivid MVT: limited view tomography using three dual-energy X-ray screener
1999	Heimann HRX: first commercial coherent X-ray scattter screener
2000	Widespread deployment by FAA of TIP-equipped X-ray scanners
2001	9/11 terrorist attacks on World Trade Center and Pentagon
2001	Aviation and Transportation Security Act: creates the Transportation Security Agency and federalizes of airport screening
2002	TSA implements 100% checked bag screening at US airports

3.1. Early history

Attacks on commercial aviation were regarded as unthinkable until the 1960s although a few incidents had occurred in the United States and abroad. Indeed, a commercial aircraft had been bombed in 1955 by Jack Graham in a bizarre scheme to expedite his inheritance by murdering his mother. The first skyjacking of a US flight was to Cuba in 1961, 2 years after Castro had established a communist regime. Toward the end of the 1960s, skyjackings became rampant with Cuba being the most frequent destination. Metal detectors and manual baggage inspection were the first measures put in place by the Federal Aviation Administration (FAA), but were relatively ineffectual. The epidemic of skyjacking was finally stemmed after the FAA issued an emergency order in 1972 to inspect all baggage by manual means or X-ray screening. The Air Transportation Security Act legislatively legitimized these measures in 1974. In 1973, an agreement was reached between the United States and Cuba stipulating the return of skyjackers, which further served to deter potential offenders.

X-ray equipment for inspection of baggage existed in a rudimentary form at this time. The US Postal Service had investigated X-ray screeners for package inspection in the aftermath of President Kennedy's assassination, tragically accomplished using a mail-order rifle. The US military had utilized fluoroscopic systems for examining parcels and this technology was adapted for airport use. First-generation equipment featured a side-shooting X-ray source collimated into a broad rectangular beam, then transmitted through an article of baggage and finally sensed by a fluoroscopic screen. The operator viewed the screen through a leaded glass window, or later on, through a series of mirrors to avoid being exposed to excessive radiation. The latter strategy was soon improved by using a charge-coupled device (CCD) device to view the fluoroscopic screen. An image was then presented to the operator on a monitor via CCTV. Addition of leaded curtains at the entrance and exits of the conveyor permitted the cabinet X-ray system to fully contain scattered radiation. Of course, the baggage itself was exposed to a relatively high radiation dose and was not "film safe."

A remarkable innovation by AS&E in 1974 was the flying spot X-ray system, which provided a digitized raster scan image of the bag. The beam from a side-shooting X-ray source passed through a rotating lead collimator and then vertically collimated, thus sweeping the flying spot. This pencil beam traversed a bag moving continuously on a conveyor. The signal was detected by large cylindrical detector of scintillation material viewed by photomultipliers at either end. Many of the features of modern carry-on scanners were incorporated into this novel system including digitized image data adjusted for gain and offset, and low, film-safe baggage exposure levels. A number of reliability issues undermined the popularity of this system.

3.2. Linear array X-ray scanners

The availability of integrated circuits paved the way for the next generation of X-ray inspection system. These units featured a side-shooting fan beam of X-rays incident on an extended array of scintillators optically coupled to photodiodes or phototransistors. The resulting low-level electric currents were then amplified, integrated, and electronically sampled and digitized. Such systems were under development by ScanRay and Picker in 1977. By 1979, Picker was marketing the Linetec 256 [29]. ScanRay, which had acquired Astrophysics, a leading manufacturer of diode arrays, first marketed its System 1 in 1980. This system was a huge commercial success. It employed a down-shooting source and a straight array of 480 elements below the conveyor. In 1982, ScanRay introduced its System 4 with an innovative folded-L array of detectors, which provided full tunnel coverage for the first time. The System 5, released shortly thereafter, offered dual views at right angles, each displayed on a separate monitor. Throughout the 1980s many image enhancements, which are now standard features, were introduced. These included reverse video, zoom, edge enhancement, variable contrast and penetration, pseudo-color and later on, dual-energy color-coded imaging and organic and metallic stripping.

The 1985 tragedy of Air India Flight 182, which exploded off Ireland en route from Montreal to London, stimulated an intensified effort to thwart terrorists. The International Security and Development Act of 1985 provided for air marshals and expanded FAA's R&D for airport security. Thermal neutron analysis (TNA) and a number of sniffer technologies for trace explosives detection, which had been developed under FAA sponsorship, were accelerated toward commercial production.

3.3. Material discrimination

The X-ray security industry responded to the challenge with a number of advances. In 1986, AS&E's Model 101Z added a backscatter detector to supplement its transmission detector in conjunction with its flying spot beam. The backscatter detector was responsive to organic material on the beam side of baggage whereas the transmission beam was most sensitive to metals anywhere in the beam path. The Z backscatter technology had been originally developed for medical diagnostic use, to identify areas of calcification in lung tissue. The system was soon available in a two-sided (dual beam) version, the 101ZZ, which displayed backscatter images from opposite sides of the baggage. AS&E boasted that the 101Z penetrated up to 19 mm of steel, then considered state of the art. By 1987, AS&E was enhancing images with color, using red to indicate organic material and green for higher Z material, such as metals. Starting in 1989, AS&E incorporated an algorithm to identify organic lumps in the image, which provided a crude and rather ineffectual means for semi-automated detection of explosives.

By 1987, EG&G Astrophysics introduced E-Scan, which enhanced its previous Linescan systems by providing dual-energy data. The data were extracted from two adjacent detector arrays having thickness and filtration designed to respond respectively to the higher and lower energy parts of the incident X-ray spectrum. Atomic number for each pixel was coded in color, while attenuation was still displayed through intensity. Orange-brown was used for organic material, and metals and inorganic material were shown in blue. Green indicated areas of high attenuation. This dual-energy concept was adapted from the field of bone densitometry. Companies such as Hologic and Lunar had been using dual-energy imaging to generate separate bone and soft tissue images computed from a single diagnostic X-ray scan. By 1990, EG&G Astrophysics innovatively offered FIP (false image projection) on its E-Scans, randomly inserting the image of a Glock 17 gun inside a bag image [30].

The German manufacturer Heimann, then a division of Siemens, came out with its Hi-Mat dual-energy system around 1988. Like E-Scan, it originally employed paired front/back detectors to provide spectral separation. Heimann touted their system's crisp image quality, for example, the ability to see 34 AWG wire and penetrate 15 mm of steel. Heimann introduced a new color scheme for its dual-energy scanners, using orange for organic material (Z below $\sim$10), green for inorganic material (then referred to as "organo-metallic") and blue for metals (Z above $\sim$18). This color scheme has become standard for today's dual-energy systems.

3.4. Automated detection

After the downing of Pan Am Flight 103 over Lockerbie in December 1988, the quest for effective explosives detection gained added urgency. Founded in 1989, Vivid Technologies released its side-shooting system H-1 in 1991. This was the first X-ray system that automatically detected plastic explosives in checked baggage. This system precisely measured dual-energy attenuation at each pixel within a bag. A background subtraction procedure carried out in basis function space allows determination of Z_{eff} for individual objects within the bag. This differs from regular dual-energy imaging that reflects the composite Z_{eff} of all material along the beam path associated with each pixel. Other characteristics of the object, such as its thickness and mass, were also used in the automated detection process. This technology was soon recast for the British Airports Authority (BAA) as the down-shooting VIS, offering fully automated detection on checked baggage lines running at 0.5 m/s. Operation of automated inspection for conveyor lines in the baggage handling area is illustrated in Figure 11.

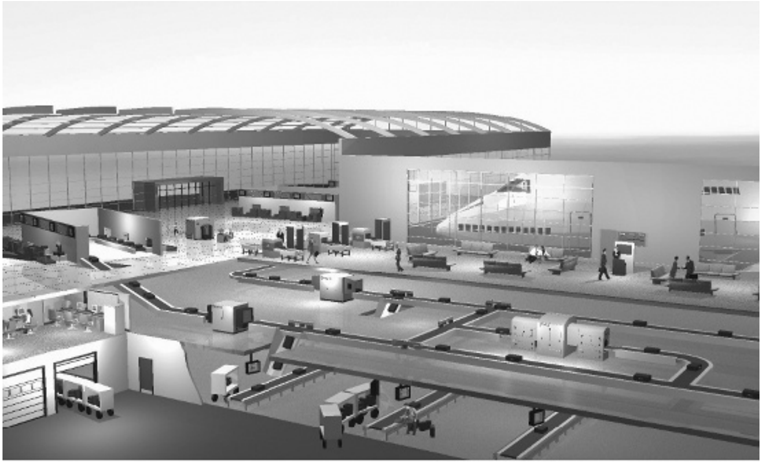

Figure 11 Artist's rendition of a conveyor line system in the baggage handling area. Bags are automatically screened at Level 1. Rejected bags are diverted and further inspected up a hierarchy of Levels until the potential threat can be resolved.

Figure 12 Level 1/Level 2 screening system, the L-3 VIS108. An automated decision on threats is made at Level 1. Operators can examine images of rejected bags at Level 2.

Rejected bag images are viewed by remotely located operators, who then decide whether to clear the bag for loading or reject it for additional inspection. Eventually, the bag-screening methodology was generalized to a matrix architecture so that a variable-sized team of operators could oversee a variable-sized number of automated X-ray systems. Other manufacturers, such as EG&G, Heimann, Rapiscan and AS&E, produced competing systems, but Vivid dominated the automated system marketplace throughout the 1990s. The VIS108 system, which is used at many airports worldwide for automated Level 1/Level 2 screening of checked baggage, is shown in Figure 12.

As early as 1991, Vivid demonstrated that its systems could automatically detect certain contraband, such as narcotics and currency [31]. Other companies followed with similar products and by 1996, these systems were tested for effectiveness by US Customs in detecting various drugs packed within luggage. Detection at reasonable false alarm rates was regarded as insufficient to warrant widespread deployment at that time. Later on, the Department of Agriculture bought Vivid systems adapted to detect restricted fruit stowed in passenger baggage.

In 1993, the FAA established a standard of performance for certifying X-ray systems. The key technological challenge is to achieve suitably high detection rates on a number of categories of explosives while maintaining a sufficient throughput and low false alarm rate. The FAA ordered, in 1990, that the detection performance characteristics of bomb detecting equipment be classified as secret. Details regarding machine performance will consequently not be discussed herein. Currently, the only machines to have passed the rigorous FAA (now TSA) certification standard for detection and throughput are CT-based X-ray systems manufactured by GE-Invision, L-3 Communications, and Analogic. In 1994, Invision's CX5000, developed with funding from the FAA, was the first system to pass FAA certification.

Starting in 1995, a collaboration between Vivid Technologies and Gilardoni led to inclusion of real-time explosive detection in carry-on baggage machines. Heimann, EG&G, and Rapiscan soon produced machines with this feature, which became known as "operator assist." The FAA performed detection testing on such systems in 1997 and although the results were reasonably good, they did not meet certification

Figure 13 The MVT screening system incorporates three separate X-ray views and merges the image information to produce a 3-D analysis of baggage contents.

levels. The decision was made not to mandate the use of "operator assist" based on its sub-optimal detection capability and various operational reasons. At the time, it was commonly presumed that terrorists would not knowingly bomb their own flights.

In 1996, the FAA contracted L-3 Communications to develop a second source for certifiable baggage inspection. This system achieved certified performance by 1998. During this period, Vivid Technologies developed a high-throughput, quasi-tomographic device, which is currently marketed as the MVT (multi-view tomography) system. This system has much greater capabilities than the dual-axis, dual-energy EG&G Z-scan system, which performed a very rudimentary 3-D analysis [32]. By providing three coplanar scanners, with views separated by roughly 60°, the MVT can perform realistic 3-D reconstruction. An MVT system is shown in Figure 13. Using sophisticated image processing, backscatter detection, and a patented method for accurately computing density, the MVT achieved certified detection levels, though at elevated false alarm rates. Heimann subsequently entered the market with its EDtS, which employs three X-ray tanks and five collimators, to generate three coplanar and two skewed-plane views.

The importance of human factors in the X-ray screening process has received increasing attention. In 1988, unannounced FAA testing of domestic screeners revealed a failure rate of 22% of screeners to spot weapons emplaced in carry-on bags [33]. Poor performance was attributed to lack of training, low wages, and attention fatigue. FAA addressed these human factors issues in 1992 through its proposed program SPEARS (Screener Proficiency Evaluation and Reporting System). A key aspect of this program was fictional Threat Image Projection (TIP). The idea is to motivate operators by sporadically presenting bag images modified by superimposing stored images of actual weapons. An information management system allows supervisors to keep track of the performance of individual operators against a variety of threat categories. Performance can be evaluated in terms of both missed threats and false alarms. TIP has proved an effective means to heighten screener performance. From 2000 onward, the TSA has placed increased emphasis on TIP capability being included on its X-ray equipment purchases.

The new century has seen the development of low-price, low-throughput CT systems under the FAA ARGUS project. These systems currently meet TSA certification except for TSA's targeted bag throughput. Several new companies have aspired to enter the CT market including Reveal and Surescan. A number of technology fusion systems have been proposed including coupling of X-ray scanners with nuclear quadrupole resonance (QR) systems.

3.5. Other advancements in X-ray screening

In 1989, the FAA fielded six state-of-the-art explosives detection systems for operational testing at airports. These thermal neutron analysis (TNA) systems, SAIC's Model EDS-3, worked in conjunction with EG&G Astrophysics System 3 prescanners. The combined system was labeled XENIS for X-ray Enhanced Neutron Interrogation System. This X-ray pre-scanner increased system throughput by communicating suspicious regions of interest on which the TNA system could concentrate. A number of other X-ray systems were being investigated as candidates for explosives detection by 1989. Imatron, later spun off as Invision, adapted its CT technology for use in scanning bags. Dual-energy CT had been investigated as early as 1978 for explosive identification [34]. However, throughput constraints and penetration requirements focused attention on single-energy CT, as used in medical imagers.

By 1989, Scan-Tech had fielded its Dynavision 900, which included a variable contrast slide switch. Another X-ray method dating from this era was developed in Israel by Soreq and eventually was marketed in the 1990s as the Magal AISYS 370. This system found elemental lead used in blasting cap initiators (lead azide, for instance). The X-ray beam was rapidly filtered by means of a high-Z Ross filter on a rotating drum. The difference image greatly accentuates areas having lead content. The AISYS system eventually fell into disfavor as many blasting caps do not contain lead-based initiators. In 1988, the Israeli company Isorad marketed the SDS400, which was an advanced fluoroscopic X-ray system equipped with CCTV imaging. The inspected bag could be rotated on a platform to give relatively unobstructed views of objects of interest. Array Systems Computing Products, a Canadian company, introduced its X-Array Vision software module for use as an add-on to X-ray scanners for automatic recognition of guns and knives. X-Array Vision never gained wide acceptance because of limitations in its detection ability.

Ultra-low-dose X-ray screeners for personnel were announced in 1991 [35, 36]. AS&E demonstrated its Model 101P "Personnel Inspector," which later was dubbed BodySearch. IRT Corp. acquired similar backscatter imaging technology from AGS Corp., which was developed into the SECURE 1000 model. These units effectively displayed objects, such as weapons, explosives, or drugs, concealed on the body. However, they were deemed too anatomically revealing for public use and the radiation exposure, though infinitesimal, presented another public relations issue. These objections still remain and have inhibited their deployment for screening the general public.

In 1987, the idea of using CXRS for explosives detection was advanced by a group at Philips in Hamburg [37]. X-rays had long been used as a crystallographic technique, dating back to the theoretical and experimental research of the Bragg's in 1913 [38]. Historically, such work was done on refined samples, but by the early 1980s medical researchers were using CXRS for characterizing bone in vivo. Philips granted a 5-year license on the technique to Scan-Tech, but they were unable to productize the method. Eventually, the license was transferred to Yxlon, which was later acquired by Invision. After a long development period, CXRS has become a viable means for detecting explosives and possibly other contraband. Starting in 1999, Heimann offered the HRX system, a CXRS unit, as a Level 2 system for inspecting regions of interest previously identified at Level 1. Yxlon subsequently developed a means for examining an entire suitcase with a CXRS system, but throughput remains low in comparison with X-ray scanners. By its nature, CXRS systems specialize in detecting crystalline material, which makes detection of certain explosives difficult.

3.6. Cargo scanners

The impetus for screening cargo likewise grew in the mid-1980s as the terrorist threat expanded. By 1986, a number of companies were developing large X-ray scanners for inspecting cargo, operating in the megavolt range. These scanners used linear accelerators to achieve energies ranging from 2 to 16 MeV. Alan Akery had designed early fluoroscopic cargo systems monitored by CCTV cameras. By 1986 two such systems, developed by British Aerospace, were in use in Qatar for inspecting trucks [39, 40] Bio-Imaging Research (BIR) developed its first MeV range systems in 1986 [41]. In the same year, Bechtel, Varian, and AS&E announced their collaboration to create a 6 MeV unit [42], marketed as Cargo-Search. This system was eventually installed in Vodkinsk, USSR in 1989 for missile warhead verification as part of the SALT II arms treaty.

In 1992, Schlumberger installed its first SYCOSCAN system at Charles de Gaulle airport outside Paris [43, 44]. This system used a 2.5 MeV electrostatic electron accelerator and employed 2048 detectors in the form of multi-wire proportional chambers filled with pressurized xenon gas. It was soon appreciated that such systems were helpful in spotting smuggled drugs as well as explosives and weapons. In 1991, China deployed two massive cargo scanning systems in Shenzhen, near the Hong Kong border, designed by British Aerospace and BIR. Each system employs a 9 MeV Linatron, solid-state detectors and platen-based conveyors. Their utility for spotting smuggled goods and other discrepancies against shipping manifests yielded a substantial increase in customs revenues.

By 1992, Heimann introduced its 8 MeV HI-CO-SCAN system. DARPA tested experimental dual-view 10 MeV cargo scanners, which used two Siemens Vanguard linear accelerators and Heimann imaging systems, first in Houston, TX (1992) and then in Tacoma, WA (1993) [45]. In the late 1980s, Heimann marketed its 300 keV down-shooting CAR-SCAN and CAR-CO-SCAN units for vehicle and container inspection, respectively [46]. Low-cost, medium-energy (420 keV) systems based on high-voltage metal–ceramic X-ray tubes were being developed around this time by British Aerospace [47]. AS&E's CargoSearch, used by US Customs starting in 1994 at Otay Mesa, CA, employed a 450 keV beam (and eventually dual view beams) with a flying spot beam, which imaged both X-ray transmission and backscatter [48]. By 1996, their MobileSearch system adapted this technology by mounting it on a truck [49]. An example of a current mobile cargo scanner operated in the 3 MeV range is shown in Figure 14. Governmental evaluation of cargo systems was conducted at test facilities in Tacoma, WA and the Thunder Mountain Evaluation Center at Fort Huachuca, AZ.

Figure 14 The CX3800M, a 3 MeV mobile cargo scanner. With the ability to penetrate over 25 cm of steel, this truck is used to X-ray other vehicles, pallets, and containers. The resulting high-definition image can be compared against the archived cargo manifest.

Performance of cargo systems was assessed in terms of five indicators based on ASTM standards, namely Wire Image Quality Indicator (wire visibility behind steel), Contrast Indicator (visibility of added steel expressed as percent), Steel Penetration, Absorbed Dose, and Throughput [50]. Later on, Resolution of grid test pieces was added as another indicator. Hole-based Image Quality Indicators are also employed for assessing performance. Safety concerns about irradiating food stuffs and activating materials in the scanner itself led to acceptance of 9 MeV as the upper energy limit for X-ray cargo scanning [51].

4. X-RAY INSPECTION SYSTEMS

X-ray inspection of baggage can be divided into a number of technologies, depending on the physical principles employed and whether computer automation used for detection. A number of publications have discussed the variety of options available to do this task [52–60]. Many of these technological systems are in common use at airports, government buildings, and other security checkpoints.

4.1. Conventional transmission

Conventional X-ray systems are used in conjunction with operators who view the images looking for threats or illicit substances in the X-ray image. The term generally refers to relatively low kilovoltage systems (less than around 150 kVp)

Figure 15 The PXM, a state-of-the-art screening system for examining parcels and carried baggage. The remote workstation can be conveniently positioned.

and is typically used for inspection of carry-on items at airports and public buildings, incoming parcels to businesses and agencies, and items shipped through the mail or via other carrier. Figure 15 shows a device used for screening carry-on items at airports.

Carry-on inspection systems expose baggage to a dose of roughly 0.2 mR and typically operate at 0.5 mA tube current and 150 kVp tube voltage. At this voltage, the efficiency of X-ray tubes for producing X-ray is estimated roughly at 3×10^8 photons/cm^2/(mA-s) at 1 m. Assuming representative operating conditions of 0.5 mA tube current, detector sampling rate of 250 Hz, detectors size of 0.04 cm^2, and source-to-detector distance of 1 m, the number of X-ray photons impinging on a detector during each sample would be 24,000. This estimate for X-ray interactions should be adjusted for added filtration (near the source and from the conveyor belt) and for the detector quantum efficiency (DQE), which for a spatially uniform absorber corresponds to the efficiency of the detector to interact with X-rays. So, each pixel is expected to receive about 15,000 X-rays in the absence of any item on the belt, i.e., in AIR. For lightly attenuating materials, the X-ray count will be almost the same number. A useful, but somewhat simplistic model for pixel signal-to-noise ratio (SNR) is based on counting statistics, which assumes a uniform output response from each detected X-ray event:

$$S = cN \tag{9}$$

$$\sigma_S = c\sqrt{\mathrm{N}} \tag{10}$$

$$SNR = S/\sigma_S = \sqrt{N} \tag{11}$$

where S is the signal from the detector, σ_S is the standard deviation (noise) in repeated samples of S, N is the number of X-rays producing the signal, and c is a response constant. This simple model suggests that 15,000 X-rays would yield a $SNR = 122$. Realistically, each X-ray event's output response varies because X-rays are not monoenergetic, and even the response of monoenergetic X-rays with the detector is distributed in its energy deposition. This effect causes a 10–15%

degradation in *SNR* known as *Swank noise* [61]. This degrades typical *SNR* to around 100. This noise creates a mottled appearance when a uniform X-ray exposure is imaged. The capability of systems to image fine wires or thin shims is limited by this quantum mottle. For beam angles that differ significantly from the normal to the plane of the anode, additional loss of beam strength and *SNR* are seen because of the so-called "heel" effect, which refers to the increased X-ray absorption within the anode at such emission angles.

Imaging systems normally convert the signal from the detectors into attenuation values by means of "LOG" conversion. Attenuation is a more natural variable for imaging, as the thickness of an absorber is closely proportional to attenuation. The proportionality becomes exact for monoenergetic X-ray beams. LOG conversion may be performed in the electronic circuitry, e.g., through logarithmic A/D converters, or by look-up tables in the software or firmware. The conversion employs the steps of offset subtraction and gain normalization. Electronic offsets are added to amplifier circuits to prevent drift and random fluctuations from leading to cutoff in A/D values. Gain normalization is necessary as absolute detector response will vary because of factors such as distance to the X-ray source, intrinsic scintillator brightness, and amplifier gain.

System drift due to time and temperature necessitate periodic updates of the dark offset and AIR gain correction factors stored in memory. The desired frequency for updating will depend on the electronic design and environmental operating conditions. Attenuation may be approximately computed with offset and gain correction using the following equation:

$$A = \mathrm{LOG}(S_{\mathrm{AIR}} - DK) - \mathrm{LOG}(S - DK) \tag{12}$$

where S is the digitized signal, S_{AIR} is the stored signal for AIR, and DK is the stored dark offset signal. At very high attenuation, S will be approximately equal to DK and statistically S may attain values even below DK. Because the mathematical LOG function is undefined when the argument is zero or negative, the look-up table must deviate from a true LOG table to handle these situations. Simple truncation of the argument to a minimum positive value may suffice although more sophisticated methodologies can be implemented. Some systems employ additional calibration procedures, for example, tabulating the attenuation from a known thickness of some absorber, to compensate for non-linearities in detector response.

In the high attenuation domain, very few X-rays penetrate through the absorbing material and the signal will be only slightly greater than the DK value. Areas that are totally dark, still receive a random signal arising from the electronic noise of the system. This noise "floor" sets the level of the smallest actual signal that can be visualized. Normally, this noise mostly comes from the first stage amplification, which converts photodiode current to a voltage by using an operational amplifier. A number of noise sources contribute, including shot noise for biased photodiodes and amplifier noise in the form of the input referred voltage, but ultimately the limiting noise factor is the thermal or Johnson noise of the feedback resistor. The dynamic range of the system is taken as the ratio of maximum signal ($S_{\mathrm{AIR}} - \mathrm{DK}$) to the minimum visible signal (noise floor). Dynamic range is improved by using the maximum feedback resistor, which in practice is taken in the range of 10–100 MΩ. At room temperature, with a sampling rate of 250 Hz, the electronic noise amounts to a random charge flow of a few thousand electrons per sample. For highly responsive scintillators, only a few X-ray interactions are required to generate an equivalent signal. In this regard, the brightest scintillators offer an advantage, which favors CsI(Tl) and rare-earth ceramic scintillators.

Penetration is typically measured as the thickness of steel that an X-ray beam can penetrate. The idea is to still be able to visualize a Pb beam blocker behind this thickness of steel. The penetrating ability has grown from around 12–15 mm of steel for early scanners of the 1980s to 30 mm or more for today's state-of-the-art carry-on systems. X-ray tube voltages and currents have not substantially changed, so the increased performance is attributable mostly to improved electronics. A number of systematic effects can decrease penetration performance of the system and attention must be paid to minimize their influence. These effects include X-ray scatter, scintillator afterglow, offset drift, and electronic pickup. Essentially, the same design is applied for single-energy cargo scanning, except that the system size and X-ray energy are increased by roughly an order of magnitude. A false color X-ray image obtained by scanning an entire truck is shown in Figure 16.

The detector scintillator material is an important factor in the design of scanning systems. Table 2 presents key properties of some commonly used scintillation materials [62, 63]. The mean free path (inverse of the linear X-ray absorption coefficient) versus energy is shown in Figure 17 for a number of scintillators. For a specified X-ray energy, two to three mean free path lengths is sufficient to absorb most of the incident X-ray photons. Some factors that enter into the choice of a particular material are cost, light output and spectral emission, primary decay constant, afterglow characteristics, temperature output stability, radiation stability, hygroscopic nature, and X-ray stopping power.

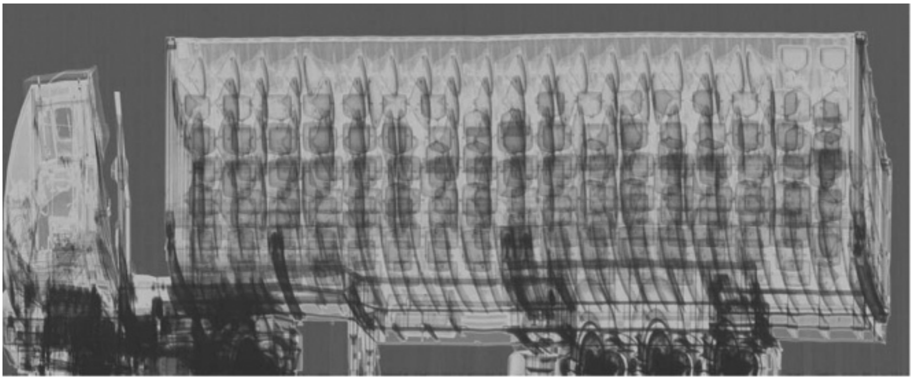

Figure 16 Scanned image of an entire trailer truck. This B/W image is typically presented as a false color image to enhance attenuation information about the contents. The imaging system is optimized to accommodate the characteristics of human visual response.

Table 2 Properties of some crystal scintillators

Material	Photons (keV at 293°C)	Decay time (μs)	Emission wavelength (nm)	Index of refraction	Density (g/cm3)	Hygroscopic?
Anthracene	16	0.03	450	1.62	1.25	No
BaF	12	0.63	310	1.49	4.89	No
BiGeO	8.2	0.3	480	2.15	7.13	No
CaWO	6	6	430	1.92	6.10	No
CdWO	15	15	470	2.30	7.90	No
CsI	2.3	0.016	315	1.79	4.51	Slight
CsI(Tl)	64	0.8 and 6	550	1.79	4.51	Slight
GdOS(Tb)	$\sim$50	3	510	2.20	7.34	No
GdSiO(Ce)	10	0.06	440	1.85	6.71	No
LaCl	49	0.025	340	1.94	3.86	Yes
LaBr	63	0.035	370	1.88	5.29	Yes
LuSiO(Ce)	30	0.04	420	1.82	7.40	No
NaI(Tl)	38	0.23	415	1.85	3.67	Yes
YAlO(Ce)	20	0.03	390	1.94	5.35	No
ZnWO	10	5	480	1.19	7.87	No
ZnS(Ag)	50	0.11	450	2.36	4.09	No

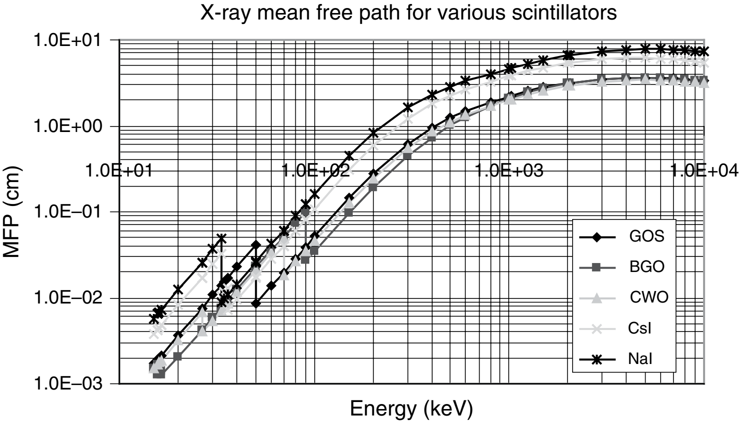

Figure 17 The mean free path (MFP) of X-rays in various scintillators as a function of photon energy. The MFP is the distance needed to attenuate an X-ray beam to 1/*e*. The absorption curves differ due to the different density and elemental composition of the scintillators.

4.2. Dual-energy transmission systems

Dual-energy systems provide two transmission images of the inspected item, taken at different X-ray energy ranges, designated HI and LO. As shown in Section 2.4, the attenuations from these measurements allows for determination of the effective atomic number, Z_{eff}. A number of different means have been employed to obtain the HI and LO images. The so-called true dual-energy systems actually vary the X-ray source spectrum. This is accomplished either by using two separate imaging systems operated at different energies or by rapidly alternating the kVp in a single view. Filtered dual-energy systems, use a single-energy spectrum but employ detectors that are responsive to different parts of this spectrum. This is implemented by varying the type, thickness, and filtration of the detectors. Generally, the true dual-energy systems are capable of better discrimination of Z_{eff}.

The method for converting dual-energy data into a color-coded image is a task that embodies many subtleties [64]. Conceptually, the X-ray image can be broken down according to an optimized attenuation, which sets a pixel's intensity, and Z_{eff}, which sets the hue. The optimized attenuation is a combination of HI and LO attenuations. Each pixel's attenuation is a composite of the attenuation produced by all objects in that line's path from the X-ray source and to the corresponding detector. This "projection" X-ray view superimposes a 3-D collection of objects into a 2-D data–space representation.

Construction of the 2-D attenuation map displayed to the operator is a key step in building useful screening systems. One basic imaging challenge is that the accuracy of the attenuation data is sufficient to distinguish roughly 500 gradations in thickness, which somewhat exceed the 256 gray levels available on color monitors, but more significantly, exceeds by an order of magnitude the capability of the human eye, which can distinguish only about 50 levels of gray. The solution is to present a fused image to the operator, one that represents "base" attenuation and the other that represents "edge" information. This compromise works because the operator requires only a general sense of the absolute attenuation of a sub-area within the image, whereas the fine details within such a subarea are well displayed by the edge image.

For dual-energy systems, SNR will further depart from the estimate made for single-energy systems. For example, for filtered dual-energy systems, the LO energy detector is typically made thin so as to decrease its sensitivity to higher energy photons. A DQE of around 50% is typical. The HI energy detector, though thick enough to stop most X-rays, has its DQE lowered by an added filter (typically by a shim of copper alloy or high-Z metal) used to decrease the detector's sensitivity to lower energy photons. Of course, if the HI detector is directly behind the LO detector, the LO detector itself will act as a filter, which may be supplemented by an added shim filter. Thus, for dual-energy detectors, *SNR* is typically around 60.

The default image also includes Z_{eff} information that is incorporated in a color display. Most security inspection vendors use somewhat similar color encoding schemes. The appeal of color is not only because of its attractiveness to the human eye, but also because of its ability to convey much more information to the operators than gray scale image [65]. Color is used to distinguish different Z_{eff} materials, such as sugar, salt, and metal, and this helps guide the eye in recognizing disparate materials as separate objects in the image. Physiologically, color vision is the natural mode for human perception in environments where sufficient light is present. Operators actually experience less visual fatigue when balanced color images are presented for inspection. The color image processing algorithm provides Z_{eff} information to the operator, while simultaneously representing attenuation in a color invariant way. Figure 18 shows the same bag in black-and-white and "color" (represented for illustrative purposes by added contrast). Discernment of objects by operators is simplified by the use of color.

Dual-energy X-ray information allows for the estimation of Z_{eff} on a pixel-by-pixel basis in the image [66]. Polychromatic beams from X-ray tubes undergo hardening as they pass through absorber, which complicates the computation of

Figure 18 The image of a typical bag rendered in "color" and in gray scale. The "color" image, shown here with boosted contrast, helps guide the operator's eye to recognize objects. Organic materials are color-coded in orange, inorganic material in green, and metals in blue.

Z_{eff}. Methods for handling these complications were worked out in the early 1970s. In practice, a look-up table can assign hue to each HI/LO pair of attenuation measurements. Traditionally, orange is assigned to organic material ($Z_{\mathrm{eff}} < 10$), green to inorganic material ($10 < Z_{\mathrm{eff}} < 18$) and blue to metallic material ($Z_{\mathrm{eff}} > 18$). The use of hues "in-between" these three categories has been found to be effective in guiding the human visual system in tasks of discerning objects in the images.

Effects such as detector cross talk and afterglow will negatively impact system performance. Cross-talk is visible by examining the image produced by sharp, metallic edges. Excessive cross-talk will result in edges appearing blurred. Cross-talk is a result of leakage between adjacent channels, which can be caused by poor containment of scintillation light or sub-optimal electronic isolation between channels. Afterglow is a phenomenon wherein scintillators do not release all of their light promptly, in some cases hundreds or even thousands of milliseconds after X-rays are turned off or blocked. Certain scintillators are known to exhibit significant afterglow. In extreme cases, afterglow will limit the ability to visualize highly attenuated areas of the image.

Other important factors affecting X-ray images are tube voltage, milliamps, and sampling rate. Higher tube voltage is used when greater penetration is sought. Higher beam voltage is generally more efficient for producing X-rays at a given tube power. Current also helps imaging through reduced quantum noise. At high currents, larger focal spots may be needed to handle the power dissipation, resulting in loss of resolution. Both higher voltage and higher current have the undesirable effect of increasing radiation dose to the baggage. Film safety issues may arise. Most single-view X-ray security systems operate with bag doses in the range of 0.1–0.3 mR per inspection. Faster sampling is generally a positive, but may result in peculiar aspect ratios (elongation of the time dimension) if used naively. Generally, the sampling rate is determined by the belt speed and is set to give a realistic aspect ratio. The conveyor distance advanced per sample (belt speed) should be matched to the scan width viewed by the detector array.

Means for computing Z_{eff} of objects in the presence of background clutter was worked out in the early 1990s [67, 68]. These methods were applied in high-quality, dual-energy systems for automatically detecting explosives in actual baggage. The technique was soon extended for similarly identifying contraband substances such as narcotics and currency. The method calls for computerized segmentation and objectization of the image followed by analyses involving Z, density, mass, and other features. Specialized methods for recognizing detonators and sheet explosives exist as well. Parameter tuning, conducted on an extensive database of "clean" bags and bags with threats, determines effective feature conditions for automated threat decisions.

The dual-energy technology for baggage inspection can be extended to cargo scanning by using dual-energy photon sources in the MeV range to achieve the greater penetration required. Baggage systems make use of the property that low-Z materials attenuate X-rays primarily by Compton scattering while higher Z materials show a relatively greater attenuation by photoelectric absorption. For a given mass thickness, the Compton process, expressed as a mass attenuation coefficient, is

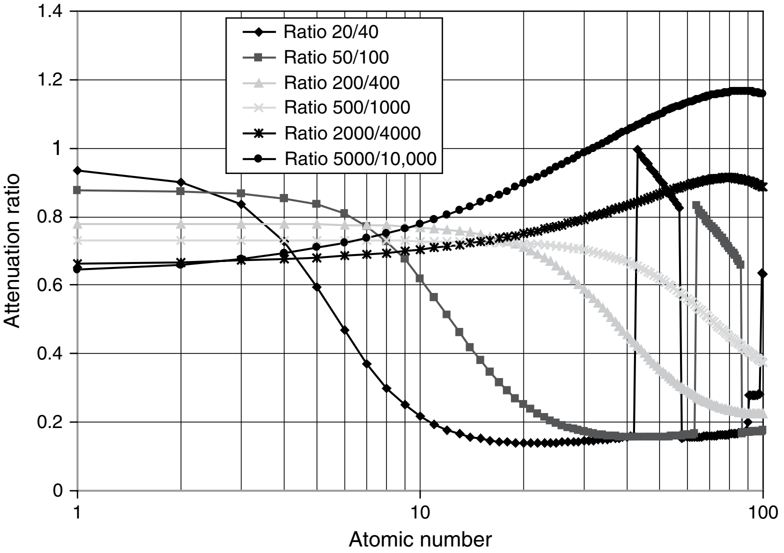

Figure 19 The Z dependence of the ratio of attenuation coefficients of a monoenergetic HI beam to a LO beam of exactly half its energy. The curves strongly depend on the energy of the HI beam, here shown at various values from 40 keV to 10 MeV. With HI energies below 1 MeV, the ratio falls with increasing Z, but above 1 MeV the ratio rises. In either case, the ratio is heuristically seen as a means for determining Z.

roughly independent of Z and E while the photoelectric effect exhibits roughly a $Z^{3.5}$ dependence and falls off like $1/E^{3.2}$. This provides a basis for distinguishing materials having differing effective atomic numbers by measuring HI and LO energy range attenuations.

The Z-dependent behavior of dual-energy systems over a variety of energies is illustrated in Figure 19. Here, ratios of monoenergetic HI attenuation to LO attenuation (taken as half the HI value) for a wide variety of HI energy choices are plotted as a function of atomic number Z. This heuristically shows that Z can be determined from such a ratio. For HI energies up to around 400 keV, the ratio falls with rising Z. Interestingly, for HI energies over roughly 4 MeV, the ratio is seen to increase as Z rises. The behavior for polyenergetic beams is more complicated, but the observed trends are still valid.

In the 1–10 MeV range, the most important attenuation processes are Compton scattering and electron–positron pair production. The mass attenuation coefficient for this latter process is roughly proportional to Z and rises very roughly as $E^{1.5}$. As before, materials of differing Z can be distinguished by measuring HI and LO energy photon beam attenuation, but now with energies in the MeV range. Established accelerator technology can readily produce such beams. The efficacy of dual-energy data acquisition coupled with sophisticated image processing has recently been demonstrated in experiments conducted at the Efremov Institute [69].

4.3. Multi-view systems

Multi-view systems make use of two or more stationary scans that view the baggage at differing view orientations. The EG&G Z Scan, which originated around 1990, used two dual-energy views, one from below and the other from the side. The incentive for this system was to increase the chance that one view would offer an unobstructed image of an object of interest. Two views constrain the volume of an object of interest to be within the associated quadrangle of intersection of the endpoint rays. This enables a rough estimation of density; however, the accuracy is too poor to be effective for threat detection. Systems based on two views suffer from an inherent ambiguity in locating point masses as illustrated in Figure 20. Note that observed attenuation from the two point sources can be attributed to the two masses denoted with circles or alternatively to the two masses denoted with triangles.

Adding a third view removes this ambiguity and offers significant advantages in image analysis. The L-3 Communications' MVT was the first system to adopt this approach and uses three X-ray tanks separated by roughly 60°, two below the conveyor plus a side-shooter. Detector arrays are arranged into sequential parallel planes. Using this system and a patented method for performing tomosynthesis, the MVT system demonstrates excellent performance. In fact, the system achieved certified levels of detection under tests performed by the FAA, albeit at a somewhat elevated false alarm rate. The system is capable of processing bags at throughput rates exceeding 1500 bags per hour.

The MVT extracts 3-D characteristics by examining feature points from pairs of projection views [70]. Each pair of projection views, selected from among the three possible pairs of projection views, produces respective triangulation points associated with the edges of objects. Bag contents are reconstructed via a tomosynthetic process. Knowledge of an object's mass (from attenuation) and its volume (from tomosynthesis) yields a reasonable estimate of its density.

In the early 1990s a group at Nottingham Polytechnic developed technology for viewing bags in a stereoscopic model [71, 72]. They employ a system using a single

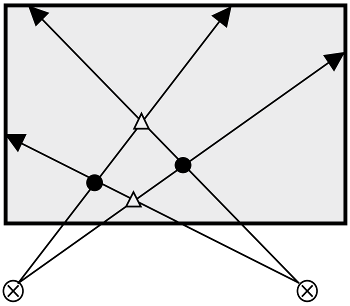

Figure 20 Ambiguity in locating point masses from two X-ray views. The observed X-ray attenuations may equally well be attributed to the two masses shown as the circles or alternatively to the two masses shown as the triangles. A third X-ray view would resolve this ambiguity.

X-ray source collimated into two diverging fan beams and viewed by two folded arrays of detectors. The data are stored and various means of presenting the images to viewers were developed. One method utilizes glasses with passive oppositely polarized lenses for each eye. The stereo images are presented on a monitor that rapidly alternates (100 Hz) images that are synchronized with a pi-cell in front of the screen. This allows the two image views to be presented alternately, switching between left- and right-polarized monitor illumination. The folded array geometry creates complications that require compensating distortion of the image data. The lateral offset or registration is an addition parameter that needs to be adjusted. The resulting image is stereoscopically 3-D although somewhat different from visual-light stereoscopic images. With the latter, objects are opaque whereas with the former, they are semi-transparent.

A novel use of multiview systems is to present a sequence of views in rapid succession to an operator. The views can be gotten by successive scans obtained in a number of ways involving sequential translations/rotations of the object and/or the source and/or the detectors. The technique is known today as “motion parallax” and previously as the kinetic depth effect [73]. Such scans are efficiently generated by using a single X-ray source viewed by multiple linear collimators and folder arrays. Image Scan Holdings employs this technology in its recently commercialized Axis-3D system.

4.4. Scatter-based systems

Since the mid-1980s, X-ray scatter information has been used for baggage inspection, often as a means to supplement transmission imaging. X-rays are scattered primarily by Compton (incoherent) interactions. The technique makes use of the difference in scattering behavior between organic and metallic materials. Low-Z materials scatter X-rays quite effectively, whereas higher Z material preferentially absorbs X-rays via photoelectric absorption and hence show less scatter. The method is most readily implemented by using a flying-spot X-ray beam and large area off-axis detectors. The detectors may be placed beyond the target (forward scatter) or behind the target (backscatter).

A schematic of a generic scatter imaging system is showing in Figure 21. The scatter detectors are preferably quite large. Typically, photomultipliers are used as transducers because of their inherently low noise characteristics. The read-out is synchronized with the flying-spot scan. In this way, a raster scan image is constructed. Organic materials show up in the scatter images as bright areas that have relatively high photon counts. Scatter is most strongly seen from the bag surfaces closest to the detector, partly because of the geometric efficiency factor but more significantly because of self-absorption within the bag. Scattered photons are “softened” and thus have more limited penetrating power, particularly in the backward direction. Backscatter images are more easily interpretable than forward-scatter images since the rear surface receives a relatively uniform X-ray flux whereas the front surface flux is reduced unpredictably by contents within the bag. By examining the ratio of scattered intensity to the attenuation seen in the transmitted image, it is possible to estimate Z. Organic material shows more scatter signal than metals do for the same attenuation of the transmission beam. This can be used to create

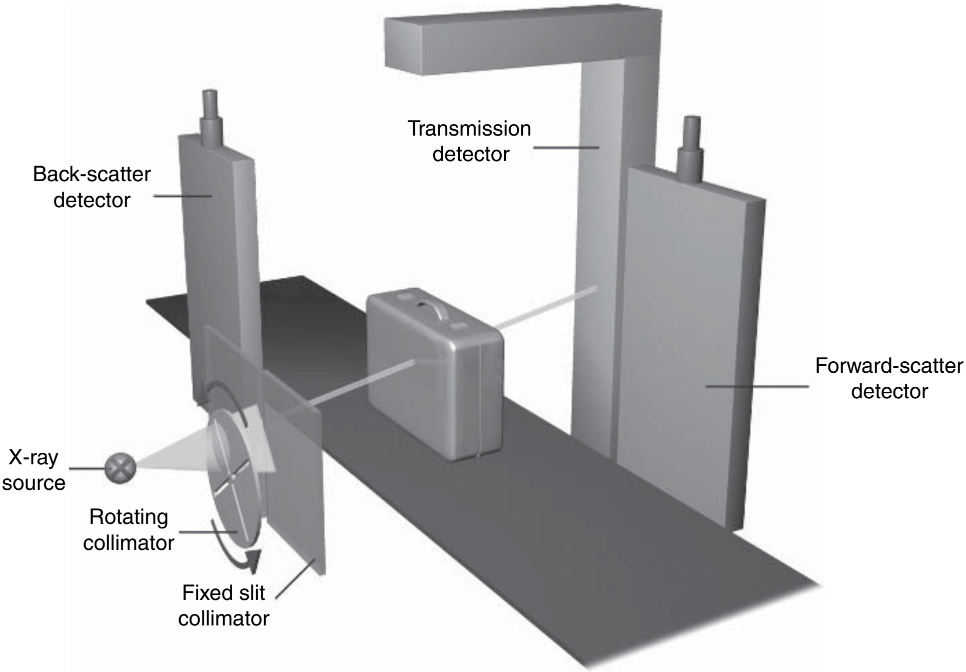

Figure 21 Artist's depiction of a system for imaging scattered X-rays. A fixed collimator slit and a rotating collimator slit produce a scanning pencil beam. A transmission detector monitors the transmitted beam, whereas large-area detectors respond to forward-scattered and backscattered X-rays emanating from the bag.

color-coded images of *Z*, but the images from dual-energy systems are more definitive as they do not suffer from the geometric dependencies cited above.

The technique works at higher energies as well. Here the *Z* dependencies are much less pronounced because Compton scatter is the dominant mode of interaction regardless of *Z*. Nevertheless, concentrations of material still show up strongly. The geometric position of the scatter source modulates the signal intensity and imparts a visual perspective to objects in backscatter images. Accurate material discrimination power is not possible, but the technique provides a means for visualizing illicit material that may be hidden near the surfaces of a cargo container.

Backscatter images have been utilized for personnel screening. This technology was developed in the early 1990s. The dose is extremely low (approximately 10 μR) and a person could undergo hundreds or even thousands of screenings per year without significantly elevating his naturally occurring radiation burden. An artist's composite image of a person harboring concealed weapons is shown in Figure 22. The technique is clearly effective for identifying weapons concealed on the body or in clothing worn. Privacy issues would be a concern if the method were used for screening the general public. Likewise, the intentional exposure to ionizing radiation is problematic, even though the doses are minimal, given the sensitization of the public toward radiation and the possible risk of malfunctions.

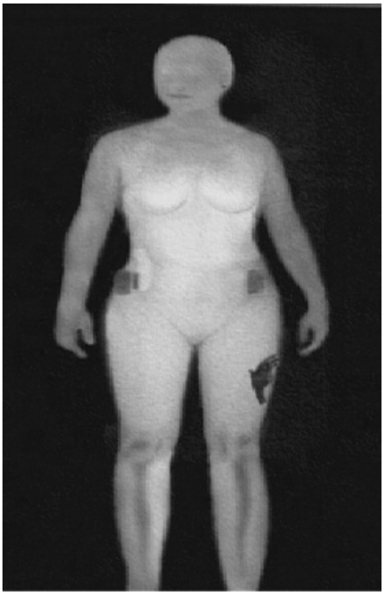

Figure 22 Artist's rendition of a person with concealed weapons seen using an ultra-low-dose backscatter system. Imaging is effective, but radiation safety and privacy issues may arise.

A flying-spot beam, though ideal for scatter applications, is highly inefficient in its use of X-ray tube flux. Fan beams contain roughly 100–500 times more total photons for the same tube operating conditions. This extra flux per pixel allows fan beam systems to produce much clearer (less mottled) images or alternatively to produce images much faster. Fan beam systems, such as L-3s MVT and VIS108, have been equipped with scatter detection for enhanced detection of sheet explosives [74]. The basic idea is to have an array of collimated scatter detectors, such that each detector is responsive to a limited volume within the bag. These systems employ a backscatter array under the tunnel conveyor in conjunction with an up-shooting X-ray beam. The scatter detection system requires initial calibration. Used in combination with the transmitted image, the dual-energy backscatter information provides an effective means to enhance explosive detection. The same technology would be applicable to the detection of concealed contraband such as narcotics.

4.5. Coherent X-ray scatter

CXRS entered the commercial market in the mid-to-late 1990s after a long development period. The basic principles have been known for many years, but practical development faced many hurdles. Most explosives have a crystalline structure. Because the crystals are small and randomly orientated, the structure is sometimes referred to as polycrystalline. These crystals exhibit a strong coherent scatter at certain angles that depend on the X-ray energy and the crystal lattice spacing. This coherent scatter (also called diffraction) is a property of the crystal lattice and is unrelated to

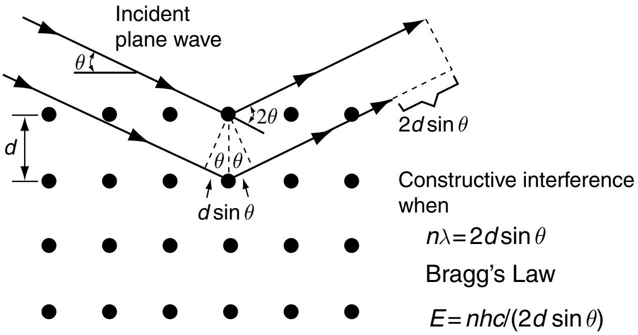

Figure 23 Bragg relation for crystalline coherent scatter. The atomic distances are comparable to the X-ray wavelength. When the difference in path lengths from reflections off adjacent crystal planes is a multiple of the wavelength, reinforcement occurs. Scatter is significantly favored when the X-ray energy and scatter angle obey the Bragg Law.

coherent scatter that occurs off atomic nuclei. The term "coherent" merely denotes that the scattered photon has the same energy as the incident photon.

Crystalline coherent scatter obeys the Bragg relation that is shown schematically in Figure 23. The photon energy, E, at which coherent scatter will occur off a target crystal is

$$E = \frac{nhc}{2d \sin \theta} \tag{13}$$

where n is an integer, h is Planck's constant, c is the speed of light, d is the distance between adjacent crystal planes, and θ is the angle between the crystal plane and the incident photon. Scatter off polycrystalline material is represented in Figure 24, which shows a number of small crystals that are randomly orientated. A schematic illustration of the arrangement for energy-dispersive CXRS is shown in Figure 25. The X-ray beam provides a broad spectrum of X-ray energies. A highly-energy-resolving X-ray detector, such as a germanium or CZT detector, is needed to identify the coherent-scatter peaks. The energy and amplitude of such peaks can be matched against a library of known polycrystalline explosive materials to determine the presence of such threats. The same technique is effective for identifying other illicit material, such as certain polycrystalline narcotics.

If the angle of observation is Θ relative to the incident beam, then only those crystals orientated at (or very near to) the angle $\theta = \Theta/2$ will contribute because the angle of incidence equals the angle of reflection for Bragg scattering. At this angle, only those photon energies that obey the Bragg relation will scatter toward the point of observation. The predominant scatter is for the first harmonic, $n = 1$. Higher harmonics require more energetic photons and their contribution to coherent scatter tends to be substantially weaker, both because of reduced scatter efficiency and reduced beam flux at these energies.

CXRS can also be employed in an angular dispersive mode (or both angular dispersive and energy dispersive). In this mode, a single-energy photon source,

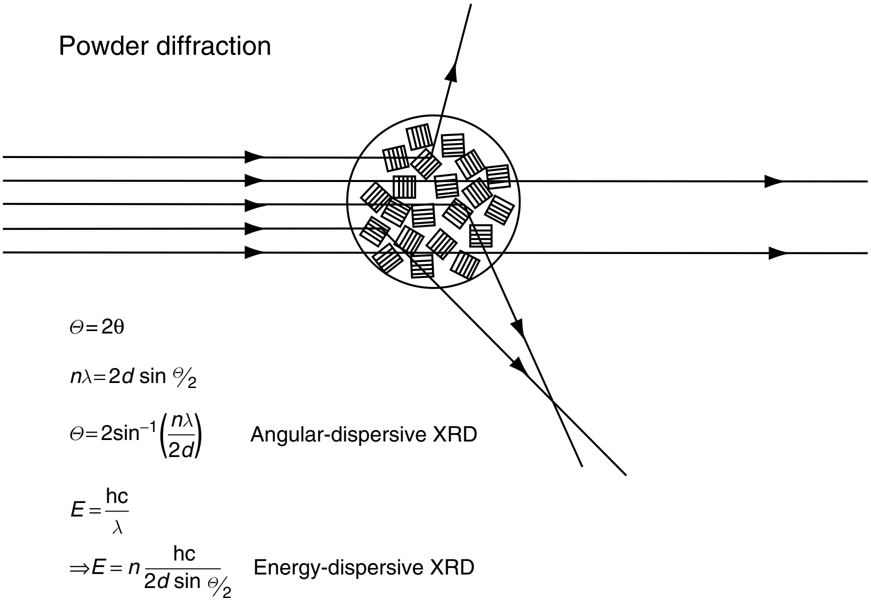

Figure 24 Scatter off polycrystalline material. The small crystals are randomly distributed resulting in reinforced scatter in the forward direction in a series of rings concentric with the incident beam.

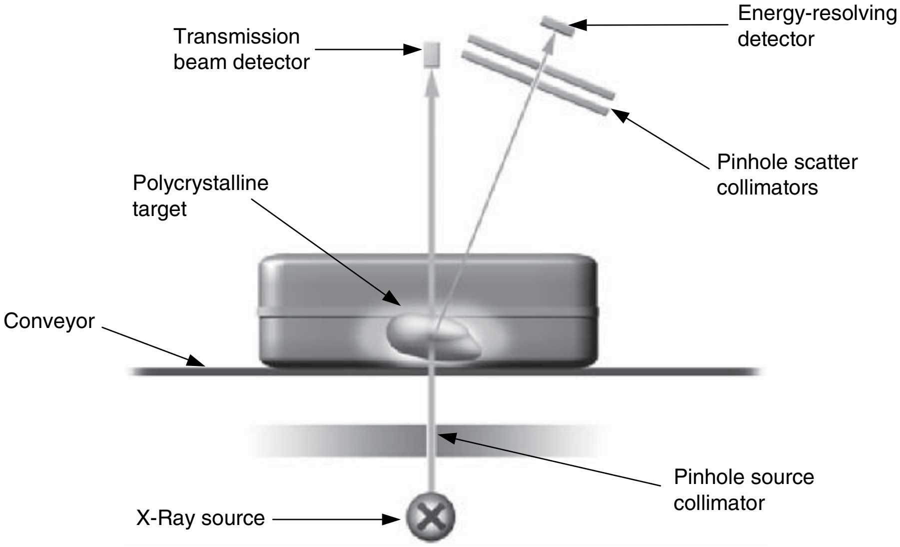

Figure 25 Schematic illustration for a system based on energy-dispersive coherent X-ray scatter (CXRS). Observation of the scattered photons is restricted to a fixed angle via a pinhole collimator. The spectrum from a highly energy resolving detector will show peaks at particular energies that are characteristic of the polycrystalline target. Computerized identification techniques can be used to identify the target substance.

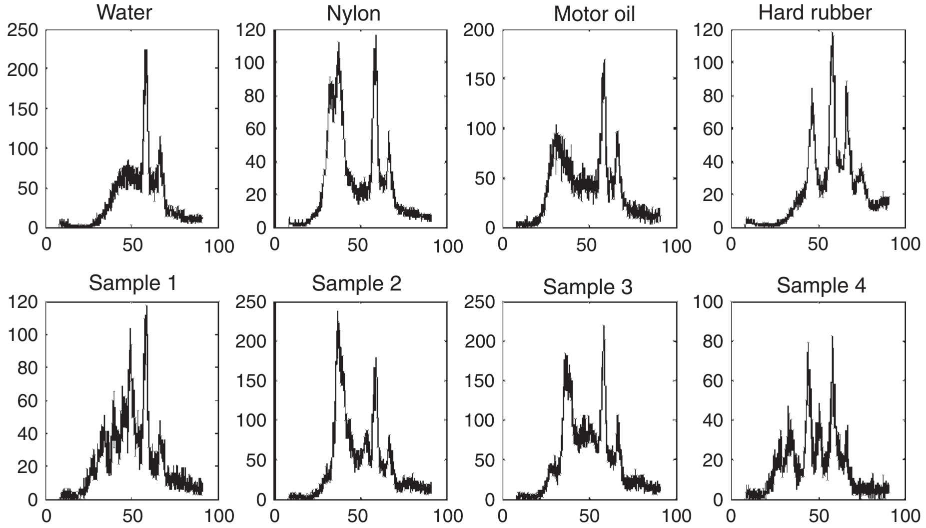

Figure 26 Spectra from four explosive samples and four non-threat materials. The differing structures of these spectra form the basis for identifying the target material. Incoherent scattering contributes to the background continuum and produces two peaks associated with the X-ray fluorescence off the tungsten anode. This is seen most clearly in the spectra with water or motor oil as targets.

which may be obtained from a radioactive source or Ross-filtered X-ray beam, impinges on the target of interest. The scatter is viewed by an extended array of collimated detectors covering an angular spread. In this case, the array indexes the scatter angle, and characteristic peaks will be observed at certain angles for each polycrystalline material. Since the energy-dispersive technique is more commonly employed, we will focus on this approach hereafter.

Figure 26 shows the spectra from four explosive samples and as well as non-threat materials. These spectra exhibit strong peaks slightly below 59 and 69 keV, which are unrelated to coherent scatter. These peaks arise from incoherent (Compton) scatter of fluorescent radiation at 59 and 69 keV, which is produced from tungsten anodes. Scatter off water shows no apparent CXRS peaks. The four explosive samples clearly show characteristics peaks, which differentiate them from the non-threat materials and from each other. Heuristically, the location and relative amplitudes of these peaks provide an effective means for detecting explosives.

A number of hurdles have made CXRS difficult to deploy in practical systems, although these difficulties are being overcome. The scattered X-ray flux has a low-intensity level because of the geometric distances involved and the restricted set of crystals that have the right orientation to contribute Bragg scatter. This demands high beam currents and/or long exposures to achieve the desired sensitivity. Compton scatter and atomic coherent scatter form a continuum background, which necessitates high-resolution detectors to observe the CXRS spectral features used for identification. Self-absorption of incident and exiting photons within the baggage tends to distort the spectrum in ways that require normalization. Attenuation measurement of the transmission beam, for example, can supply this normalization, but compensation is imperfect. Finite collimator apertures, X-ray beam spot width, and finite detector size degrade angular resolution, which contributes to loss in energy sharpness in the CXRS peaks. Carefully controlled mechanical movement of the detectors is necessary to track target voxels throughout a range of lateral and height positions in the inspection tunnel. The spectrum-matching algorithm must be robust, and include as many explosive materials as possible without false alarming on an innocuous material or a composite of innocuous materials. Nevertheless, CXRS vendors have been resourceful in overcoming these difficulties and making the technique effective. Recently, TSA certification levels of detection have been achieved with a CXRS system although at a relatively low baggage thoughput rate.

5. CONCLUSION

X-ray techniques are extremely valuable for the detection of explosives and other illicit substances. X-ray screening systems were among the first methods employed to protect airlines from hijacking and terrorist actions. Their use has continued to expand and they are widely recognized by the public as an effective means for security, particularly at airports and public buildings. In the last 15 year, X-ray detection has been automated, so that airline checked bags are now routinely examined for explosives. This analysis is done rapidly, in a matter of seconds, with high accuracy, and with a reliability level that has made these systems true workhorses. X-ray systems have expanded beyond routine imaging. Specialized techniques such as backscatter and CXRS offer a new range of applications. There is a rapidly growing interest in the inspection of cargo. Large-scale, MeV energy systems are now being adopted for use by customs authorities as well as other agencies interested in examining large cargo containers. X-ray technologies will surely remain an important means for security inspection and illicit substance screening in the foreseeable future.

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CHAPTER 7

CT TECHNOLOGIES

R.C. Smith *and* J.M. Connelly

Contents

1. INTRODUCTION

X-ray computed tomography (CT), initially developed for medical diagnostics, is now also being used extensively in airports, worldwide, to find hidden explosives in checked airline luggage. The population of CT systems deployed at US airports as of January, 2008, numbers more than 1700.

CT images provide a large amount of detailed information about each individual object packed in articles of luggage. This information is not available in images produced by conventional X-ray scanners.

This chapter discusses the features of CT imaging and outlines how the images are formed. Several different technical approaches are described along with examples. Finally, issues to be considered in designing luggage scanners are presented.

2. FEATURES OF X-RAY CT IMAGING

CT is an X-ray imaging technique that has unique capabilities in security applications. Presently, its main use in the security arena is to locate hidden explosives in airline luggage. It can also be used for finding other contraband material.

In locating contraband the CT approach has two major advantages over conventional X-ray imaging. First, and most importantly, it can measure and record, unambiguously, the material property μ of individual objects packed in a bag. The quantity μ is the X-ray attenuation coefficient, which is proportional to a material's density and is also a function of the material's atomic number. Accordingly, the CT process can differentiate among a wide variety of materials.

This ability is in contrast to that of conventional X-ray imaging, which provides only a line integral of μ across the entire thickness of a bag. A thick piece of low-μ material can give the same X-ray reading as a thin piece of high-μ material. Thus two different materials can give the same reading and cannot be distinguished from one another. CT, however, can determine μ for each individual object even if the bag is populated with numerous overlapping items that would further confuse a conventional X-ray assessment.

Since μ is proportional to material density (g/cm^3), it is common to refer to the CT image as a density image.

The second advantage of CT is its ability to generate a full three-dimensional (3D) image of a bag and its contents. The 3D image takes the form of a data set of the density values for each point in a bag specified by the three rectangular coordinates x, y, and z. The 3D density image allows computer software to isolate every object in the bag from its neighbors and to test each one for properties of explosive materials.

A CT baggage scanner generates density maps in thin planes that slice through a bag. (The word "tomography" comes from the Greek word *tomos*, meaning "a piece cut off."[1]) These planes are perpendicular to the direction of motion of a bag as it moves through the scanner on a conveyor belt. An analogy is a loaf of thinly sliced raisin bread, where inspection of the slices reveals the locations and color of all the raisins.

Some scanners do not generate full 3D bag images, but instead they generate CT slices only at optimum locations. These systems use a computerized conventional X-ray first-stage screener whose software identifies where candidate threat objects are located in a bag. The location information is passed to a CT stage that subsequently interrogates the bag with several slices through the suspicious object(s). Its software assesses the resulting density values for consistency with threat material. This approach uses the density-measurement capability of the CT process but does not use its 3D feature.

Other CT scanners do not use a first-stage screener, but instead they continuously generate contiguous slice images of the bag as it moves at a constant speed through the system on the conveyor. The system's software stacks these slices, one next to the other, to form the 3D density image. The software then searches the entire 3D image for threat objects.

Figures 1 and 2 contrast the conventional X-ray and CT X-ray image processes. Figure 1 schematically shows the formation of a 3D bag image from CT slices.

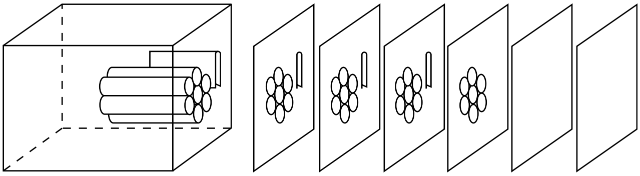


Figure 1 Schematic drawing of the slice-by-slice generation of a 3D CT image of a bag containing seven sticks of dynamite and one book.

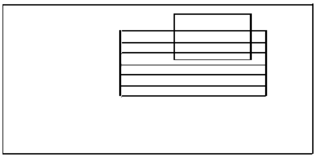


Figure 2 Schematic drawing of the conventional 2D X-ray image of the same bag as shown in Figure 1. There is not enough information for accurately determining density, volume, mass, and location of the individual objects.

In the figure, the right-most two slices show only the outline of the bag. The third slice from the right intersects seven sticks of dynamite, which can be seen to be touching each other. Each of their densities can be measured separately. The fourth slice shows the end of a book, which clearly does not touch any of the dynamite sticks. From the full collection of slices (the 3D image) one can determine the density, volume, and position in x, y, and z of all the objects. Knowing the volumes and densities allows one to compute the masses of each object.

Figure 2 schematically shows a conventional X-ray image of the same bag shown in Figure 1. Even though the upper portion of the book has no interference with other objects, one still cannot compute its density, for there is no information as to its thickness. The multiple overlaps of the dynamite sticks make their characterization even harder. The boundaries of the dynamite sticks could even lead to the mistaken conclusion that there are only six of them. The CT process makes possible the determination of object material and configuration information that is impossible for conventional 2D X-ray approaches.

3. PRINCIPLES OF CT IMAGING

Numerous texts and a wealth of literature exist that describe many approaches to X-ray CT imaging. Examples include Refs [2–4]. All approaches involve a large number of X-ray transmission measurements of the item being imaged. In addition to measuring transmission at different positions of the item, all these measurements are then repeated at a large number of different trajectory directions of the incident X-ray beams.

The approach used in all presently fielded explosives detection systems is known as "third generation." A third-generation CT imager has an X-ray source on one side of the item to be imaged and a large number of small X-ray detectors arrayed on the other side. The source and detectors are mounted on a single vertically oriented disk that rotates about its center. The disk's center has a large hole in it through which passes, e.g., a bag riding on a conveyor belt (Figure 3). The figure depicts a typical geometry for making a single-slice CT measurement.

3.1. Single-slice CT

Single-slice CT refers to a configuration where the system passes an individual, vertical, CT slice through a pre-selected region of interest in a bag. To prepare for

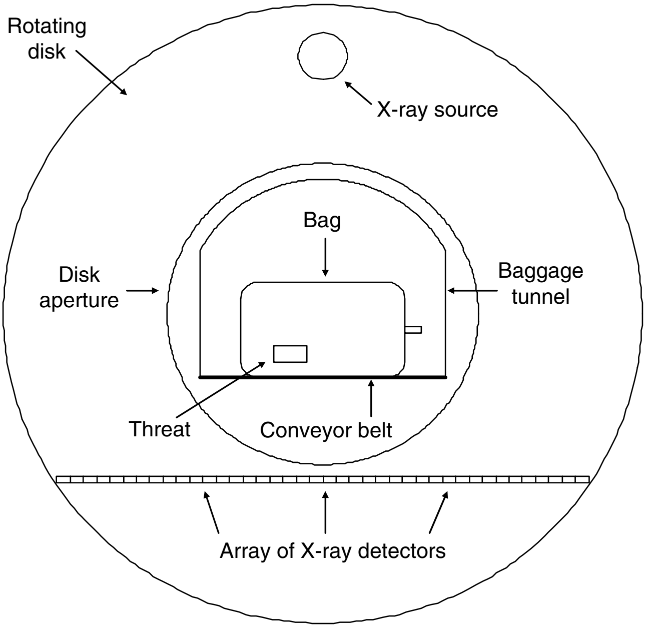


Figure 3 A third-generation CT baggage scanner typically has a conveyor belt for the bags that passes through a hole in a rotating disk that supports an X-ray source and an array of detectors. The conveyor motion direction in this drawing is into the page.

the measurement the conveyor comes to a complete, temporary halt such that the region to be imaged sits in the plane defined by the source's emission point and the line formed by the X-ray detectors. The process in making the single-slice image is fundamental to all other CT image types and is outlined here as an illustrative example.

Figure 4 shows the coordinate systems associated with the example shown in Figure 3 The horizontal axis is x, and the vertical direction is y. The conveyor belt is perpendicular to the y axis and moves in a direction into the page. The disk rotation angle, θ, is measured counter-clockwise from the y-axis. This example has 501 detectors in a straight line, which is defined as the s direction. The straight lines running from the source to the detectors represent rays of radiation detected at each detector location. There are 501 such rays that the figure represents with 21 lines. (The detector geometry is often modified to place individual detectors along an arc of a circle centered on the X-ray source.)

The disk rotates at a uniform speed. The system's electronics capture all the detector readings simultaneously, typically several hundred times per second. Each such collection corresponds to a single value of θ. Shortly thereafter the electronics capture a subsequent set of readings, this time associated with an angle $\theta + \Delta\theta$. The value of $\Delta\theta$ is typically 1° or less. The process repeats until every point in the bag has been sampled with rays from 0° to 180° in increments of $\Delta\theta$. To accomplish this requirement, the disk must rotate through an angle of 180° plus the angle at the

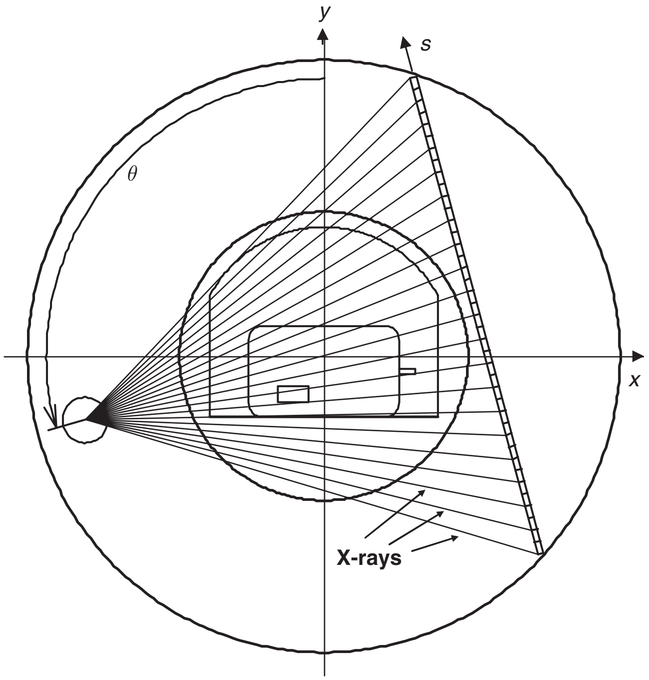


Figure 4 A third-generation CT measurement exposure geometry where the disk rotation angle, θ, is 105° (see Figure 3). Typically, from 200 to 1000 such measurements are made, depending on the design of the scanner, at equally spaced angular intervals in order to generate one CT slice.

source subtended by the line of detectors (63° in this example). Accordingly measurements are made over an angular interval of 243°.

The measured data for a CT slice form a mathematical rectangular matrix of X-ray detector readings. Each matrix row corresponds to a single rotation angle, θ. If the increment between angle values were $\Delta\theta = 0.5°$, then there would be $243°/0.5° = 486$ rows. Each matrix column corresponds to an individual detector. Thus each row comprises an ordered list of detector readings representing X-ray attenuation as a function of distance, *s*, along the detector array.

X-ray attenuation affects a detector reading according to Eq. (1). For the case when there is no object in a beam path between the source and a detector, the detector reading is I_0. With the insertion of a bag the detector reading becomes I because of X-ray attenuation in the bag contents. In Eq. (1) the exponent magnitude is the line integral of the attenuation coefficient, μ, along the ray from the source to the detector. The integral is necessary because μ is a function of position (x, y) in the bag.

$$I = I_0 e^{-\int \mu(x,y)\mathrm{d}l} \tag{1}$$

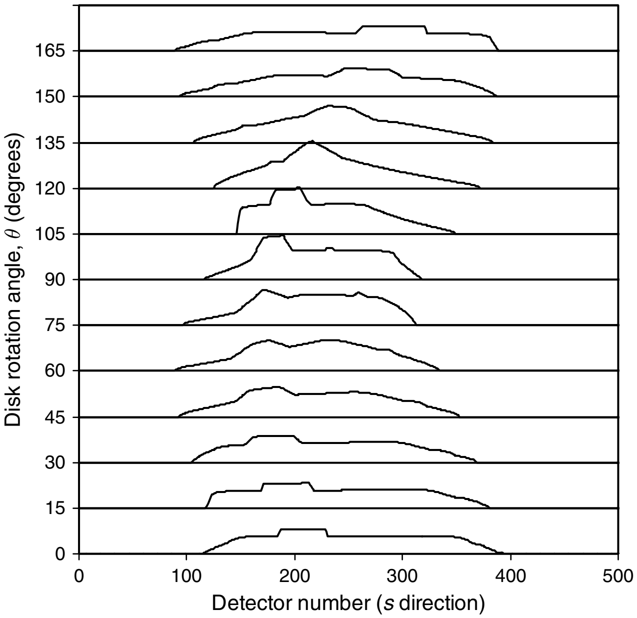


Figure 5 Example plots at 15° intervals of the θ–s detector-reading matrix for a single-slice measurement using the geometry of Figures 3 and 4. Detector readings are from Eq. (2).

In the θ–s detector-reading matrix, the values tabulated are $\ln(I_0/I)$ as given in Eq. (2), which is the line integral of μ. It has the property that higher values mean higher thicknesses and densities of material.

$$\ln\left(\frac{I_0}{I}\right)=\int \mu(x,y)\mathrm{d}l \tag{2}$$

(In actual practice, one uses modifications to Eq. (2), which include the so-called beam-hardening corrections to account for deviations from Eq. (1) caused by the broad-spectrum nature of the incident X-ray beam.)

Figure 5 illustrates the nature of the θ–s detector-reading matrix. It is based on the geometry of Figures 3 and 4 under the assumption that the attenuation coefficient of the bag contents is $1.0\,\mathrm{cm}^{-1}$ and the threat's attenuation coefficient is $3.5\,\mathrm{cm}^{-1}$. The figure shows the results of Eq. (2) for selected rows at 15° intervals.

Even with the simple bag model of Figure 3, there is a large variability among the projections at different angles. At 0° one sees that the left and right sides are almost mirror images of each other with the exception of a small rightward protrusion because of the bag handle. The threat is clearly visible as a nearly rectangular region near detector number 200. At 90° the threat has become narrower and stronger, while the handle is now located at the center of the detector array. At the 105° angle, from detector 1 to 146 there is essentially no attenuation, but a steep increase is seen starting at detector 147. This effect is illustrated in Figure 4 where one sees a ray running nearly parallel to the bag's bottom surface, suffering no attenuation, and a neighboring ray running through the entire length of the bag near the bottom suffers a very high attenuation.

There are a number of different methods of converting the θ–s detector-reading matrix into a 2D density map to produce the slice. These methods are known as reconstruction algorithms. They are covered in detail in many references including Refs [2–4]. They convert the θ–s data to 2D images comprised of pixels. The value assigned to each pixel is normally a measure of the X-ray attenuation coefficient, μ, at the x, y position represented by the pixel. Typically, pixel dimensions are from 0.5 to 4.0 mm, depending on the design of the equipment.

The reconstruction methods used most often are variations of the filtered backprojection algorithm [2–4]. Often the algorithms require re-sorting the rays and performing interpolations to arrive at a set of equally spaced parallel rays for each of the θ values from 0° to 180°. Occasionally, a full 360° scan is used along with strategies to enhance the spatial resolution of the image. The choice of reconstruction algorithm is based on many factors including trade-offs among image accuracy, spatial resolution, required image-generation rate (throughput), available computer speed and capacity, and system cost.

3.2. Multislice CT

CT slices are the bases for generating 3D density maps. A large number of 2D CT slices assembled back to front serves to form a 3D image. Figure 1 shows this relationship schematically. There are many approaches to this process, each having its own features and drawbacks.

The spatial resolution along the slice-stacking direction, z, is typically, though not necessarily, the same as the pixel-to-pixel spacing in the 2D slices. The 3D image is therefore made up of numerous, small, cubical or rectangular volume elements called voxels. The value assigned to each voxel is normally a measure of the X-ray attenuation coefficient, μ, at the x, y, z position represented by the voxel. A voxel's height and width in the x and y directions match the pixel dimensions in the 2D slices, and its length equals the inter-slice spacing.

The conceptually simplest multi-slice 3D imaging process is known as the "step-and-shoot" method. Using this method the scanner (i) halts its conveyor, (ii) collects projection data for a single slice, (iii) resumes belt motion, (iv) halts the belt after having advanced by one voxel length, and (v) collects new projection data for the next slice. The scanner repeats the process until it has covered the desired image length. To maintain a desired baggage throughput rate the reconstruction computer processes data from each slice during the time the subsequent slice data is being collected. Thus at the end of a bag scan the entire 3D image is available for contraband detection processing. A drawback of the step-and-shoot approach is the mechanical complexity needed to increment the bag position accurately and rapidly up to 1000 times to maintain both image quality and baggage throughput.

The next level beyond the step-and-shoot method is the helical-scan approach. The conveyor belt of a helical-scan system moves continuously at a uniform speed and is synchronized with the rotating disk that holds the X-ray source and detectors. The synchronization ensures that by the time a bag has advanced by one voxel length, the system has collected enough angle-dependent exposure data to generate a single CT slice.

Both the step-and-shoot and single-detector-row helical-scan methods suffer from low throughput. If a typical bag and inter-bag gap represent together a length of 80 cm, in order to achieve a throughput of, e.g., 675 bags per hour, the conveyor belt would need to run at 15 cm/s. If the desired image spatial resolution along the belt was 1/3 cm, then slices would need to be generated at a rate of 45 slices per second. If the fan angle subtended by the line of detectors when looking from the source was 60°, then each slice would need a disk rotation interval of $180° + 60° = 240°$ per slice. Accordingly, each slice would need $240°/360° = 2/3$ of a revolution. Therefore 45 slices per second translates into 30 revolutions per second or 1800 RPM. The centrifugal load at the edge of a 2 m diameter disk would then be in excess of 3660 Gs, which would tear most equipment apart. Presently, some of the fastest systems are being designed for rotation speeds of up to 120 RPM, which is nowhere near 1800 RPM. At 120 RPM the centrifugal load is in excess of 16 Gs, which is manageable, but such a configuration would only be able to maintain a throughput of 45 bags per hour. Accordingly, even with a helical-scan design, systems employing a single row of detectors cannot come close to meeting realistic throughput requirements while generating 3D images.

The method to avoid such high rotation speeds is to supplement the single row of detectors with many such rows placed next to each other. Accordingly, instead of a single row of detectors, as shown in Figures 3 and 4, the system uses a 2D array (Figure 6). If there were 20 detector rows, the conveyor belt could advance by 20 detector widths for each 240° of disk rotation. In the example of the previous paragraph using 20 detector rows would allow the disk to rotate at $1800\,\text{RPM}/20 = 90\,\text{RPM}$. At 90 RPM the centrifugal load would be only 9 Gs, which is an acceptable value.

Multi-row detector systems are referred to as "cone-beam" systems. With a moving conveyor they become "helical cone-beam" systems. The cone-beam designation is in contrast to the fan-beam geometry used in Figures 3 and 4, where the source and detectors are all in a single plane.

There are numerous associated helical cone-beam image reconstruction methods. They range from approximating the helical cone-beam projections by a series of flat, tilted planes [5] to methods derived explicitly for the translating 3D measurements [6]. Most of these methods draw on the principles underlying the filtered backprojection algorithm. One makes the choice among the various approaches according to trade-offs in image quality, processing speed, and computer cost.

3.3. Dual-energy CT

Dual-energy is a CT imaging approach aimed at generating and extracting additional information beyond material density from image slices. The additional information, a second material property, is known as the effective atomic number, Z_{eff}. Although the X-ray attenuation coefficient μ is proportional to a material's density ρ, it is also a function (i) of the atomic number Z of each of the material's

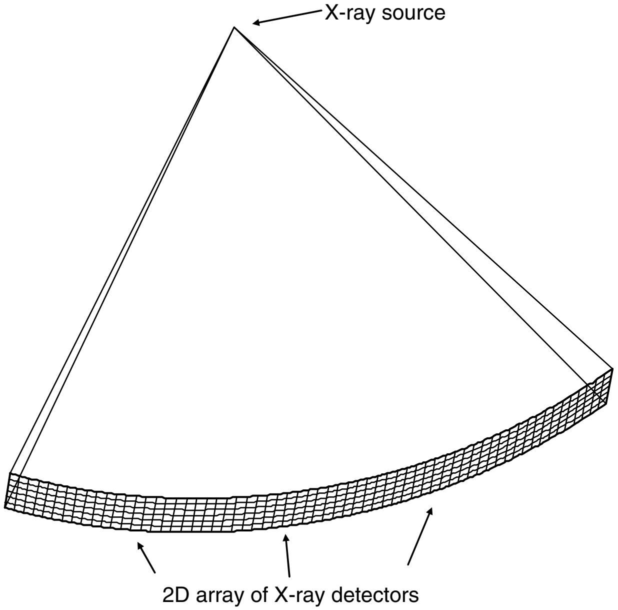


Figure 6 A multi-row detector array is used in a cone-beam system. In this case, the detector rows fall along circular arcs centered on the X-ray source's x, y coordinate values. Detectors of equal size therefore subtend equal angles with respect to the source. This characteristic and other system and data-analysis considerations often make curved detector rows more attractive than straight ones like those of Figures 3 and 4.

constituent elements and (ii) of the energy E of the X-ray photon. The attenuation for an X-ray photon of energy E by a pure elemental material of atomic number Z and of density ρ is thus characterized by an attenuation coefficient $\mu(\rho, Z, E)$. Mixtures and compounds share the characteristics of each elemental component and therefore behave as if they were characterized by an intermediate value of atomic number, Z_{eff}. Accordingly, the attenuation coefficient becomes $\mu(\rho, Z_{\text{eff}}, E)$.

Dual-energy methods appear in many references. Examples include Refs [7–10]. The underlying approach is to measure two corresponding sets of X-ray projection data for each slice. For each of the two sets the shape of the incident X-ray energy spectrum is markedly different. One way to achieve such a difference is to use two markedly different X-ray tube voltages for each set. The high-voltage exposure is called the high-energy data, and the low-voltage exposure is called the low-energy data. Therefore, the method is referred to as dual-energy.

Through understanding the joint ρ, Z, and E dependence of μ, one uses the high- and low-energy attenuation measurement of each ray to compute two new corresponding ray values, one being the line integral of density and the other being the line integral of effective atomic number. The two new sets of ray data then serve to generate two new image slices, one being a 2D map of ρ and the other being a 2D map of Z_{eff}.

Figure 7 shows one way to generate the dual-energy measurements. In this example, projection data are collected for each half-degree of disk rotation. The

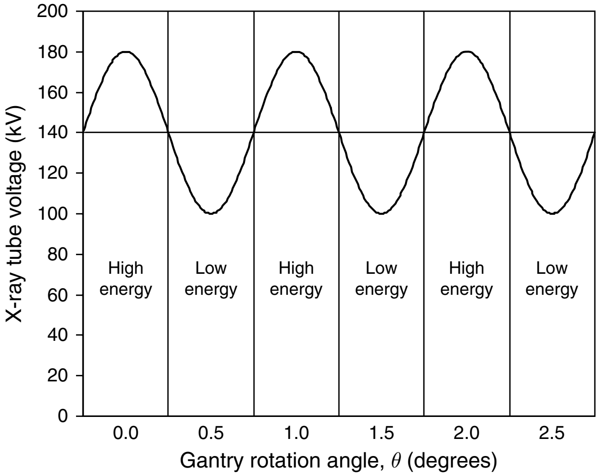


Figure 7 In one example of a dual-energy process, where Gantry denotes the rotating disk, the X-ray tube voltage swings between 180 and 100 kV, with peaks and valleys synchronized, respectively, with integral and half-integral disk-rotation angles.

X-ray tube high-voltage power supply is synchronized with the rotation. Its output is a 40 kV sine wave superimposed on a 140 kV DC level. The timing is such that the high-energy peak of the sine wave (180 kV) occurs during data collection for integral values of projection angle and the low-energy valley (100 kV) falls during the half integral angle values. A high-energy ray's corresponding low-energy ray comes from averaging of the two half-integral values measured on either side.

Dual-energy CT capability, providing measurement of a second, independent material quantity Z_{eff} of candidate threat objects, is expected to aid significantly in reducing false alarm rates and thereby to improve performance over single-energy CT systems.

4. CT SCANNER OPERATION

A photograph of a typical CT scanner appears in Figure 8. It is an L-3 Communications eXaminer® 3DX 6500, which has the same envelope as its predecessor, the eXaminer® 3DX 6000. This is a TSA-certified explosives detection system that makes and assesses full 3D, single-energy, X-ray images of airline luggage. The configuration shown is for stand-alone operation. It can also be integrated into the conveyors of an airport baggage-handling system.

As depicted, the luggage moves from left to right after being placed on the tilted entrance conveyor, which then transitions to a horizontal motion for scanning. The larger structure in the center is the CT scanner section. Next comes the exit conveyor that transitions downward for ease in retrieving bags. Conveyors in the entrance tunnel, in the scanner section, and in the exit tunnel all run at the same speed. The two conveyor tunnels at either end each contain several sets of leaded

Figure 8 Example of an X-ray CTexplosives detection system that generates and analyzes 3D images of airline luggage.

curtains for X-ray shielding. Accordingly, the conveyors can move closely spaced bags through the system without stopping while still keeping X-ray exposure to personnel well below the safety limits.

A block diagram of a typical CT system appears in Figure 9. The heart of the system is the X-ray scanner, whose processes are monitored and controlled by computer. In all cases, the X-ray components include source and detector-array components mounted on a rotating disk. The X-ray components for a selected 2D-slice-type scanner often also include a stationary source–detector pre-screener assembly. Detector readings enter the Image Reconstruction Computer at a high rate and are converted into CT slice images that move to a computer called the Image Analysis System.

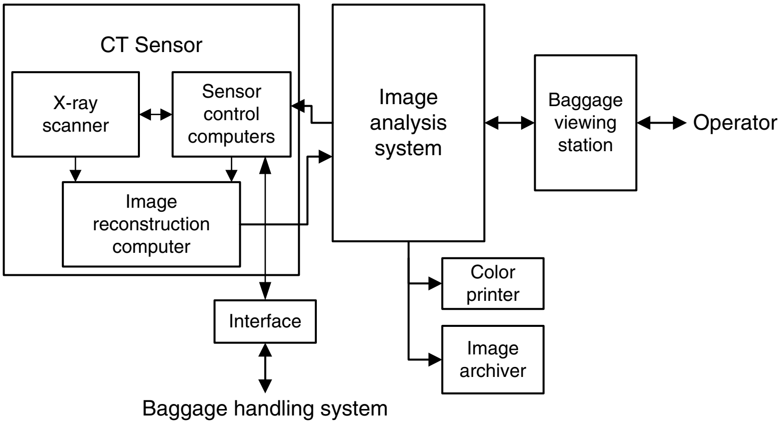
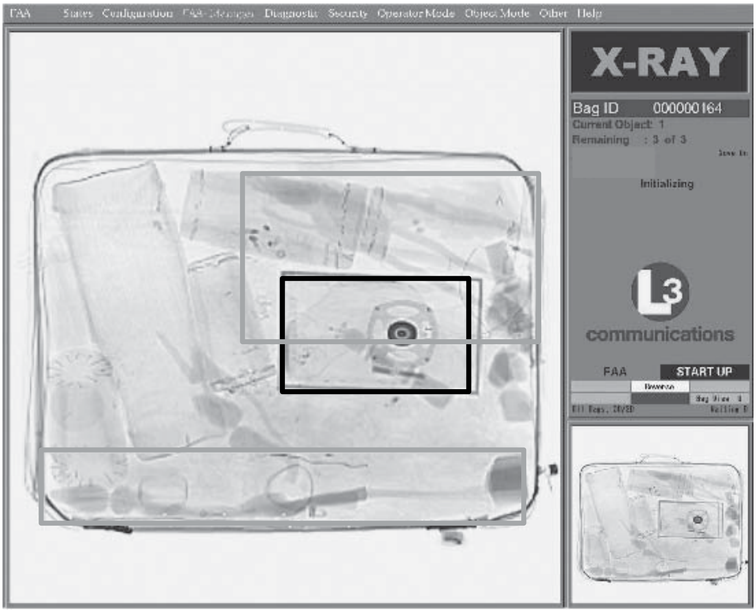


Figure 9 A typical CTscanner system (i) accepts bags for inspection, (ii) makes images in terms of material properties such as density, (iii) analyzes the images for signatures of contraband, (iv) makes annotated images available to the operator for viewing and disposition, (v) prints selected image hard copies, (vi) electronically stores selected images, and (vi) ensures a smooth flow of baggage via communication with the external baggage handling system.



Bag ID 000000164
Current Object: 1
Remaining : 3 of 3

Figure 10 Baggage Viewing Station 2D projection view of a bag containing three potential threats. The black rectangle (normally displayed as turquoise on a color display) identifies the object to be assessed in 3D as shown in Figure 11.

The Image Analysis System segments the bag image into objects, each of which it then analyzes for characteristics of contraband [11]. Finding contraband triggers an alarm situation. The Image Analysis System then annotates the alarmed images and makes them available for operator viewing at the Baggage Viewing Station. (Operators have the ability to view any aspect of any bag, alarmed or not, at their discretion by means of the Baggage Viewing Station.) Hard-copy images can be provided by the dedicated printer, and electronic storage is available to archive bag images. In addition, there is an interface to the external baggage handling system to ensure the smooth flow of bags as well as baggage information, such as ID number and alarm status.

Gray scale versions of a typical Baggage Viewing Station display appear in Figures 10 and 11.

They are from an eXaminer® 3DX 6500 explosive detection system. Figure 10 shows a 2D projection of an entire bag whose 3D image was processed by the Image Analysis System. The black and gray rectangular frames highlight three suspicious regions that have caused automatic alarms and that need to be reviewed by the human operator. (On a color display, the black rectangle would normally be turquoise and the gray rectangles would normally be yellow).

The black rectangle, in Figure 10, surrounds the first object for the operator to assess. It is a sheet explosive stuffed randomly into a small, wooden, loudspeaker enclosure. Figure 10 shows a clear representation of the speaker's metallic frame.

Bag ID 000000164
Current Object: 1
Remaining : 4 of 4

Figure 11 Baggage Viewing Station 3D projection views of the bounding box containing the sheet threat inside a loudspeaker enclosure.

Four of the enclosure's wooden walls are approximately aligned with the black frame. The explosive material causing the alarm, however, is not readily apparent.

3D information of the loudspeaker box appears in Figure 11. The Image Analysis System has already determined that the sheet contained inside is, very probably, a threat. It would accordingly render the sheet in red, thereby indicating to the operator exactly what is the source of concern. The metal of the speaker would be blue, and the threat's detonator would be rendered as green. In the gray scale version shown in Figure 11, the dark gray region represents the area the computer has highlighted as a possible explosive (normally shown in red on a color display).

The small image at the lower right of Figure 11 repeats the image of Figure 10 to remind the operator which object he or she is reviewing.

In the large white area the three images in the lower-left, upper-left, and upper-right corners are orthogonal projections of a 3D rectangular region inside the bag that completely encloses the threat. The region is known as the bounding box. Each of these three images is a projection of the voxels that are only inside the bounding box. Therefore they eliminate clutter from material located outside the region of interest. The lower-left projection is from the side, the upper-left one is from the top, and the upper-right one is from the end.

The lower-right image in the main viewing area of Figure 11 is a 3D, semi-transparent rendering of the bounding box's contents. Using the computer mouse one can click and drag so as to rotate the 3D image into any orientation. This ability, unique to full 3D systems, aids the operator in understanding the physical relationships among objects. For example, the operator can ascertain that the sheet threat is not planar, but has been worked into the enclosure with curving bends to accommodate the cramped quarters.

The ability of X-ray CT scanners to capture information from the third dimension and to measure material properties directly gives them the ability to markedly surpass conventional 2D X-ray systems in automatically discovering contraband and in making it visible to human operators.

5. CT SCANNER DESIGN CONSIDERATIONS

Designing X-ray CT scanners for contraband and/or threat detection involves a large number of trade-off decisions aimed at meeting the desired performance capability at a reasonable cost. The main performance parameters are acceptable detection capability and false alarm rates, maximum bag size, and baggage throughput rate. These in turn depend on machine characteristics such as image spatial resolution, signal-to-noise ratio (SNR) in the image, beam hardening and other artifacts in the image, belt speed, and the image assessment algorithms. Additional trade-offs include those among (i) using a full 3D image of each bag, (ii) using 3D data from only a portion of the bag, or (iii) relying on selected CT slices passed through the bag based on a pre-screener's 2D image. Other important performance parameters include reliability, maintainability, and operating cost.

Major trade-offs must be made involving the rotating system, the X-ray system, and the detector package. The minimum size of the disk opening is set by the cross section of the largest bag to be scanned. Spatial resolution is dictated by the needs of the image assessment algorithm in meeting targeted detection/false alarm criteria. This resolution and the required size of the disk opening determine the individual X-ray detector size.

Using small detectors to achieve good spatial resolution has the drawback of reducing the detector SNR. For a given X-ray source strength, and a given source-to-detector distance, reducing an individual detector size reduces its measured X-ray signal and thus adds noise to the signal because of photon statistics.

A loss in detected X-rays can be offset by using a stronger source. Increasing the X-ray tube current raises the photon emission rate, raises the measured X-ray signal, and can therefore restore the SNR for a detector of reduced size. The drawbacks of increasing the X-ray tube power, however, include (i) additional power capacity of the high-voltage power supply, (ii) additional heat removal capacity needed for the tube cooling system, (iii) reduced X-ray tube lifetime, and (iv) additional centrifugal force on the disk due to the extra weight of the more powerful source and its supporting equipment.

In a full 3D imaging system the tradeoff between the number of rows in the detector array and the disk's rotation speed was discussed in Section 3.2. The desired baggage throughput rate dictates the conveyor belt speed, and the image assessment algorithm dictates the spacing of the CT slices. These parameters taken together specify the rate at which CT slices are taken. Key considerations are (i) enough photons per detector for adequate SNR, (ii) reasonable centrifugal loads on disk-mounted hardware, and (iii) a tractable, rapid, and accurate cone-beam reconstruction algorithm. Additional tradeoffs needed in considering how many rows to use include the detector electronics system complexity, the computer hardware needs of the reconstruction method, and the system cost.

There are also trade-offs in the choice of X-ray spectral distribution, which is adjusted mainly by filtration characteristics and by choice of tube voltage. For single-energy systems, an excess of low-energy photons can increase image degradation from beam-hardening artifacts. Excessive high-energy photons can lead to loss in contrast and the need for thicker detectors. In dual-energy applications the two energy distributions need to be widely separated. The lower energies need to be low enough to sample the photoelectric region of low-atomic-number elements. The energies must not be too low, however, or too few photons will penetrate the bag.

These and other trade-offs have been successfully balanced by the design teams of currently certified X-ray CT explosives detection systems. The final sets of design parameters have been incorporated into CT inspection systems that are both effective and affordable.

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CHAPTER 8

ANALYSIS AND DETECTION OF EXPLOSIVES BY MASS SPECTROMETRY

J. Yinon

Contents

1. INTRODUCTION

Mass spectrometry has become a routine technique for forensic analysis of explosives and one of the technologies used for vapor and trace detection of hidden explosives.

Mass spectrometry is the field dealing with separation and analysis of substances according to the masses of the atoms and molecules of which the substance is composed. The principle of mass analysis is that parameters of time and space of the path of a charged particle in a force field in vacuum are dependent on its mass-to-charge ratio (m/z).

The two main types of mass spectrometers used for analysis and detection of explosives are the quadrupole and the ion trap. These two types of mass analyzers are relatively small, when compared with magnetic sector instruments. They can be miniaturized to make mobile detectors weighing less than 15 kg.

The quadrupole mass analyzer [1] consists of four parallel metal rods arranged as in Figure 1.

Two opposite rods are electrically connected and have an applied potential of $U+V\cos\omega t$, and the other two rods, also electrically connected, have a potential of $-U+V\cos\omega t$, where U is a d.c. voltage and $V\cos\omega t$ is an RF a.c. voltage. The applied voltages affect the trajectory of ions traveling down the flight path centered between the four rods. For given d.c. and a.c. voltages, only ions of a certain mass-to-charge ratio pass through the quadrupole analyzer and all other ions are thrown out of their original path. A mass spectrum is obtained by monitoring

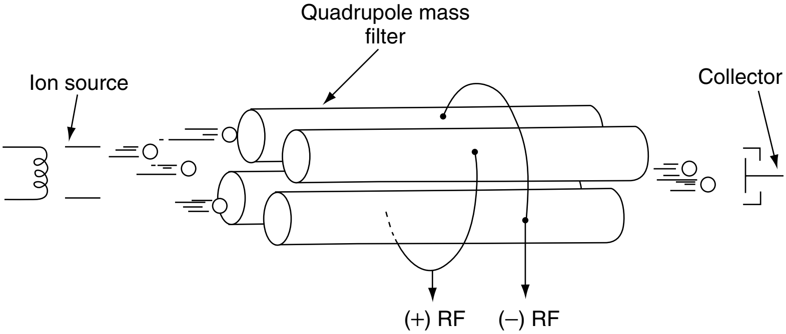

Figure 1 Quadrupole mass analyzer.

the ions passing through the quadrupole analyzer as the voltages on the rods are varied. There are two methods: varying the frequency ω while holding U and V constant, or varying U and V but keeping U/V constant.

The ion trap mass analyzer (Figure 2) [2] consists of two end-cap electrodes, held at ground potential, and an interposed ring electrode, to which a d.c. and RF a.c. voltages are applied. The ring electrode is a single surface formed by a hyperboloid of rotation. The end-caps are complementary hyperboloids having the same conical asymptotes: z is an axis of cylindrical symmetry. These electrodes form a cavity in which it is possible to trap and analyze ions. Both end-cap electrodes have a small hole in their centers through which the ions can travel. The ring electrode is located halfway between the two end-cap electrodes.

Ions produced in the source enter the trap through the inlet focusing system and the entrance end-cap electrode. Various voltages are applied to the electrodes to trap and eject ions according to their mass-to-charge ratios.

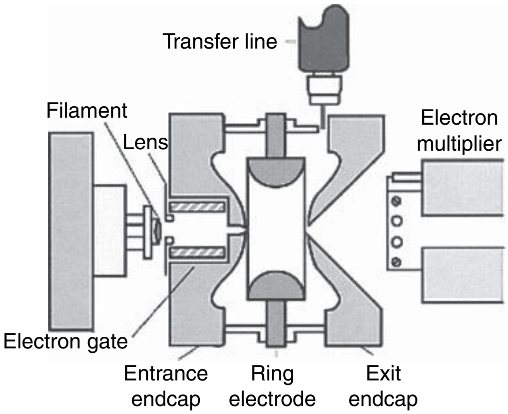

Figure 2 Ion trap mass analyzer (Reproduced from http://www.wpi.biz/initiatives/2002/20020903.asp. With permission from Varian, Inc.).

The ring electrode RF potential, an a.c. potential of constant frequency and variable amplitude, is applied to the ring electrode to produce a three-dimensional quadrupolar potential field within the trapping cavity. This will trap ions in a stable oscillating trajectory confined within the trapping cell. The nature of the trajectory is dependent on the trapping voltages and the mass-to-charge ratio of the ions. During detection, the electrode system voltages are altered to produce instabilities in the ion trajectories and thus eject the ions in the axial direction. The ions are ejected in order of increasing mass-to-charge ratio, focused by the exit lens and detected by the ion detector system, generating a mass spectrum.

Tandem mass spectrometry (MS/MS) (Figure 3) [3] allows one to induce fragmentation and mass analyze the fragment ions. This is accomplished by collisionally generating fragments from a selected ion and then mass analyzing the fragment ions. Fragmentation can be achieved by inducing ion/molecule collisions by a process known as collision-induced dissociation (CID) [also known as collision-activated dissociation (CAD)]. CID is achieved by selecting an ion of interest (precursor ion) with the first mass analyzer and introducing that ion into a collision cell. The selected ion then collides with an inert collision gas (typically argon or helium) resulting in fragmentation. The fragments are then analyzed by the second mass analyzer to obtain a fragment ion spectrum. The MS/MS–CID mass spectrum provides a "fingerprint" of the precursor ion and provides and additional dimension of selectivity in the identification of the analyzed sample. MS/MS systems used in analysis and detection of explosives are the triple-stage quadrupole [4, 5] and the ion trap [5].

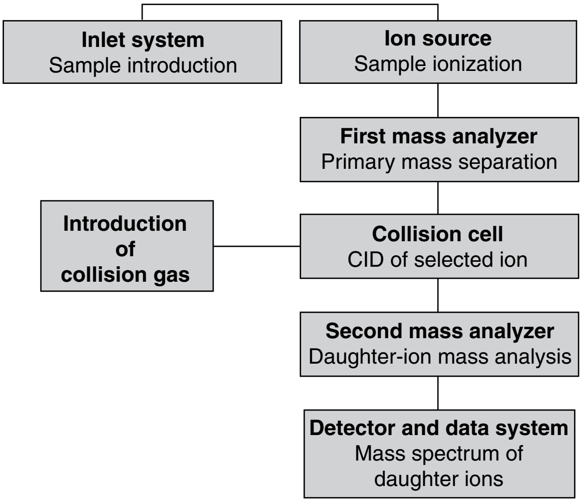

Figure 3 Block diagram of a tandem mass spectrometer (MS/MS).

2. TRACE ANALYSIS OF EXPLOSIVES

Trace analysis of explosives is of major importance in forensic and environmental applications [6]. In forensics, the applications include analysis of post-explosion residues and identification of traces of explosives on suspects' hands, clothing and other related items. The results of these analyses are not only necessary for the investigation of a bombing but can also serve as evidence in court.

In the environmental field, the applications include analysis of explosives and their degradation products in soil and water. These analyses are important because of the toxicity of most explosives and the fact that many areas in the vicinity of explosives and munitions manufacturing plants are contaminated.

The methodologies for the analysis of explosives for both forensic and environmental applications are very similar, using mainly GC/MS and LC/MS. As explosives are thermally labile compounds, LC/MS has an obvious advantage over GC/MS, as the chromatography is carried out at room temperature.

2.1. Analysis of explosives by GC/MS

Several examples illustrate the use of GC/MS for analysis of explosives: Trace analysis of explosives in water by GC/MS was carried out using a cooled temperature-programmable injector and a 15 m × 0.255 μm ID, 0.25 μm film thickness, DB-1 column [7].

Investigated explosives included 2,4,6-trinitrotoluene (TNT), 2,4,6,*N*-tetranitro-*N*-methylaniline (tetryl), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and pentaerythritol tetranitrate (PETN). The temperature of the injector, cooled with liquid CO_2, was $-5°$ C for 0.3 min, programmed from -5 to 250° C, at a rate of 200° C/min, with a final hold time of 8.4 min. The column temperature was 80° C for 2 min, programmed to 250° C at 25° C/min, with a final hold of 2 min. Electron ionization (EI) in the positive-ion mode was used. Figure 4 shows the mass chromatograms of a mixture of explosives (10 ppb each), extracted from water by liquid–liquid extraction and × 100 concentration. Identification was based on typical fragment ions for each one of the explosives.

A study comparing detection limits for GC/MS analysis of 2,4-DNT, TNT, RDX and PETN, using EI, CI and NICI, showed that NICI gave the lowest detection limits, which were between 0.18 and 1.11 ng [8].

Solid-phase microextraction (SPME) for preconcentration, followed by GC/Ion Trap MS, was used for trace analysis of explosives and their metabolites in seawater [9]. NICI was used with methane as reagent gas. Compounds of interest included RDX, TNT and two of its metabolites 2-amino-4,6-dinitrotoluene (2ADNT) and 4-amino-2,6-dinitrotoluene (4ADNT). Although the instrument sensitivity was in low-ppb range, the detection limits for SPME with GC/ITMS

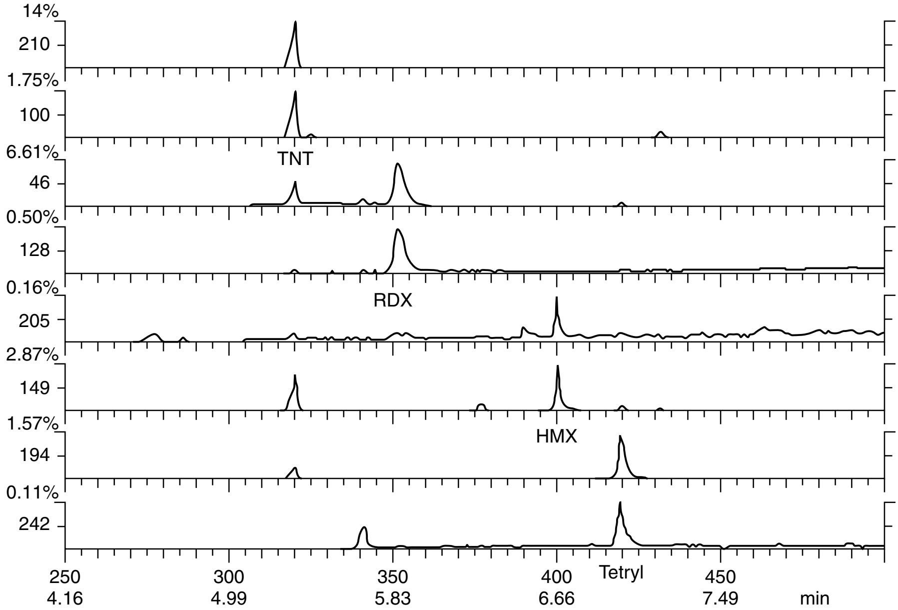

Figure 4 Mass chromatograms of a mixture of explosives (10 ppb each) extracted from water [Reproduced from J. Yinon, J. Chromatogr. A, 742 (1996) 205. Copyright 1996, with permission from Elsevier].

were in the low-ppt range. Figure 5 shows a GC/ITMS analysis of a 5 mL ocean water sample. Concentrations of explosives found in this sample were 210 ppt TNT and 1900 ppt RDX. The monitored ions for TNT were at *m/z* 227, 210 and 197, and for RDX at *m/z* 129, 102 and 85.

Triacetone triperoxide (TATP) is a powerful explosive manufactured in clandestine laboratories and used by terrorists. As TATP sublimes easily, analysis was performed by SPME trapping of its vapor, using polydimethylsiloxane/divinyl benzene (PDMS/DVB) fiber, followed by desorption into a GC/MS injector [10]. Figure 6 shows the TIC, mass chromatogram and the EI mass spectrum of headspace from a debris sample containing TATP [11]. The EI mass spectrum contains a molecular ion at *m/z* 222 and several fragment ions. In the chemical ionization mass spectrum of TATP [12], the major ions were at *m/z* 223 (100%), 222 (20%), 133 (20%), 117 (40%), 115 (20%), 103 (75%) and 100 (50%).

2.2. Analysis of explosives by LC/MS

The thermal lability of many explosives, along with the requirements of high sensitivity, especially in the analysis of post-explosion residues, makes LC/MS a method of choice for the analysis of explosives. Both electrospray ionization (ESI)

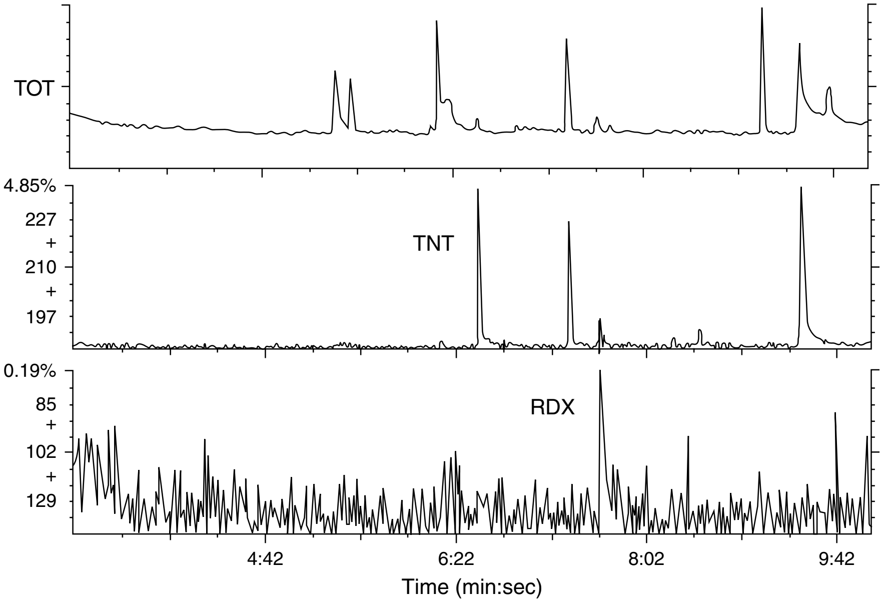

Figure 5 GC/ITMS total ion and mass chromatograms of an ocean water sample [Reproduced from S.-A. Barshick et al., Anal. Chem., 70 (1998) 3015. Copyright 1998, with permission from the American Chemical Society].

and atmospheric pressure chemical ionization (APCI) are being used, depending on the type of explosives [13].

2.2.1. Principles of ESI- and APCI-LC/MS

In ESI, a solution of the analyte, introduced into an ion source at atmospheric pressure, is pumped through a stainless steel capillary that carries a high potential, typically 3–5 kV (Figure 7). The strong electric field generated by this potential causes the solvent to be sprayed from the end of the capillary. The charged droplets pass down a potential gradient toward the mass analyzer. During that transition, the droplets reduce in size by evaporation of the solvent or by droplet subdivision, resulting from the high charge density. Ultimately, fully desolvated ions result from complete evaporation of the solvent or by field desorption from the charged droplets. This process is known as "ion evaporation" and is the primary mechanism for gas-phase ion formation in electrospray. A flow of nitrogen gas through the source helps the evaporation process and removal of the solvent. Because ESI is a soft ionization technique, there is usually little or no fragmentation, and the spectrum contains only the $(M+H)^+$ or $(M-H)^-$ ion. The presence of additives or contaminants, such as ammonium or sodium ions, can cause adduct formation with ions present in solution. Designed addition of certain additives will form intense adduct ions that will assist in the identification

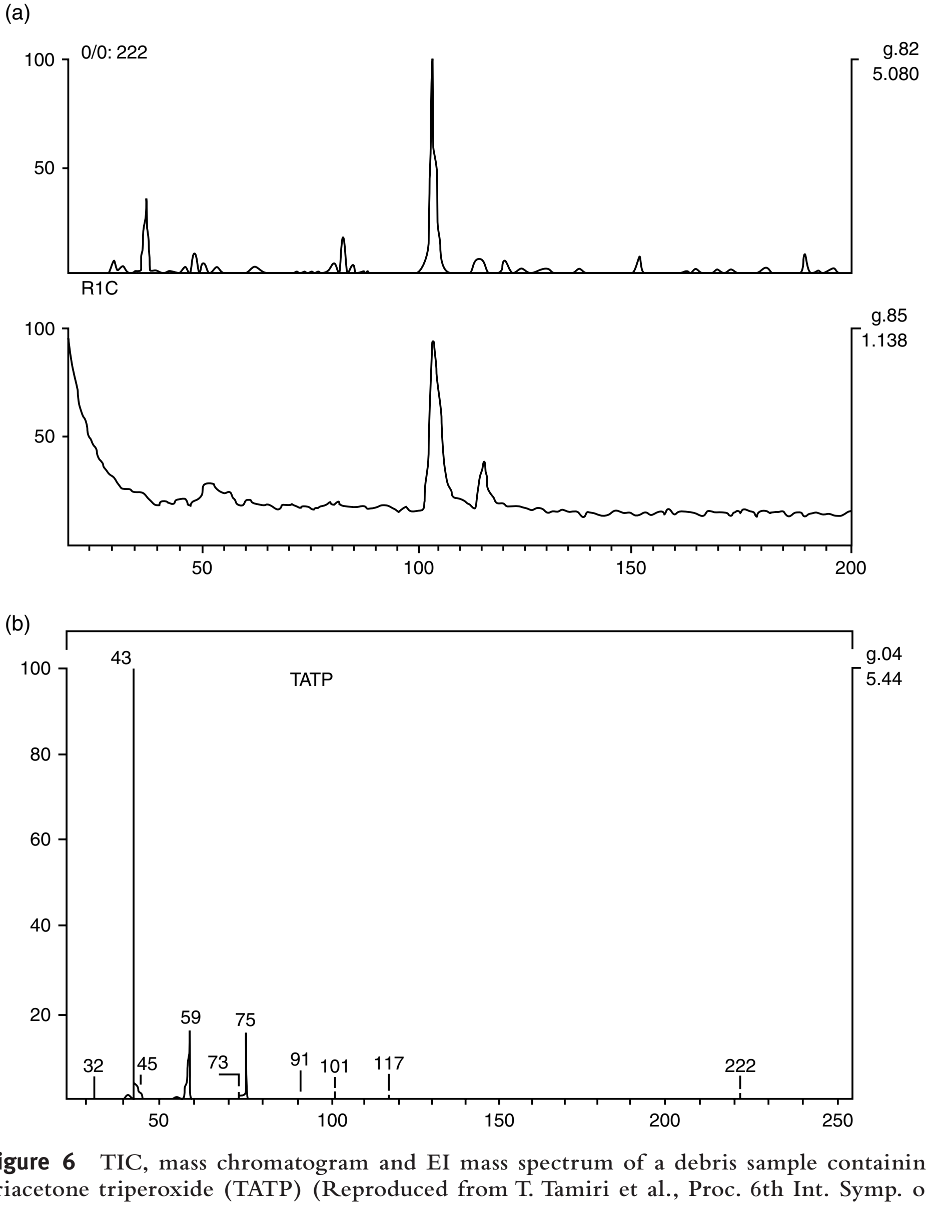

Figure 6 TIC, mass chromatogram and EI mass spectrum of a debris sample containing triacetone triperoxide (TATP) (Reproduced from T. Tamiri et al., Proc. 6th Int. Symp. on Analysis and Detection of Explosives, Prague, Czech Republic, 1998. With permission).

of the analyte. The main advantages of ESI are molecular weight information, good sensitivity and suitability for thermally labile molecules.

Ions, formed in the source, are transported into the high-vacuum system of the mass spectrometer by the use of a nozzle-skimmer arrangement. This acts as a momentum separator and heavier sample molecules tend to pass through, while lighter solvent and drying gas molecules can be more readily pumped away in this

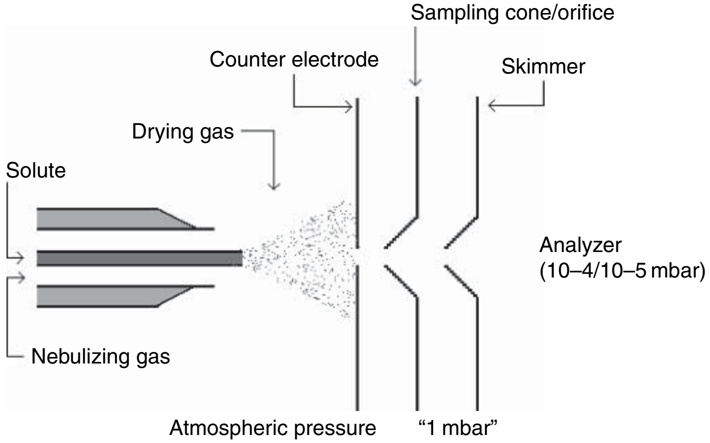

Figure 7 Electrospray ion source (From www.astbury.leeds.ac.uk/Facil/Mstut/mstutorial.htm. With permission from Dr. A. E. Ashcroft, University of Leeds, UK).

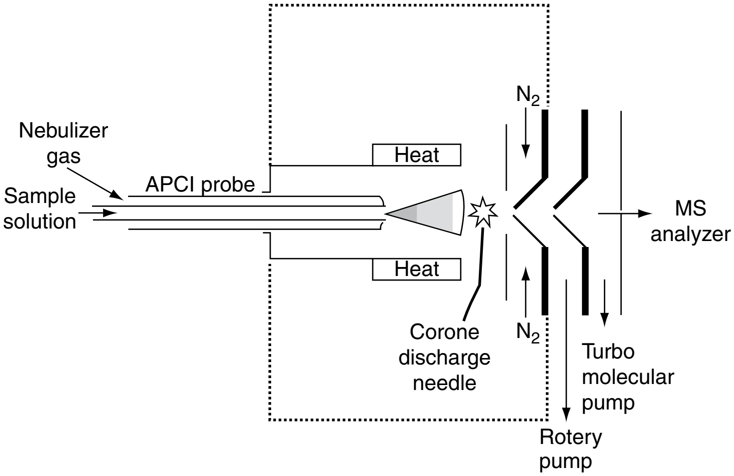

Figure 8 APCI ion source [Reproduced from R.C. Spreen et al., Anal. Chem., 68 (1996) 414A. Copyright 1996, with permission from the American Chemical Society].

differentially pumped intermediate vacuum stage. In APCI (Figure 8), there is no voltage applied to the capillary. The liquid elutes from the capillary probe, which is surrounded by a coaxial flow of N_2 nebulizing gas, into a heated region. The combination of nebulizer gas and heat forms an aerosol which begins to evaporate rapidly.

At the end of the APCI probe is a high-voltage (2.5–3.0 kV) metal needle to produce a corona discharge, causing solvent molecules eluting into the source to be ionized. Sample molecules that elute and pass through this region of solvent ions can be ionized by gas-phase ion molecule reactions. Chemical ionization of sample molecules is very efficient at atmospheric pressure because of the high collision frequency. Proton transfer, forming $[M+H]^+$ ions, occurs in the positive-ion mode, and either electron transfer or proton transfer, forming $[M-H]^-$ ions, occurs in the negative-ion mode. The moderating influence of the solvent clusters on the reagent ions, and of the high gas pressure, reduces fragmentation during ionization and results in primarily $[M+H]^+$, $[M-H]^-$ and/or adduct ions. As in ESI, ions are transported into the high-vacuum system of the mass spectrometer by the use of a nozzle-skimmer arrangement. The main advantages of APCI are that it gives molecular weight information on volatile molecules, and also allows high solvent flow rates, typically in the range of 0.2 to 2.0 ml/min. This permits direct coupling of 2.1 and 4.6 mm ID HPLC columns to the APCI interface. ESI sources can be used in the range of 5–1.0 mL/min, thus allowing also the interfacing of capillary columns.

2.2.2. Analysis of explosives by ESI- and APCI-LC/MS

The following examples illustrate the range of applications of LC/MS for trace analysis of explosives: ESI-LC/MS/MS-CID fragmentation processes of a series of nitroaromatic, nitramine and nitrate ester explosives were studied in the negative-ion mode using daughter-ion, parent-ion and neutral loss scans [14]. Table 1 shows the CID daughter ions in ESI-MS/MS of TNT.

Table 1 Collision-induced dissociation ions in ESI-MS of TNT

Parent ion		Daughter ions		Structure
m/z	Ion	*m/z*	(%)	
227	M^-	210	(100)	$[M–OH]^-$
		197	(52)	$[M–NO]^-$
		181	(5)	$[M–NO_2]^-$
		180	(7)	$[M–NO–OH]^-$
		167	(7)	$[M–2NO]^-$
		151	(7)	$[M–NO_2–NO]^-$
		137	(17)	$[M–3NO]^-$
226	$[M-H]^-$	208	(30)	$[P–H_2O]^-$
		198	(33)	$[P–NCH_2]^-$
		196	(100)	$[P–NO]^-$
		183	(23)	$[P–NO–CH]^-$
210	$[M-OH]^-$	152	(100)	$[P–NO–NCH_2]^-$
		136	(5)	$[P–NO_2–NCH_2]^-$
		124	(29)	
197	$[M-NO]^-$	180	(16)	$[P–OH]^-$
		167	(100)	$[P–NO]^-$
		151	(5)	$[P–NO_2]^-$
		150	(5)	$[P–OH–NO]^-$
		139	(20)	$[P–NO–NCH_2]^-$
		137	(5)	$[P–NO_2–CH_2]^-$

Reproduced from J. Yinon et al., Rapid. Commun. Mass Spectrom., 11 (1997) 1961. Copyright 1997, with permission from John Wiley & Sons.

Several additives were tested with a series of explosives in order to enhance ESI intensities [15–17]. Nitramine and nitrate ester explosives showed enhanced response for ammonium nitrate additive, by forming $[M + NO_3]^-$ adduct ions in the negative-ion mode. Nitrate adduct ions were more intense than trifluoroacetate (TFA) or chloride adduct ions by a factor of 6–40. The base peak in the negative-ion mass spectrum of TNT, with 1 mM ammonium nitrate in the mobile phase was at *m/z* 226 due to the $[M - H]^-$ ion.

Figure 9 shows the LC/MS-ESI mass chromatograms of a 25 pg/μL Semtex sample (a plastic explosive containing RDX and PETN) with post-column introduction of ammonium nitrate [17]. HPLC separation was achieved with a C18 column (100 × 2.1 mm, 5 μm particle size), using an isocratic mobile phase of methanol–water (70:30), at a flow rate of 150 μL/min.

LC/MS/MS with selected reaction monitoring and ESI in the negative-ion mode was used to detect RDX and its degradation products in contaminated groundwater [18]. The detected degradation products were MNX (hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine), DNX (hexahydro-1,3-dinitroso-5-nitro-1,3,5-triazine) and TNX (hexahydro-1,3,5-trinitroso-1,3,5-triazine). The $[M + 75]^-$ and $[M + 45]^-$ were the most intense ions in the mass spectra of RDX and its degradation products. In the CID mass spectra, the base peak for RDX, MNX and DNX

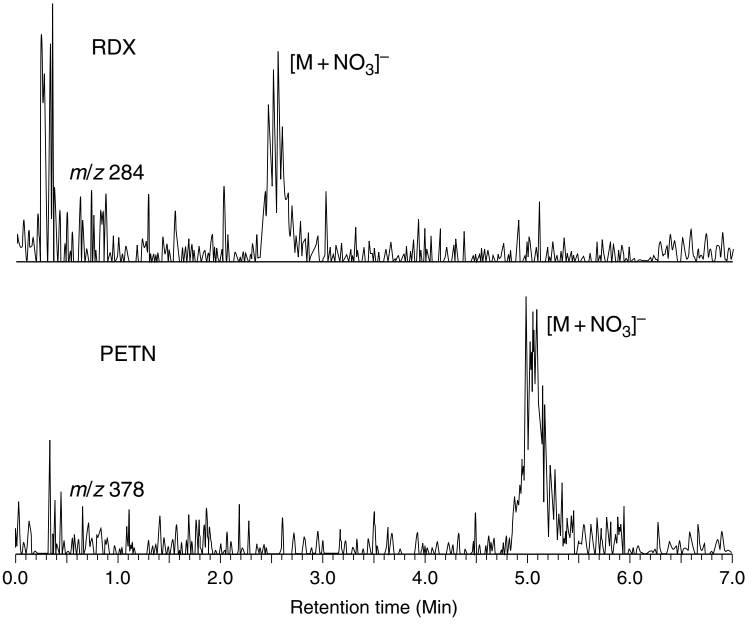

Figure 9 LC/MS-ESI mass chromatograms of a Semtex sample [Reproduced from X. Zhao and J. Yinon, J. Chromatogr. A, 977 (2002) 59. Copyright 2002, with permission from Elsevier].

was at *m/z* 46, $[NO_2]^-$, while for TNX, which does not include a NO_2 group, it was at *m/z* 113.

The formation of RDX cluster ions in LC/MS and the origin of the clustering agents have been studied in order to determine whether the clustering anions originate from self-decomposition of RDX in the source or from impurities in the mobile phase [19]. Isotopically labeled RDX ($^{13}C_3$-RDX and $^{15}N_6$-RDX) were used in order to establish the composition and formation route of RDX adduct ions produced in ESI and APCI sources. Results showed that in ESI, RDX clusters with formate, acetate, hydroxyacetate and chloride anions, present in the mobile phase as impurities at ppm levels. In APCI, part of the RDX molecules decompose, yielding NO_2^- species, which in turn cluster with a second RDX molecule, producing abundant $[M+NO_2]^-$ cluster ions.

Figures 10, 11 and 12 show the ESI mass spectrum of RDX, $^{13}C_3$-RDX and $^{15}N_6$-RDX, respectively. The ions $[M+45]^-$, $[M+59]^-$, $[M+75]^-$, $[2M+59]^-$ and $[2M+75]^-$ are adduct ions formed as a result of the presence

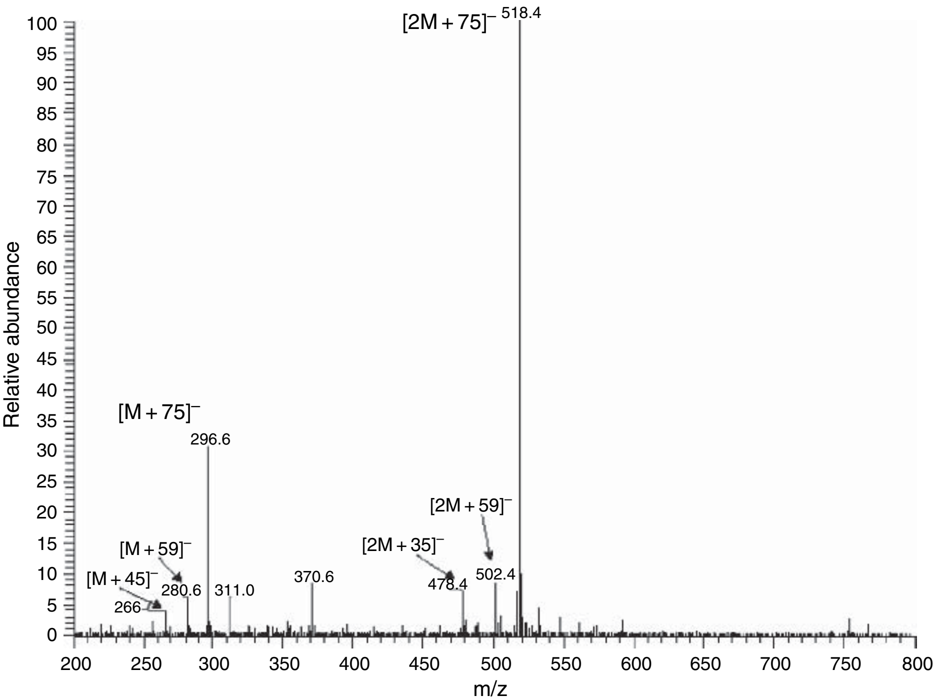

Figure 10 ESI mass spectrum of RDX [Reproduced from X. Zhao and J. Yinon, Rapid. Commun. Mass Spectrom., 17 (2003) 943. Copyright 2003, with permission from John Wiley & Sons].

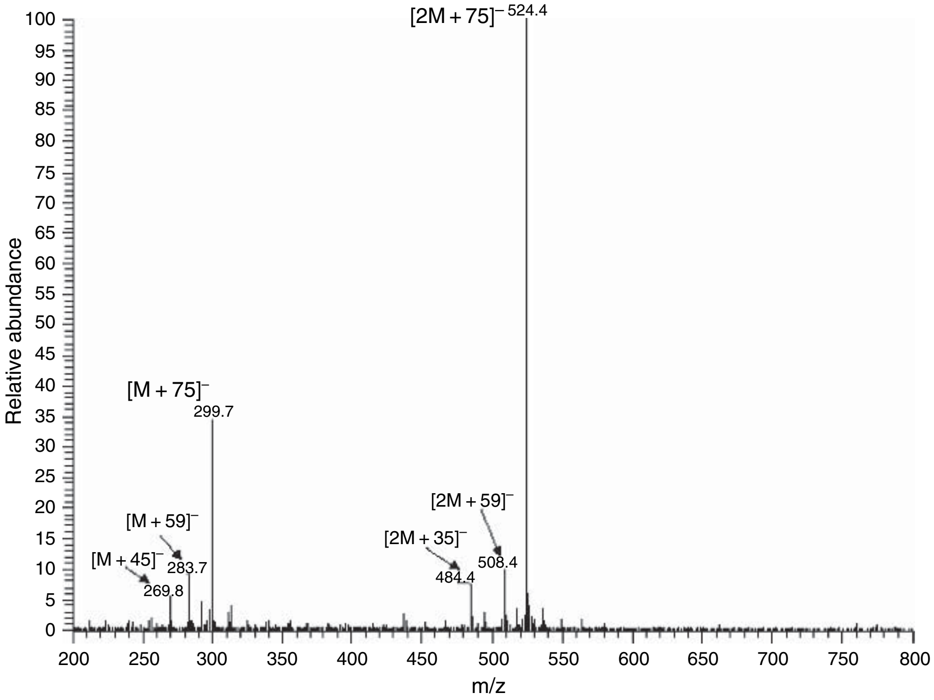

Figure 11 ESI mass spectrum of $^{13}C_3$-RDX [Reproduced from X. Zhao and J. Yinon, Rapid. Commun. Mass Spectrom., 17 (2003) 943. Copyright 2003, with permission from John Wiley & Sons].

of these impurities, probably in the HPLC-grade methanol of the mobile phase.

LC/MS-APCI in the positive ion mode was used for trace analysis of TATP [20]. Chromatographic separation was carried out with a C18 (150 × 2.0 mm, 3 μm particle size) column, with a mobile phase of methanol–water (70:30) with 5 mM ammonium acetate buffer, at flow rates between 0.1 and 0.2 mL/min. Samples were injected as acetonitrile solutions.

The peaks observed in the LC/MS mass spectrum were at *m/z* 75, 89, 90, 91, 102, 107, 194, 240 and 252. The ion at *m/z* 240 is believed to be the $[M + NH_4]^+$ adduct ion, formed because of the use of nitrogen drying gas. This ion was enhanced when using ammonium acetate buffer. Figure 13 shows the LC/MS/MS mass spectrum of TATP (parent ion *m/z* 240). Lowest detection limit, 100 pg/μL, was obtained by using MS/MS-SIR (single ion reaction) between the parent ion at *m/z* 240 and the daughter ion at *m/z* 89 (Figure 14).

Characterization and origin identification of explosives is important in forensic analysis of post-explosion residues. In addition to the type of explosive used in a

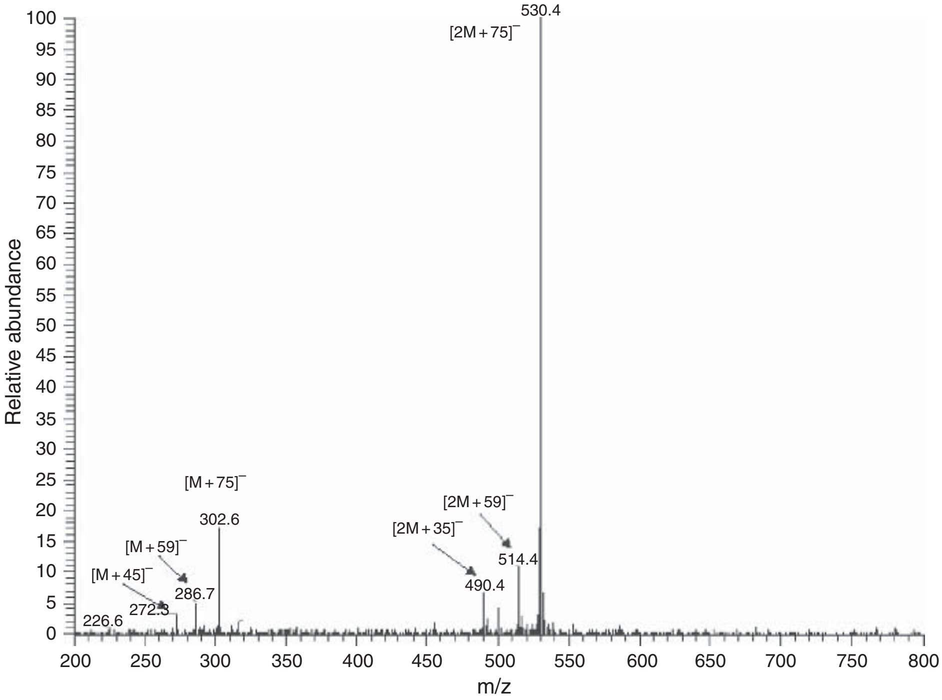

Figure 12 ESI mass spectrum of $^{15}N_6$-RDX [Reproduced from X. Zhao and J. Yinon, Rapid. Commun. Mass Spectrom., 17 (2003), 943. Copyright 2003, with permission from John Wiley & Sons].

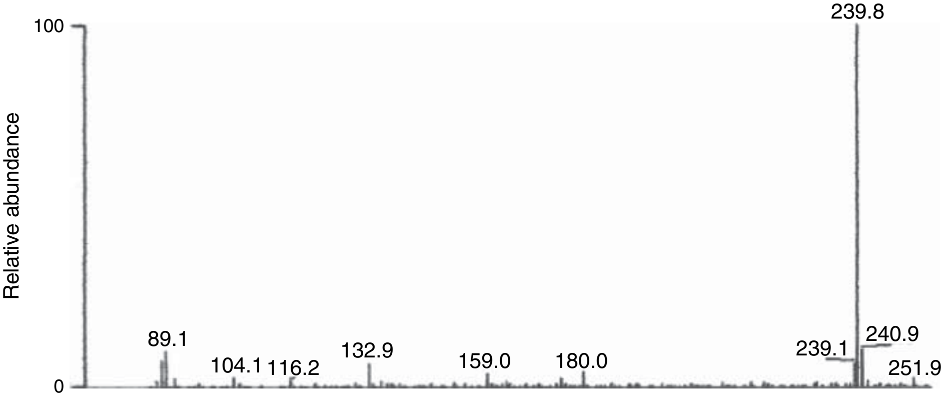

Figure 13 LC/MS/MS mass spectrum of triacetone triperoxide (TATP) [Reproduced from L. Widmer et al., Analyst, 127 (2002) 1627. With permission from the Royal Society of Chemistry].

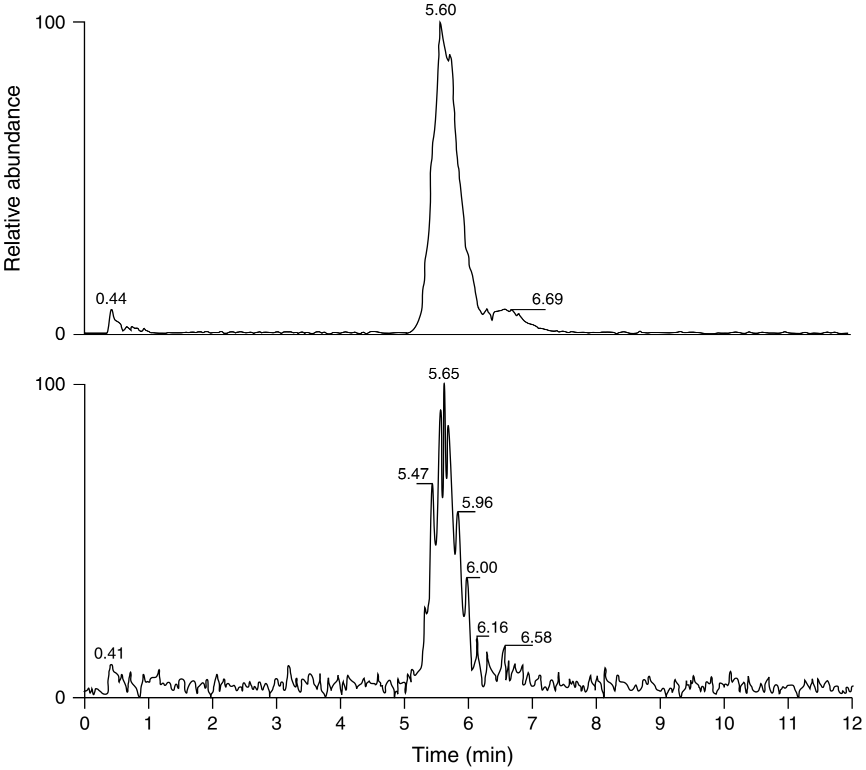

Figure 14 MS/MS-SIR mass chromatograms of triacetone triperoxide (TATP) [Reproduced from L. Widmer et al., Analyst, 127, (2002) 1627. With permission from the Royal Society of Chemistry].

bombing, the investigators would like to know its country of origin and preferentially its manufacturer. Each manufacturer will produce the explosives with characteristic differences in the type and amount of by-products, impurities and additives, depending on the purity of the raw materials and solvents used and the type of manufacturing process, thus resulting in a typical profile of by-products, organic impurities and additives.

The by-products of industrial TNT, including isomers of trinitrotoluene, dinitrotoluene, trinitrobenzene and dinitrobenzene, were investigated using LC/MS-APCI in the negative-ion mode to build a profile for the characterization of TNT samples from various origins [21]. MS/MS-CID was used for further identification of some of the nitroaromatic isomers.

The MS/MS-CID results of *m*/*z* 227 of the individual TNT isomers are summarized in Table 2.

Table 2 MS-MS-CID data of TNT isomers

Parent ion		Daughter ions		Tentative identification
m/z	Ion	*m/z*	%	
		2,4,6-TNT		
227	M^-	210	100	$[M–OH]^-$
		197	48	$[M–NO]^-$
		181	5	$[M–NO_2]^-$
		167	4	$[M–2NO]^-$
		151	5	$[M–NO_2–NO]^-$
		137	13	$[M–3NO]^-$
		2,4,5-TNT		
227	M^-	197	100	$[M–NO]^-$
		181	2	$[M–NO_2]^-$
		2,3,5-TNT		
227	M^-	197	100	$[M–NO]^-$
		3,4,5-TNT		
227	M^-	197	49	$[M–NO]^-$
		2,3,6-TNT		
227	M^-	197	100	$[M–NO]^-$
		181	10	$[M–NO_2]^-$
		2,3,4-TNT		
227	M^-	197	60	$[M–NO]^-$
		181	100	$[M–NO_2]^-$
		151	3	$[M–2NO]^-$

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Figure 15 shows the mass chromatograms of a standard mixture of six TNT, three DNB, four DNT and one TNB isomers in methanol–water (50:50) at a concentration of 1 μg/mL each. Figure 16 shows the LC/MS-APCI mass chromatograms of two samples from different sources, demonstrating the capability of this method to characterize TNT samples.

Inorganic oxidizers are widely used as blasting agents in mining and construction explosives and also in improvised explosive devices utilized by terrorists. Ammonium-nitrate-based explosives (e.g., ammonium nitrate and fuel oil – ANFO) have almost completely replaced the majority of dynamites. In addition, slurry and emulsion explosives, which contain mostly ammonium nitrate and a small amount of other oxidizers, have become widely used.

Mass spectra of ammonium nitrate and of a series of additional inorganic oxidizers were studied in both positive- and negative-ion mode by ESI-MS and ESI-MS/MS-CID [22, 23]. Characterization of ammonium nitrate by a series of typical cluster ions was confirmed by using isotopically labeled ammonium nitrate (ammonium-^{15}N, nitrate-^{15}N and nitrate-^{18}O) and deuterated water [22]. It was found that, at heated capillary temperatures in the range

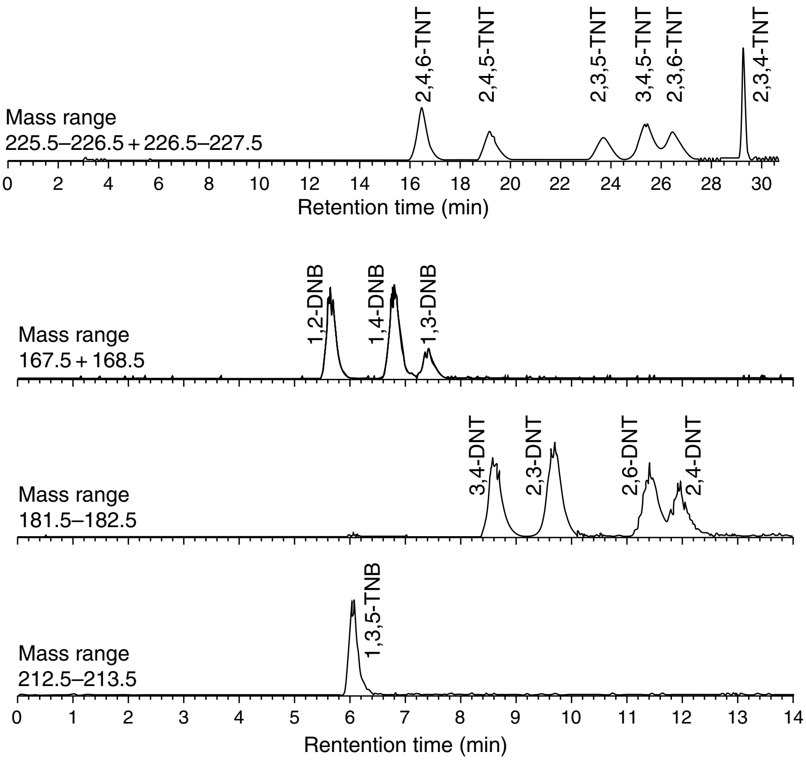

Figure 15 Mass chromatograms of a standard mixture of six TNT, three DNB, four DNT and one TNB isomers [Reproduced from X. Zhao and J. Yinon, J. Chromatogr. A, 946 (2002) 125. Copyright 2002, with permission from Elsevier].

55–150° C, in the positive-ion mode, cluster ions of the type $[(N_4NO_3)_nNH_4]^+$ ($n = 1$–3) were dominant in the mass spectrum, which enables the characterization and identification of the integral ammonium nitrate molecule. Figure 17 shows the positive-ion ESI mass spectra of (a) 1 mM NH_4NO_3, (b) 1 mM NH_4 $^{15}NO_3$, (c) 1 mM $^{15}NH_4NO_3$ and (d) 1 mM NH_4N $^{18}O_3$ in methanol–water (50:50) introduced by syringe pump infusion. Temperature of heated capillary was 100° C.

The investigated oxidizers [23] included sodium nitrate, potassium nitrate, ammonium sulfate, potassium sulfate, sodium chlorate, potassium chlorate, ammonium perchlorate and sodium perchlorate. Figure 18 shows the positive- and negative-ion ESI mass spectra of 1 mM sodium perchlorate in methanol–water (50:50), at heated capillary of 220° C. The cluster ions obtained are $[(NaClO_4)_nNa]^+$ and $[(NaClO_4)_nClO_4]^-$. Figure 19 shows the positive-ion (upper trace) and negative-ion (lower trace) ESI mass spectra of a Black Powder sample at a heated capillary temperature of 220° C. Ions correspond to those of potassium nitrate, $[(KNO_3)_nK]^+$ and $[(KNO_3)_nNO_3]^-$.

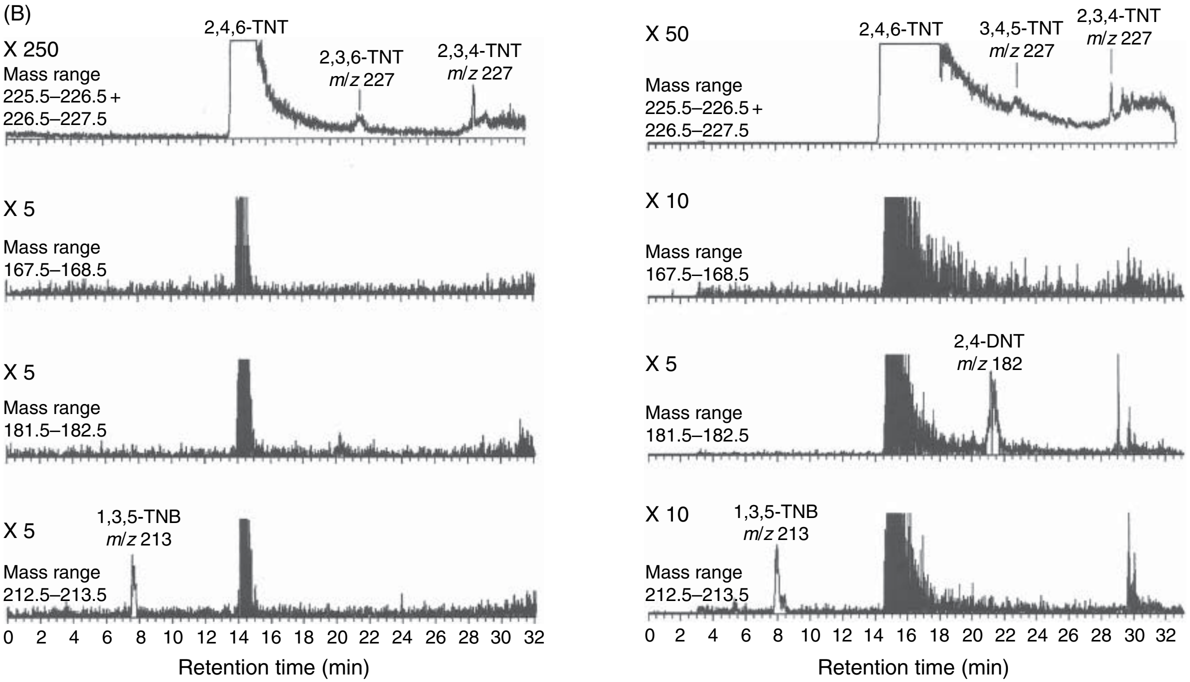

Figure 16 LC/MS-APCI mass chromatograms of two TNT samples from different sources [Reproduced from X. Zhao and J. Yinon, J. Chromatogr. A, 946, (2002) 125. Copyright 2002, with permission from Elsevier].

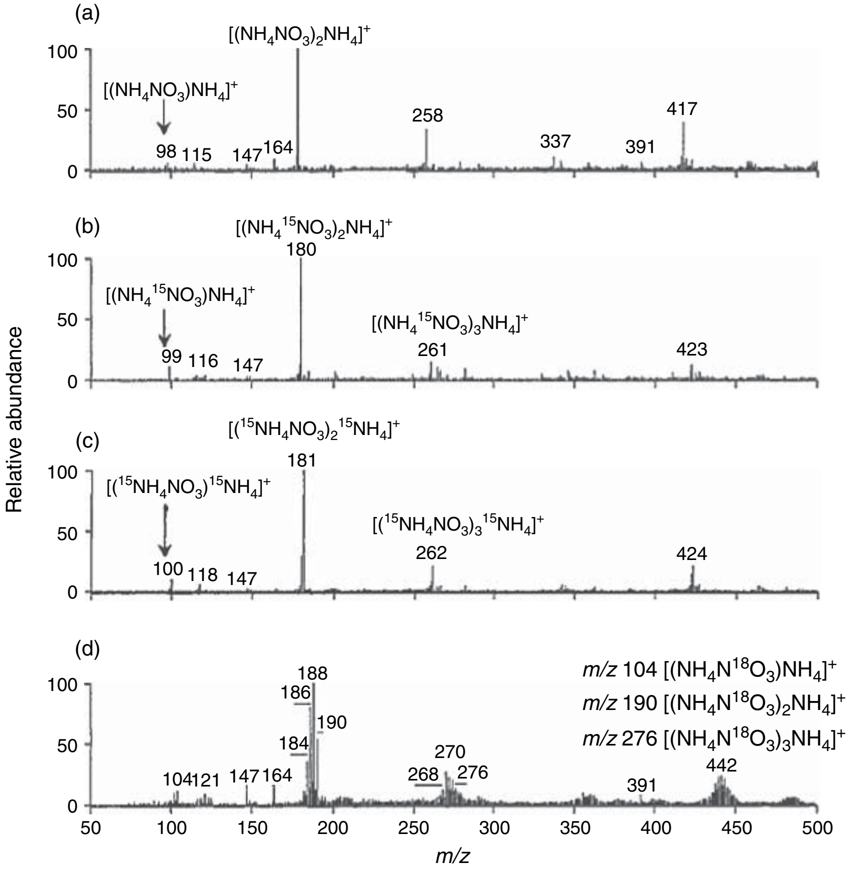

Figure 17 Positive-ion ESI mass spectra of (a) 1 mM NH_4NO_3, (b) 1 mM $NH_4{}^{15}NO_3$, (c) 1 mM $^{15}NH_4NO_3$ and (d) 1 mM $NH_4N{}^{18}O_3$ [Reproduced from X. Zhao and J. Yinon, Rapid. Commun. Mass Spectrom., 15 (2001) 1514. Copyright 2001 with permission from John Wiley & Sons].

3. DETECTION OF HIDDEN EXPLOSIVES

Detection of explosives is of major importance in several applications related to homeland security, such as detecting hidden explosives in airport luggage, in vehicles and in mail and screening of personnel for concealed explosives.

The main performance requirements of an explosive detection system are sensitivity, selectivity and speed of analysis. The mass spectrometer meets these requirements. Additional requirements are mobility and cost. During the last years, mass spectrometers have become smaller and mobile, but the prices are still relatively high. However, despite the complexity of the mass spectrometer, its performance as an explosives detector is more reliable than most existing vapor and trace detectors.

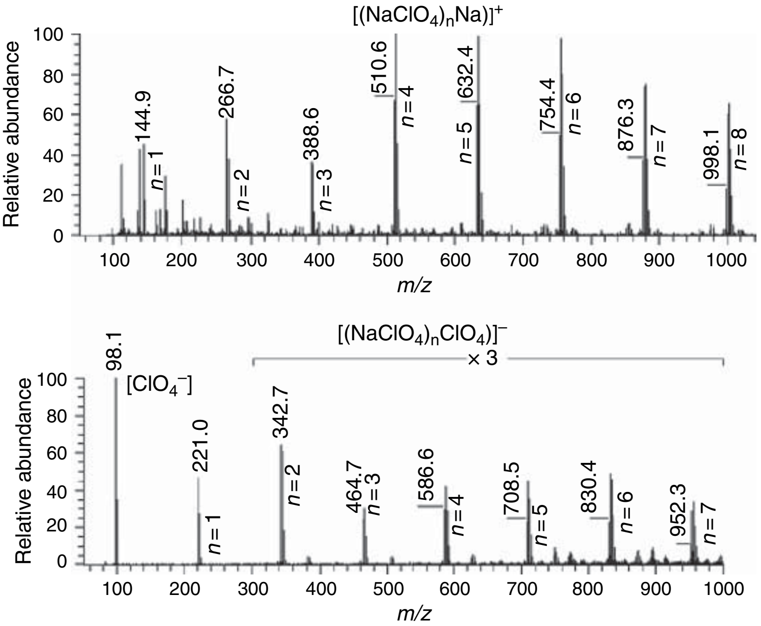

Figure 18 Positive- and negative-ion ESI mass spectra of 1 mM sodium perchlorate in methanol–water (50:50), at heated capillary of 220° C. [Reproduced from X. Zhao and J. Yinon, Rapid. Commun. Mass Spectrom., 16, (2002) 1137. Copyright 2002, with permission from John Wiley & Sons].

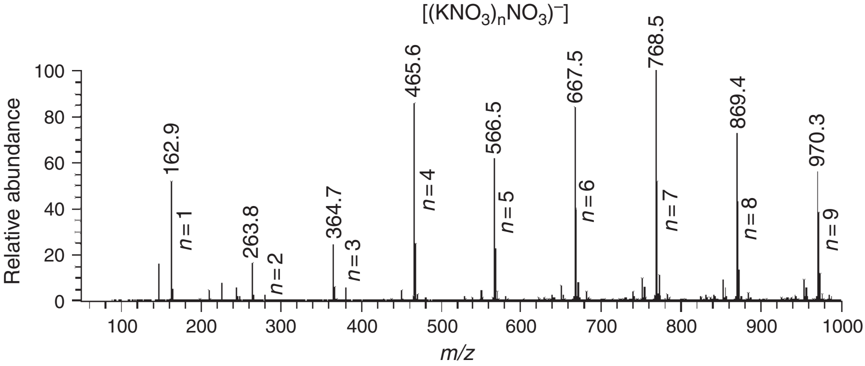

Figure 19 Positive-ion (upper trace) and negative-ion (lower trace) ESI mass spectra of a Black Powder sample at a heated capillary temperature of 220° C [Reproduced from X. Zhao and J. Yinon, Rap. Comm. Mass Spectrom., 16, (2002) 1137. Copyright 2002, with permission from John Wiley & Sons].

Various mass spectrometer configurations have been used for the detection of explosives, such as ion traps, quadrupoles and time-of flight mass analyzers and combinations as MS/MS systems. The ionization method is usually APCI with corona discharge [24, 25]. An example is given in Figure 20, which shows the schematic diagram of an explosive mass spectrometer detector [25]. It is based on an ion trap mass analyzer, an APCI source with corona discharge and a counter-flow introduction (CFI) system. The direction of the sample gas flow introduced into the ion source is opposite to that of the ion flow produced by the ion source.

A mass spectrometer system for the detection of trace explosives residues on airport boarding passes was developed [26]. Desorption of explosives from the boarding passes was done by short wave infrared radiation. The vapors produced are drawn into a Sciex API 3000 triple quadrupole MS/MS system, operated in the multiple reaction monitoring (MRM) mode. Negatively charged chloride adduct ions are formed in the corona discharge APCI source as a result of introduction of dichloromethane. Precursor ions formed are $(M + {}^{35}Cl)^-$ and $(M + {}^{37}Cl)^-$, where M is RDX, PETN or nitroglycerin (NG). TNT does not form an adduct ion, but only a molecular ion, M^-. MRM transitions produce product ions at *m/z* 46 for NG, PETN and RDX and a product ion at *m/z* 197 for TNT. All four investigated explosives were detected at below 100 pg from the surface of boarding passes. The system was able to analyze 1000 passes per hour.

A personnel screening portal (Figure 21) was developed using a MS/MS mass spectrometer detector [27]. The MS detector consisted of ion trap and time-of-flight mass (IT-TOF) analyzers with a discharge ionization source (Figure 22). MS/MS product ions of the various explosives were used for identification.

Detector sensitivity for TNT, RDX and PETN was 1, 5 and 20 pg, respectively.

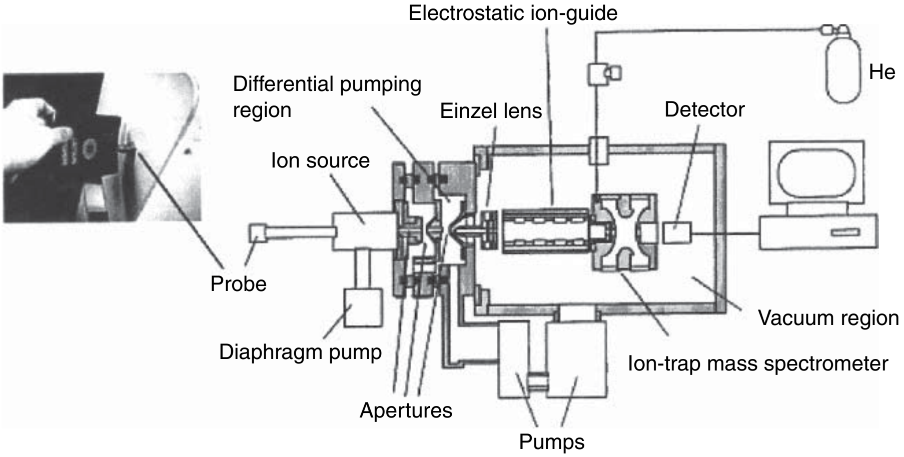

Figure 20 Schematic diagram of a mass spectrometer for explosive vapor detection [Reproduced from Y. Takada et. al., Propellants, Explosives, Pyrotechnics, 27 (2002) 224. Copyright 2002, with permission from Wiley-VCH].

Figure 21 MS-based personnel screening portal (Reproduced from www.syagen.com/LitReq/Pres1102/portal.pdf. With permission from Sandia National Laboratories, Albuquerque, NM).

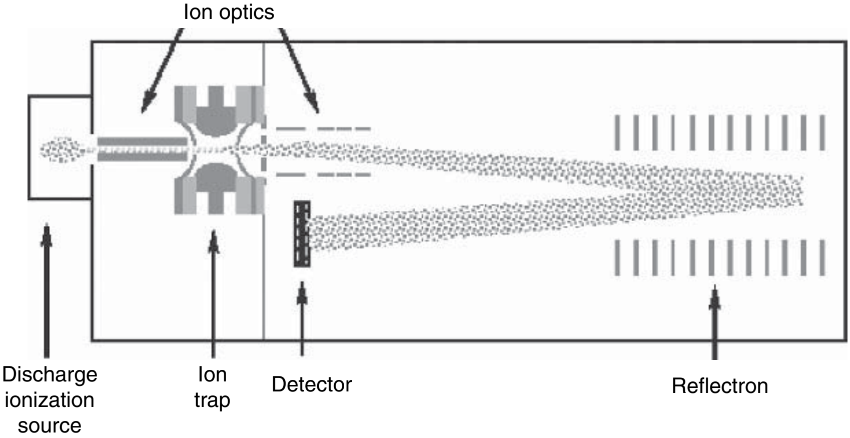

Figure 22 IT-TOF MS/MS portal detector (Reproduced from www.syagen.com/LitReq/Pres1102/portal.pdf. With permission from Syagen Technology).

4. CONCLUSIONS

Mass spectrometry, and especially LC/MS, is a major technique in the analysis of explosives. It combines good sensitivity and selectivity, and in addition to MS/MS, provides an excellent identification tool for the forensic analyst.

Mass spectrometry has not been accepted as a universal technology for the detection of hidden explosives. However, it has been used in the MS/MS configuration in some specific applications for the detection of hidden explosives.

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CHAPTER 9

ADVANCES IN ION MOBILITY SPECTROMETRY OF EXPLOSIVES

G.A. Eiceman *and* H. Schmidt

Contents

1. INTRODUCTION

Ion mobility spectrometers have become prominent trace detectors of explosives and can be seen in airports worldwide at security check points where hand bags, and other small articles, to be carried onboard aircraft are screened for explosives. Surfaces of such articles are wiped using a cloth strip to collect residues or particulates of explosives; when these samples are placed in a heated anvil and warmed rapidly to ~200°C, vapors are generated and swept into the central component of the mobility spectrometer, the drift tube. In the drift tube, sample vapors are mixed with gas phase ions and yield, through chemical reactions, product ions derived from the sample. Ions are pulsed into an electric field of ~200 V/cm, and the resulting ion swarms acquire characteristic speeds, or drift velocities, through a supporting atmosphere, usually purified air. The drift velocities are measured by determining the time required for the ion swarms to move between the point of injection and the end of the drift tube where ion impact on a detector generates a current flow. The analytical signal, or mobility spectrum, is a plot of detector current flow versus time (usually in milliseconds). The entire measurement, including the thermal desorption step, can be completed in several seconds with the automated interpretation of the mobility spectrum. When the product

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M. Marshall and J.C. Oxley (Editors)

ions characteristic of explosives are observed in a mobility spectrum, a visual or audible alarm for the presence of explosives is given.

This summary of events in a mobility spectrometer illustrates the apparent simplicity of a determination of target analytes by ion mobility spectrometry (IMS) where both ion formation and ion characterization occur at ambient pressure without any requirements for a vacuum system, as found with mass spectrometers. In comparison with mass spectrometers, IMS instrumentation can be regarded as simple, low maintenance, portable, and inexpensive. The attractions of high speed, simple operation, and cost alone are not enough to explain the widespread acceptance and the use of IMS analyzers for explosives screening in airports. What makes IMS a compelling technology is the characteristic response toward explosives that is seen as low limits of detection (routinely approaching picogram levels) and as selectivity governed by the two dimensions of ionization chemistry and ion mobility. The low demand for consumables, excepting the cloth associated with sample collection, means low operating costs; however, the need for humans to collect samples and place samples in the analyzers makes the current generation of instruments somewhat labor-intensive. Over 16,000 IMS analyzers are in operation worldwide for explosives monitoring, placing IMS in a position of importance and routine use unrivaled by chemical instruments of such sophistication.

This chapter is intended for those with some familiarity of IMS or for those who can benefit by reference to several reviews on IMS, including some with an emphasis on explosives detection [1–6]. Another compact and detailed description of principles, practices, and technology of IMS may be found in a second edition of the monograph *Ion Mobility Spectrometry* published in 2005 [7]. This chapter is intended rather as a critical survey of recent developments where the analytical capabilities for explosive measurements or the scope of applications of IMS with such analyses have been advanced. The order of discussion will follow roughly the steps involved in the determination of an explosive by IMS and will be concerned only with references directly associated with IMS. Although IMS measurements are generally regarded as reliable with low false positives and negatives, improvements in all aspects of technology and practice can be made. The number of recent publications referenced in the discussions below suggests that IMS is not a stagnant technology and that the past decade has been full of technical innovations and expanded use of IMS for explosive screening. A significant amount of the literature cited in this chapter is available only as patents or proceedings and the level of disclosure or discussion of performance in such monographs is limited. Nonetheless, patents and proceedings are included in the discussion below to provide a record of the developments in IMS and a context to assess contemporary and future advances. In other instances, detailed descriptions of analytical performance are neither desirable nor prudent.

2. SAMPLING, PORTALS, AND INLETS

The concept of obtaining a sample by wiping an article or object with a cloth strip to collect particulate of explosives, with subsequent heating of the sample in an anvil to desorb explosive vapors, is a general practice and has been described in a patent [8]. This approach to the analysis of hand-carried items was developed after extensive discussion in the 1970s and 1980s that vapor pressures of certain high explosives, a main threat for commercial aviation, were too low for the direct measurement of vapors. Consequently, particulate matter is the principal means by which low vapor pressure explosives can be sampled. The attraction of this method at security checkpoints is its sheer simplicity, speed, and convenience of wiping surfaces of hand luggage with disposable cloth strips. The complication is also related to this simplicity: such methods are not suitable for sampling inside luggage, are unacceptable for screening whole bodies, and are not easily automated. These considerations have motivated other strategies for obtaining samples of vapor and particulate inside luggage as described in a patent [9], although little of the practice and performance of this innovation can be gleaned from the patent. In this, a suitcase is opened enough for a sampling probe to be inserted into the suitcase. Air is drawn into the probe and passed to a pre-concentrator before analysis for explosives. The importance of this disclosure concerns the technical requirement with IMS to bring samples to the analyzer. Unfortunately, the approach as described will be labor-intensive, rendering the method unsuitable to automatic or even semiautomatic screening of suitcases in large numbers.

The difficulties of sampling objects for dislodged particulate are aggravated by the large volumes of air normally associated with moving particulate matter off or through samples. As mobility spectrometers function with gas flows of several hundreds of milliliter per minute and measurements occur over a few seconds, direct sampling of explosives in large volumes of air into an IMS drift tube is not a plausible method for sampling and analysis. The differing regimes of flow rate, sample volumes, and time of operation create conflicts with interfacing a high-volume sampler and an IMS drift tube. Instead, sample collectors can be operated independently with liters/s gas flows for perhaps 10 s, greatly enriching samples and improving the possibilities of collecting particulate matter. Then samples can be transferred to the IMS drift tube under conditions favorable for IMS measurements. This has been approached during the past decade with pre-concentrators [10, 11], where particulate matter is carried in a flow of air from the object sampled and sample is accumulated on a metal mesh as the large flow of air is drawn onto and through the mesh. This pre-concentrator design, as shown in Figure 1, was developed at Sandia National Laboratories (SNL) and is based on porous stainless steel mesh bounded on either side with metal diaphragm apertures; the apertures are opened during the high-volume sample step when the sample is drawn through the filter at high flow rates. After the sampling step, the apertures are closed to isolate the mesh (Figure 2), and gas at a reduced flow rate is passed over the mesh that is simultaneously heated resistively with high current. As the temperature of the mesh is increased to ~200°C, the explosives are vaporized in the gas flow and transferred into a mobility spectrometer. In one configuration of the pre-concentrator, the desorbed gas flow is passed to a side flow IMS drift tube (Figure 3) where sample vapors are introduced into a segment of the drift tube located between the ion source and the drift region. All gas flows including the sample are withdrawn from the drift tube on the opposing side of this region [12], so that the source region and drift regions are bathed constantly in a purified gas atmosphere and desorbed vapors contact the analyzer

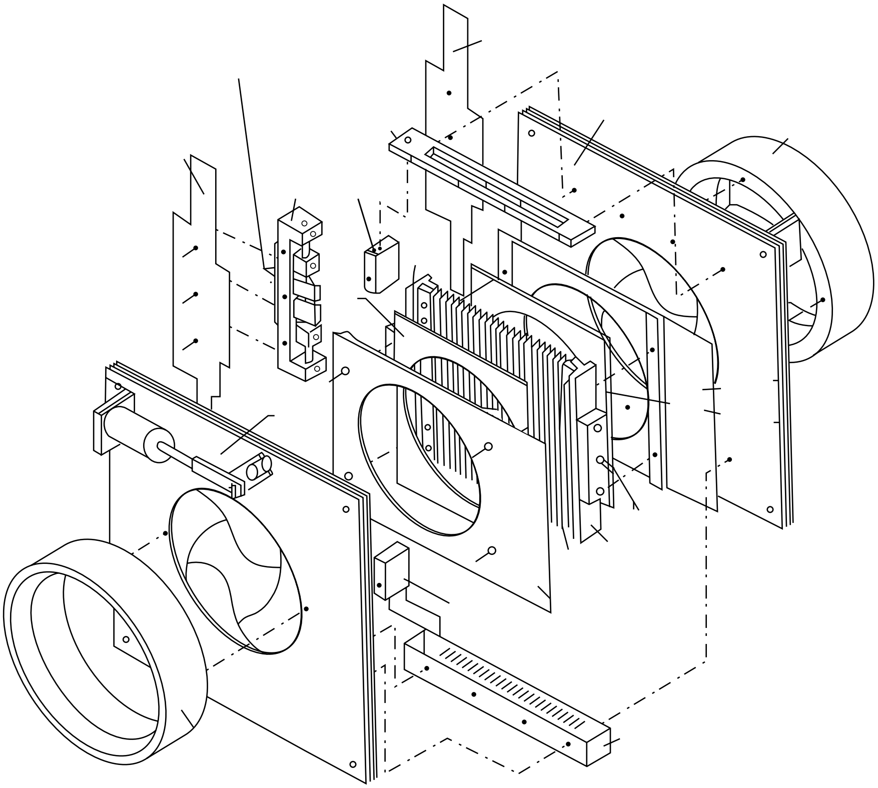

Figure 1 Schematic of pre-concentrator designed to trap particulate matter including traces of explosives on a metal mesh screen. After a sample collection step, the apertures are closed, gas is passed at a low flow rate over the mesh which is resistively heated to 200°C or more, releasing vapors into the gas flow and passed to an analyzer, commonly an ion mobility spectrometer.

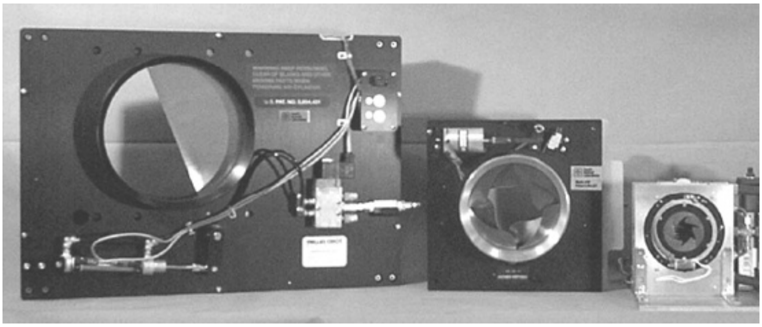

Figure 2 Photographs of pre-concentrators of various sizes. Apertures are seen in each assembly and the metal mesh is found behind the aperture. Apertures are electro-mechanically actuated and move in a manner found in some photographic equipment.

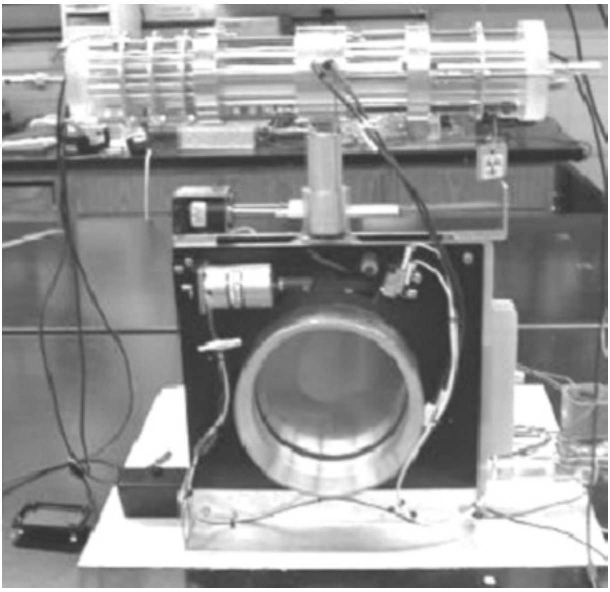

Figure 3 Ion mobility spectrometer attached to pre-concentrator module. The IMS drift tube is a side-flow design where vapors are passed into and through the side of the drift tube. In the drift tube of this photograph, ions are formed in the right portion of the drift tube and moved with an electric field through a purified air atmosphere to the region where sample vapors are introduced to the drift tube. After ionization reactions occur with sample molecules, product ions are moved under an electric field into the drift region, seen at the left of the drift tube.

only in this small region of the drift tube. Fouling of the ion source is avoided, enabling the analysis of vapor emissions from skin particulate, synthetic fibers, and other materials likely to be pulled into the filter from sampling clothing or bodies. Consequently, the drift tube can experience exposures to comparatively large concentrations of explosives and matrix vapors and is restored rapidly to a condition of clean response.

Miniaturization of IMS analyzers is attractive for applications where portability is desired, that is, the instrument is moved to the sample rather than moving samples to the instrument. However, the pre-concentrators described above and shown in Figures 1 to 3 are equal to or greater in size than some IMS analyzers. Thus, pre-concentrator sizes have been reduced further while maintaining common principles of operation. Performance naturally is affected (Table 1) by changes in size where the principal impact is on sampling rates. Eventually, a miniaturized configuration of the resistively heated metal mesh device was developed [13–15]. These small pre-concentrators have been integrated with IMS analyzers (Figure 4), first as the Hound^{TM} or Hound II^{TM} (containing a commercial handheld explosives analyzer) and then as the microHound^{TM} (equipped with an SNL-developed miniaturized IMS analyzer). A concept of resistive heated swipes was also described [16], although not subsequently developed.

Table 1 Characteristics of Pre-concentrators developed at SNL. The effect of reducing the size of the pre-concentration is seen in reduced concentration factor

Inlet sizes inches/cm	Large-volume airflow cfm	Concentration factor assuming a pre-determined gas volume for a desorption step
2/∼5	120	∼1400
6/∼15	320	∼3800
9/∼23	680	∼140,000*

* Concentration ratio based on 2nd stage pre-concentrator.

Source: Adapted from K. Linker, *Large-Volume Sampling and Preconcentration*, 3rd Explosives Detection Technology Symposium and Aviation Security Technology Conference, Atlantic City, NJ, USA, 26–27 November, 2001.

Figure 4 The miniature pre-concentrator (left) and the incorporation of the pre-concentrator with a commercial handheld IMS analyzer, known in combination as the Hound^{TM}. The metal mesh of the preconcentrator can be seen in the photo (left).

At the other extreme of philosophy for sample handling is the concept of wall-less sampling where gas flows are arranged to deliver sample to an analyzer without contact between the sample and inlet surfaces. Contact of low vapor pressure, adsorptive molecules, such as explosives with surfaces, can lead to losses in mass (i.e., signal or response in an IMS analyzer) and to prolonged memory effects. In either circumstance, response is sluggish and undependable. A design for pulling the sample into a mobility spectrometer without surface complications was described in a recent patent [17] and has become the basis for a commercial analyzer [18]. In this approach, a vortex is intended to draw sample into a mobility spectrometer after the sample surface is warmed by radiant energy. Because this device and instrument (see discussion below) are still proprietary and only patents are available for study, critical assessment of the technology is impossible and the performance of the analyzer cannot be documented or guaranteed. Nonetheless, the promise and attraction with this type of sample collection are high, and quantitative data on measured performance, when available, will be helpful to properly assess the value of this approach.

The largest sampling device or inlet for a mobility spectrometer is the human portal (Figure 5) where passengers can be screened routinely in a non-invasive way for common high explosives such as dynamite, 2, 4, 6-trinitrotoluene (TNT), C-4, and Semtex. In a portal developed at SNL [19, 20], a person stands for several seconds while puffs of air are directed against the body. Explosive vapors and particles, dislodged by the air pulses, are swept from the portal atmosphere and collected on a pre-concentrator for subsequent detection by IMS. An IMS analyzer portal apparatus showed linear quantitative response to mass for vapor samples over more than two orders of magnitude. The total time for screening each passenger, as determined in 1997 with tests at the airport in Albuquerque, NM, was ~12 s, and involved screening 2400 volunteers in a prototype portal located at the Albuquerque International Sunport. Based on favorable reactions from volunteers and analytical performance, portals fitted with IMS detectors are now commercially available from several companies (as shown in Figure 5). A next step of testing was started at JFK Airport in NY in 2004. At this writing, other airports in the testing pilot program to receive (or have received) portals include those in Phoenix (AZ), San Diego (CA), Tampa (FL), Baltimore (BWI Airport, MD), Las Vegas (NV), Miami (FL), Gulfport-Biloxi (MS),

Figure 5 Portal for sampling humans for explosives. A person enters the portal and remains for some seconds while puffs of air are directed against the body and air is drawn away from the body and through a pre-concentrator.

Jacksonville (FL), Providence (RI), Rochester (NY), and San Francisco (CA) [21]. An intention to develop portals with IMS detectors appears to be part of the US Transportation Security Administration plans, with $28.3 million allocated to purchase and install an additional 147 trace portals [22]. One feature of the portals not mentioned in the discussion above is that sample is collected from an object, here a body, automatically. This contrasts with the current generation of explosive trace detectors where swipes of samples are needed for a measurement.

3. ION FORMATION AND ION SOURCES

3.1. Gas phase ionization reactions

The first step in an overall response to an explosive inside an IMS drift tube is the conversion of sample vapor molecules into gas phase ions that reflect or disclose details of the composition of a sample. The historic method of creating ions in mobility spectrometers has been through chemical reactions between a sample and a reservoir of charge, the reactant ions. Reactant ions are formed in most commercial IMS analyzers from the release of high-energy electrons into the supporting atmosphere, purified air, in the ion source (commonly 10 mCi of ^{63}Ni) of the IMS drift tube. In negative polarity with purified nitrogen gas, the lifetime of free gas phase electrons is long enough for collisions directly with sample molecules (M) and subsequent electron capture as shown in Eq. (1):

$$\begin{array}{c} e^- + M \rightarrow M^- \\ \text{reaction in nitrogen} \end{array} \tag{1}$$

This reaction is identical to that occurring inside electron capture detectors (ECDs), which are familiar detectors with gas chromatographs. Indeed, radioactive foils in early IMS analyzers were identical to those found in ECDs. Because electron affinities for high explosives are comparatively large, ionization reactions in the negative polarity have been integral for IMS response to explosives and the suitability of ionization reactions in complex matrices to provide selectivity. When the supporting atmosphere is purified air, electron attachment to oxygen yields a reactant ion in negative polarity, $O_2{}^-$. The addition of sample with this reactant ion leads to the formation of an adduct ion, $M*O_2{}^-$ as shown in Eq. (2) and Figure 6. When molecules contain acidic hydrogens, the association between O_2^- and the acidic hydrogen can weaken the bond between a hydrogen and a neighboring carbon, C—H, in the adduct ion, with the association as C—H ····· O-O$^-$. When a C—H bond is sufficiently weak, the hydrogen can be abstracted by $O_2{}^-$, forming a product ion, $(M\text{-}H)^-$ as shown in Figure 6 and Eq. (2) [23]. Thus, the transition between an adduct ion to a hydrogen abstracted ion is controlled by the acidity of the hydrogen and can be observed for other anions such as Cl$^-$:

$$\begin{array}{l} X^- + M \rightarrow M \cdot X^- \rightarrow (M - H)^- + HX \\ (\text{in air where } X^- \text{is } O_2^- \text{ or } Cl^- \text{and M contains an acidic proton}) \end{array} \tag{2}$$

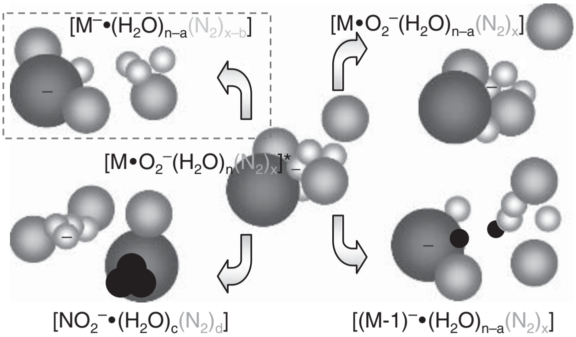

Figure 6 Summary of reactions of an explosive after the formation of an adduct ion. The nitrogens in each formula are not meant to indicate stable ion species but to highlight the clustering of ions in a dynamic manner by the supporting atmosphere. In contrast, waters of hydration are understood to be substantially bound to the core ion.

Eiceman et al. [23] determined that mixtures of product ions, $M{*}O_2^-$ and $(M\text{–}H)^-$, can be observed when ion formation and determination are fast, as with an atmospheric pressure ionization (API) mass spectrometer. In contrast, usually $(M\text{–}H)^-$ or $M{\cdot}O_2^-$ (but not both) is observed with explosives in IMS drift tubes where residence times for ions are 5 ms or greater, enough time for proton abstraction to be complete [24]. Alternatively, the $M{\cdot}O_2^-$ ion may undergo dissociation with charge retention by the analyte molecule as shown in Eq. (3) and Figure 6:

$$\begin{gathered} X^- + M \rightarrow M \cdot X^- \rightarrow M^- + X \\ \text{in air where } X^- \text{is } O_2 \text{ or } Cl^- \text{and M contains no acidic proton} \end{gathered} \tag{3}$$

Although the product ion in Eq. (3) is indistinguishable from that in Eq. (1), the supporting atmospheres and reactant ions differ. Because commercial analyzers are operated with purified air, the formation of M^- product ions will occur via Eq. (3).

Decomposition of the adduct ion can also lead to the loss of NO_2, which can be accompanied by the retention of charge to NO_2^- (an ion with *m/z* 46 and a high mobility usually faster in drift time than the reactant ion peak) as shown in Eq. (4) or to $(M\text{–}NO_2)^-$, data not shown.

$$M \cdot NO_2^- \rightarrow NO_2^- + (M - NO_2) \tag{4}$$

Another pathway is for NO_2^-, formed in Eq. (4), to attach to excess sample neutrals to form an adduct ion, $M{\cdot}NO_2^-$ as shown in Eq. (5). Although this can be a distinctive and pronounced pathway for some explosives, such as nitrogylcerin, the reaction comes at a cost – two molecules are consumed for each product ion, degrading quantitative response. One molecule provides NO_2^-, which clusters with the second molecule.

$$M + NO_2 - \rightarrow M \cdot NO_2 \tag{5}$$

The adduct ions as found with nitroglycerin (NG) are sensitive to temperature and can be seen at 100°C and below. However, the lifetime for the adduct ion is decreased as the temperature is increased and only the fragment NO_x^- per Eq. (4) is observed with NG in analyzers where drift tube temperatures are 125°C or greater. Other ions seen in IMS from explosives include NO_3^- or $M{\cdot}NO_3^-$ and may arise from reactions between NO_2 with O_2^- or NO_2^- with O_2.

Each of these product ions for a specific explosive will exhibit characteristic drift times and the patterns will be sensitive to temperature, moisture, and residence times of ions in drift tubes [25]. These patterns are unique to each explosive and are only partly described by the reactions in Eqs (1–4) and by graphics in Figure 7. A full listing of mobility coefficients and ion identities, as reported, is available in the review by Ewing et al. [25]. The discussion here is intended to illustrate the complexity of response possible with the ionization of explosives in air at ambient pressure. Naturally, the various reaction pathways and multiple product ions for a single compound can be seen as a disadvantage of ambient pressure ionization-type analyzers. Despite such complications, ambient pressure chemical ionization is compelling due to the high electronegativity of explosives and the preferential

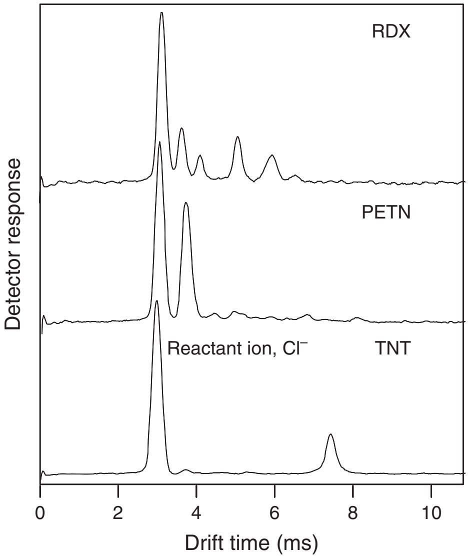

Figure 7 Mobility spectra for several explosives recorded using a mobility spectrometer equipped with a 10 mCi, ^{63}Ni ion source, methylene chloride reagent gas, moisture of 0.1 ppm, and traditional drift tube design. Ambient pressure was ~660 torr and drift tube temperature was 130°C. The presence of an intact ion for TNT is evident near 7.5 ms. Decomposition of PETN to fragment ions is extensive though some evidence of parent ions near 8 ms can be seen in baseline perturbations. Complex chemistry for RDX was observed with significant fragmentation. Increases in moisture and decreases in temperature will alter the patterns for RDX and PETN through decreases in fragmentation.*Source*: J.E. Rodriguez, *Atmospheric Pressure Chemical Ionization of Nitro-Organic Compounds in Mass Spectrometry and Ion Mobility Spectrometry*, MS Thesis, New Mexico State University, Las Cruces, NM, May 1996.

formation of product ions for explosives competitively over matrices. Additionally, the complexity described above can be simplified greatly using reagent gases.

An early example of the benefits of adding a reagent gas such as methylene chloride in the supporting atmosphere of the ion source of an IMS analyzer was the simplification of response for ethyleneglycol dinitrate (EGDN). The formation of large quantities of Cl^- from methylene chloride in the ion source can force the formation of chloride adducts, $M\cdot Cl^-$ for EGDN, and the production of an uncomplicated mobility spectrum containing a single product ion [26]. Several explosives benefit in similar ways, although other aspects of ambient pressure ion behavior cannot be avoided. For example, the $M\cdot Cl^-$ for EGDN is temperature sensitive, at 100°C, approximately 50% of the ion intensity observed at ambient temperature was destroyed through decomposition, and at 125°C, the $M\cdot Cl^-$ peak was wholly eliminated. The chemistry of ionization of explosives, although complicated by multiple pathways (Figure 6), is nonetheless a valuable and indeed essential component to IMS response. When temperature and moisture are controlled and the resultant product ions are tailored by the use of reagent gases, response can be made reliable, characteristic of each explosive, and quantitatively attractive.

One of several advances in the past few years was in understanding the molecular basis for ion formation from explosives or explosive-related substances. The associations of Cl^- to dinitroalkanes were characterized by mobility spectrometry, the thermal stabilities of adducts were measured, and the observed mobility spectrum for each substance was interpreted using ion stabilities [27]. The thermal stabilities for chloride adducts of 1,4-dinitrobutane (DNB), 2,3-dimethyl-2,4-dinitropentane (DMDNP), and 2,3-dimethyl-2,3-dinitrobutane (DMNB) decreased in the order $DNB\cdot Cl^- > DMDNP\cdot Cl^- > DMNB\cdot Cl^-$. The stabilities were governed by the cumulative association of Cl^- with the molecule, where hydrogen atoms were the points of electrostatic association. Thus, stability was correlated with the number of acidic hydrogens on the carbon-α to the nitro groups, namely, four with DNB, two with DMDNP, and zero with DMNB. The stability of the cluster was improved with increased numbers of associations between Cl^- and hydrogens of the chemical. This study illustrates the value of describing the structural or molecular basis for ion-molecule chemistry and the patterns observed in mobility spectra. In another study on ionization, Buttigieg et al. [28] found that triacetone triperoxide (TATP) exhibited favorable response in positive polarity, that is, due to proton attachment. The response was low or nil in negative polarity, highlighting the need for dual polarities with a new generation of IMS analyzer. The main peak was mass-identified at an m/z of 223 as the MH^+ of TATP. These findings were consistent with recent studies using differential mobility spectrometry described below.

3.2. Ion sources

Today, the most widely used ion source with IMS analyzers is 10 mCi ^{63}Ni, often a 1 cm diameter × 1 cm long metal cylinder, which spontaneously emits high-energy electrons (maximum energy ~ 67 keV) into the supporting atmosphere. The electrons initiate the formation of reactant and product ions as described above although the speed of forming reactant ions is slower than those reactions forming product ions [7]. A radioactive ion source such as ^{63}Ni provides reliable behavior, a stable supply of reactant ions, instant response without a warm-up period, zero maintenance, no replaceable parts, no power supply, and no supporting electronics. The analytical response for explosives is as good as any other ion source. Consequently, radioactive ion sources are the favored sources for mobility spectrometers. Against these attractions are some difficulties. Although the cost of a radioactive foil today is significant for commercial instruments at $300 per source, this is a minor cost compared with the long-term costs for the maintenance needed to conform to safety regulations. Semiannual leak tests, labor costs for documentation and record-keeping, and finally the costs for disposal of the source and analyzer at the end of a serviceable lifetime combine to elevate the costs of radioactive sources to a bearable but unwelcome level. Consequently, there is a search in research groups worldwide for a non-radioactive replacement of ^{63}Ni and a few examples, relevant to explosive determinations, are described below.

An electrospray ionization (ESI) source, where liquid is formed into a fine aerosol spray using gas flow, electric fields, and electrochemical reactions, has transformed mass spectrometry by making possible measurements of large non-volatile molecules and has also been adapted with mobility spectrometers [29]. Such an ion source might be relegated to environmental applications where interest exists in the presence or levels of explosives in aquatic environments. Solutions of explosives have been sprayed into an IMS drift tube using an ESI source, and characteristic response was found for a range of compounds including TNT, 2,4-dinitrotoluene (2,4-DNT), 2-amino-4,6-dinitrotoluene, 4-nitrotoluene, trinitrobenzene, cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), cyclotetramethylene-tetranitramine (HMX), EGDN, and NG. Mass analysis of product ions showed that product ions were mostly associated with intact molecules except for NG and such instability for NG was understandable since the drift tube was operated at 250°C. The use of liquid samples introduced some convenient flexibility not available with other ion sources. For example, adducts with chloride ions were enhanced through the addition of sodium chloride to the sprayed solution, though this is comparable to adding a reagent gas in a ^{63}Ni ion source. Detection limits were 15–190 pg/l with an ESI source. The advantage is best illustrated with the flexibility or selection possible with ESI – the chemistry of ionization might be altered through the use of reagents that are soluble in aqueous solution but not volatile. Salts and other inorganic materials might be introduced into gas phase chemistry in ways not possible with permeation or diffusion tubes used with volatile reagents. This concept was advanced one step beyond ordinary ESI practices by using the ESI source as a generator of only reactant ions [30].

Ions formed in an ESI source, with aqueous solutions free of sample, were then mixed with vapors of explosives generated through ordinary methods of volatilization. Ions from the ESI source and sample vapors, when mixed, yielded product ions through ion–molecule collisions and reactions similar to those in Eqs (2–4). This concept was demonstrated for RDX, NG, and pentaerythritol tetranitrate

(PETN), all of which exhibited the formation of NO_3^- and subsequent association to $M{\cdot}NO_3^-$. This approach to ionization was termed secondary ESI and was proposed as an alternative to radioactive ion sources even in non-environmental uses of IMS analyzers. The benefit of controlling ion chemistry with the use of reagents not usually available to IMS measurements was demonstrated with the formation of NO_3^- as a reagent ion from a nitrate salt. The initial fragmentation of PETN or RDX to NO_3^- is wasteful, requiring two molecules for the formation of each ion. However, detection limits for RDX were reduced to 5.30 μg/l in the presence of NO_3^-, presumably through suppressing the first ionization of chemical. The detection limit for RDX in the presence of a traditional volatile chloride ion was 116 μg/l. Disadvantages of this method are the need for a consumable, the reservoir of aqueous solution for the ESI process, the burden of additional instrumentation for controlling the ESI source, and the specialized drift tube design needed to dehydrate ions from the ESI source before use with sample vapors. Despite these limitations, the concept should be pursued and introduces some creativity and flexibility rarely seen in ion sources for IMS.

Electric discharges in air or nitrogen have been a long-standing interest for creating ions at ambient pressure, and a stable type of discharge, the corona discharge, can produce ions suitable for use as reactant ions in certain mass spectrometers [31] and in mobility spectrometers [32–36]. Particularly relevant here is the demonstration, under laboratory conditions, that a corona discharge was effective in the determination of explosives [37]. Corona discharges in analytical instruments are commonly operated with a constant or regulated current providing reasonably stable production of reactant ions at the expense of power and maintenance [31]. An alternative method of operation, particularly well-suitable for handheld or portable analyzers, is a pulsed corona discharge that is operated on-demand to conserve battery lifetime. A concern with corona discharges generally is that the ions formed in the negative polarity may not be the same as those from radioactive sources, thus creating two difficulties: response differs qualitatively from that historically seen with the IMS determination of explosives (a minor concern) and response exhibits degraded detection limits (a serious concern). The specific concern was that the formation of NO_x^- and ozone as ions in the reaction region would render the chemistry unfavorable for ionization of explosives. For example, the electron affinities of NO, NO_2, NO_3, O_3, and O_2 are 0.026, 2.27, 3.94, 2.10, and 0.45 eV, respectively [38]. In contrast, the electron affinities for 2-nitrotoluene and 2,4-DNT are reported as 0.92 and <1.6 eV, respectively (a value for TNT is not available). Thus, an electron on NO_2^-, NO_3^-, O_3^- will not be transferred to 2-nitrotoluene or 2,4-DNT, rendering these substances as ineffective reagent gases. However, Bell and Ross [33] discovered that the formation of NO_x and O_3 was promoted by the mixing of reactive neutrals with ions in the corona discharge zone. When flows were arranged in the source region so that reactive neutrals were swept from the corona region, ordinary and desired negative reactant ions were produced and were available for ionization reactions with the sample. Unfortunately, the performance of a pulsed corona discharge with explosive vapors has not been described and cannot at the moment be assessed despite the attractions of a low-power, non-radioactive ion source.

Direct current or continuous corona discharges can produce a large amount of ions, nearly 10^2 more than a radioactive source. However, Tabrizchi et al. [35–37] observed that the introduction of electronegative substances into the source disrupts the discharge, thus making response non-quantitative, unstable, or even extinguishing response completely. A corona discharge ion source was incorporated into a drift tube design by isolating the sample from the source region in order to maintain a clean gas atmosphere in the source region (Figure 8). Ions are extracted from the corona discharge and introduced to the sample in a separate region of the IMS analyzer. This concept was successfully demonstrated with nitrobenzene, PETN, and TNT where detection limits as low as 10 ng/m^3 were reported with a linear range of response or calibration of 10^5. In later studies with this source design, measurements were extended to other explosives with detection limits reported as 8×10^{-11}, 7×10^{-11}, and 3×10^{-10} g for PETN, TNT, and RDX, respectively. The calibration plots showed linear dynamic ranges of $\sim 10^4$. These promising results should be supplemented with longevity studies and examination of needle maintenance; nonetheless, the concept is a promising development, suggesting a

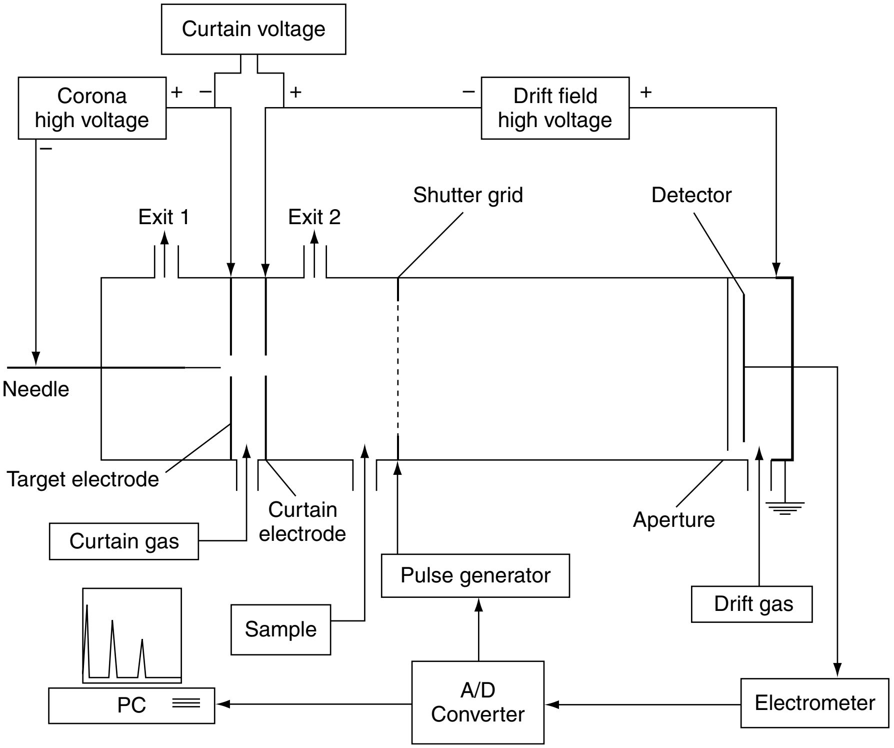

Figure 8 Drift tube design for a corona discharge ion source where sample was excluded from the source region and ions extracted from the source region were mixed with sample in a volume outside of the source. In this design, a clean supporting atmosphere of the ion source is preserved rendering stable response without fouling by sample.

non-radioactive source free of the gas phase chemistry problems associated with traditional DC corona discharges.

Photoionization, where electrons are released by molecules following the absorption of energy from photons, has long been viewed as a non-radioactive means to ionize explosives in the vapor phase [39]. In recent years, two teams have sought to employ laser ionization with IMS for explosive determinations. A team at Implant Sciences Corporation has utilized a laser (or flash lamp) for sampling surfaces and for ionization of sample vapors in an IMS analyzer [40, 41]. In their approach, the sample is removed from a surface with an increased temperature from laser exposure. Gases (and presumably particulate matter) from over the surface are drawn into an IMS drift tube using a wall-free inlet (*vida supra*). In the IMS drift tube, resonance multi-photon ionization by a laser is used to produce ions from the explosives. Their system, term QS^{TM} ionization, is not well-described in the open literature and their commercial literature discloses little on the design or performance. Some parts of the design can be seen in photographs of the Quantum Sniffer (QS-H100) from the commercial literature (Figure 9). Although not well-documented, the concept of contact-free sampling of surfaces has intrinsic attractions and should be developed independent of the choice of an ion source. Still, lasers have been recognized by others for the thermal desorption of explosives from surfaces [42] and may be viable commercially with increasing measure as laser costs decrease and convenience of operation increases.

A variation of direct photo-ionization is the use of a light source to form gas phase electrons with photoemissive materials. In this approach, electrons are generated and released into the gas phase by irradiation of a metal plate or metal-coated window by either a flash lamp or pulsed laser beam. This ion source, first described in 1991 for mobility detectors [43], has since received little development or further application. As with all alternatives to a ^{63}Ni ion source, the attendant electronics and maintenance issues can be very disadvantageous for instrumentation that is required to operate routinely with high stability and reliability,

Figure 9 An ion mobility spectrometer called the Quantum Sniffer has an inlet with laser or flash-lamp to warm a surface and a vortex sampler (left frame) to pull sample into the analyzer without contact between analyzer and surface (right frame).

and the photoemissive source concept may be difficult to transfer from laboratory studies to fieldable instrumentation.

4. DRIFT TUBES AND ANALYZER DEVELOPMENT

Mobility spectrometers may be regarded as simple ionization detectors (such as the ECD) with refinements from additional analytical information provided by the mobility characterization of ions in the drift region. In traditional mobility spectrometers, ions formed in a reaction region are extracted and injected as an ion swarm into a drift region with an electric field (E) of several hundred V/cm over a fixed distance, usually 5–8 cm long. In the drift region, an ion swarm attains a certain velocity, the drift velocity (v_d), which is characteristic of the swarm, hence the ions in the swarm. The drift velocities can be associated with the molecular structure and mass through the mobility coefficient (K), which provides a second dimension of selectivity in analysis by IMS. This is further enhanced as swarms undergo separation or resolution in the drift region. The mobility measurement is often associated with the molecule or more correctly from a combination of ion structure and a specific supporting atmosphere. The drift velocity is calculated by measuring the time needed for the ion swarm to traverse a distance (L) between the injection and detection at a metal plate as shown in Eq. (6):

$$K = v_d/E = (t_d/L)/E \tag{6}$$

The drift tubes used in commercial analyzers have demonstrated reliability and value. However, the same drift tubes contain certain design limitations or intrinsic features that could be improved for either the expanded scope of explosives detection or improved operations. These are recognized within the community of IMS developers and researchers and improvements have been under active study and development during the past decade.

One challenge with existing drift tubes is the need to maintain highly precise temperature control within the drift tube and so measurements are reproducible over hours, days, or months. However, explosives span a large range of vapor pressures and ionization properties, which are temperature-dependent. Consequently, neither a single temperature nor a particular polarity is effective or optimum for the determination of all explosives by IMS. One approach to solving the dilemma of finding a single set of conditions for a drift tube is the use of two drift tubes in a single analyzer. McGann et al. [44] used dual drift tubes with one drift tube in negative polarity for black powder and smokeless powder and a second drift tube in positive polarity for the simultaneous determination of TATP and ammonium nitrate. Temperatures were also arranged independently on individual drift tubes for best response. When an ion source is common to two drift tubes, signal artifacts apparently arise and methods were developed to overcome such interferences. Modulation of the ion intensity provided a basis to reject common background interferents [45].

Another interest in drift tube improvements is the poor performance of certain components such as the ion shutter, the device used to inject ions into the drift region from the ion source region. Whereas the commonly accepted electronic gate called the Bradbury–Nielsen shutter (and variations) is functional and satisfactory for existing analyzers, there are aspects to these ions shutters that are genuine limitations for future refinements in drift tube technology. Commonly, the ion shutter allows a 100 μs wide band of ions (the swarm) into the drift region. During this 100 μs interval, ions move through the shutter, providing an ion swarm ~5 mm in width (this is repeated at ~30 Hz or every ~30 ms). The duty cycle then is 0.1/30 ms, hence only a few percent or less of all ions formed in the ion source is actually sampled, characterized, and detected; well over 90% of all ions in the source are wasted or not measured. To improve signal-to-noise ratios, spectra are treated by digital signal averaging, which reduces noise with a cost in slightly degraded resolution from uncertainties in control of phase. This cost has been considered a normal consequence of a functioning drift tube; however, Tarver [46] has proposed that Fourier Transform operations can be applied to the ion shutter with variable frequency to improve ion throughput when software is used to simulate a second ion shutter. In this approach to the control of ion shutters, the duty cycle can be improved to 50%, providing a 7 × improvement in detection limits.

A drift tube suitable for use with the high gas flows from portals with high resolution was described [47] and characterized for response to TNT, 4,6-dinitro-o-cresol, and RDX. In this design, an 800% increase in ion current from 0.85 to 6.8 nA was accomplished by modification of the ion source region. Resolution of the device was calculated as 50–60, roughly twice of that found with commercial IMS analyzers, and was attributed to the use of a large-diameter drift tube and selective sampling of ions toward the center where field distortions are small. At the other extreme of dimensions is a miniaturized drift tube fitted onto a 6 by 10 cm circuit card that contains the drift tube, high-voltage power supply, switching control, and detection electronics [48]. This instrument is based on flexible ceramic sheeting with the drift tube components on the sheet that is rolled into a drift tube. Currently the unit is part of a micro-Hound^{TM} development at SNL. Another small analyzer tested with explosives was the palm-sized Lightweight Chemical Detector, which is equipped with a pulsed corona discharge source and two drift tubes (positive and negative polarities) [49]. The taggants DMNB and EGDN were measured using this ambient temperature analyzer and detection limits were ~10 ppb_v without complications from low vapor pressure explosives or matrices. A final mention of drift tube designs, with applications for explosives or taggants, is that of Munro et al. [50] who characterized the ion chemistry for a dinitroalkane with various reagent gases. This is noteworthy as an example of the exploration of gas phase reaction chemistry using mobility spectrometer–mass spectrometers and the influence of gas composition and temperature on observed response, for example, the mobility spectrum.

One of the most impressive developments during the past year or so with traditional drift tubes is the introduction of an IMS analyzer with authentic twin drift tubes where the sample is ionized in a single reaction region and positive and negative ions are extracted and characterized in two separated drift tubes placed at appropriate polarity. In this design, the two drift tubes can be individually controlled in temperature although the ion source is common to both drift tubes. The analyzer is derived from a patent filed in 1990 and is developed from the successful IONSCAN family of instruments [51]. The enhanced capabilities of this instrument, the IONSCAN 500DT, have not emerged widely within the trace detector community but should become a benchmark device for future developments in IMS technology.

5. FIELD ASYMMETRIC IMS AND DIFFERENTIAL MOBILITY SPECTROMETRY

Although mobility spectrometers with traditional drift tube designs, as described above, are found in explosive detectors worldwide, a new generation of mobility-based analyzers was developed in the 1990s and successful applications with explosives have been demonstrated. These developments are sufficiently significant with potential to transform explosive analyzers based on ion mobilities that a discussion separate from drift tube technology is merited. In High Field Asymmetric Waveform Ion Mobility Spectrometry (FAIMS) and Differential Mobility Spectrometry (DMS), ions are characterized for differences in mobility through a non-linear dependence of mobility on electric fields, typically between 10 and 100 Td ($1\,\mathrm{Td} = 10^{-17}\,\mathrm{V.cm^2}$). The mobility coefficient for an ion is independent or practically independent of the electric field when the field (expressed as E/N where N is neutral gas density) is ~1 to 10 Td. However, as E/N is increased above 10 Td, the mobility coefficient becomes dependent on field strength as shown in Eq. (7):

$$K(E/N) = K(0)[1 + \alpha_2 (E/N)^2 + \alpha_4 (E/N)^4 + \ldots] \tag{7}$$

where the terms are: $K(0)$, the mobility coefficient under zero field conditions and α_2, $\alpha_4 \ldots$ α_{2n}, specific coefficients of even powers of the electric field. Under normal conditions of 273.15 K and 101.325 kPa, 1 Td for E/N corresponds to an electric field of 268.67 V/cm. The α terms are an even power series for E/N so that the absolute value for ion velocity is independent of electric field direction. The expression in Eq. (7) can be simplified as a function per Eq. (8):

$$K = K(0)(1 + \alpha(E/N)) \tag{8}$$

where $\alpha\,(E/N) = \alpha_2(E/N)^2 + \alpha_4(E/N)^4 + \ldots$ and $\alpha\,(E/N)$ is understood to be a function derived from plots of mobility versus E/N.

In a FAIMS or DMS analyzer, ions in a flow of gas are carried through a narrow gap between two electrodes, which may be cylindrical or planar. A high-frequency, high-voltage asymmetric waveform is applied to the electrodes, resulting in an electric field or separation field that affects ion motion through different coefficients of mobility via Eq. (7) or (8). Ions undergo oscillations perpendicular to the gas flow in response to the separation field. The instrument is originally configured so that ions that have no field dependence will undergo oscillations with net displacement of zero. If an ion has a mobility dependence on the electric field, a slow net displacement or drift toward an electrode will occur and the absolute displacement depends on field amplitude, field waveform, and α function for an ion. Ions that collide with the wall of the analyzer are neutralized and swept out of the analyzer.

An ion that is displaced from the center of the analyzer can be restored to the center of the gap (i.e., compensated) when a DC potential from, for example, ~–20 to ~10 V is superimposed on the separation field. This second potential is called the compensation voltage and will allow an ion to be passed through the DMS drift tube and to a detector. A scan of the compensation voltage provides a measure of all ions in the analyzer and is termed a differential mobility spectrum as shown in Figure 10. This method is now understood as a technique for separation of ions based on ΔK rather than K as seen with conventional drift tubes.

The α functions for ions can be obtained experimentally and two general behaviors can be observed: positive α and negative α functions. Processes responsible for positive α functions are understood to be the dynamic transitions of ions between unclustered and clustered or short-living associations, with corresponding changes in collision cross-sections between these two ion forms or conditions. This can be seen in the ion size or cross-section at an effective temperature ($\Omega_D(T_{eff})$) as seen in the formula for mobility in Eq. (9) where an unclustered ion at high electric fields will have a comparatively small $\Omega_D(T_{eff})$ and the ion at low fields in a clustered form will have a higher $\Omega_D(T_{eff})$:

$$K = \frac{3e(2\pi)^{1/2}(1+\alpha)}{16N(\mu k T_{eff})^{1/2}\Omega_D(T_{eff})} \tag{9}$$

If all other terms are constant, ΔK is linked principally to $\Delta\Omega_D(T_{eff})$ and to changes in effective reduced mass, $\Delta\mu$. The effects of the clustering–declustering process lead to changes in K of approximately 2–8%. Negative α functions arise from

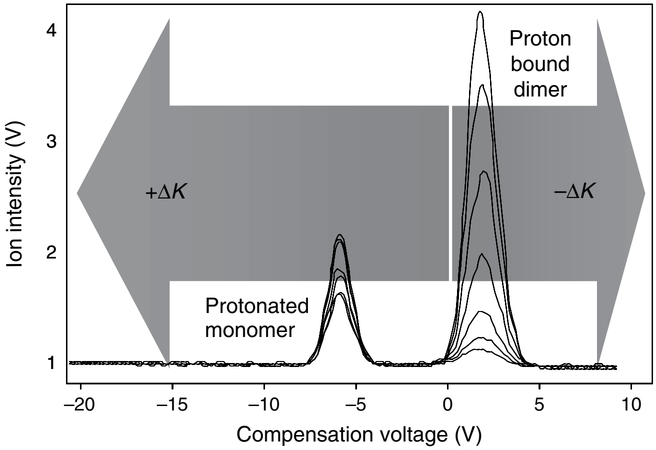

Figure 10 Differential mobility spectrum showing the characterization of ions by compensation voltage, the separation of protonated monomer (MH^+) from proton bound dimers (M_2H^+) and the relationship between compensation voltage and K for ions. Ions with positive (left moving) and negative (right moving) functions are strongly related to ion mass. Negative ions are also easily detected with a DMS analyzer (see below) and are characterized simultaneously with positive ions in the same analyzer. A DMS analyzer is equipped with two voltage biased detectors for detecting positive and negative ions.

increased collisions experienced by an ion with increased drag and decreased mobility. Although differences in mobility with negative α functions are usually below 1%, ions can be characterized and separated when they are subjected repeatedly to a large number of oscillations or cycles.

Although methods of ion characterization using asymmetric electric fields are relatively recent developments, explosives were among the first chemicals characterized, and favorable analytical response was reported for both resolution and detection limits. Buryakov [52, 53] showed the FAIMS response to 1,3-dinitrobenzene, 1,3,5-trinitrobenzene, p-mononitrotoluene, 2,4-DNT, and TNT and PETN. Analytical response was astonishing with reported detection limits near 2 ppt for DNT, 0.4 ppt for TNT, and 0.6 ppt for PETN [52]. In the use of FAIMS for explosives detection, Buryakov [54] employed high-speed chromatographic pre-separation of sample before the analyzer to improve selectivity and reliability of response. The column of choice for this team has been a multi-capillary column [55]. The GC-FAIMS analyzer was used for contraband and chemical warfare agents with a maximum detection limit of 5 pg/ml for cis-α-LW, and a best value of 0.001 pg/ml for cocaine. The maximum value of linear dynamic range (LDR) equal to 1000 was registered for sarin and the lowest one of 150 was for the ions of lewisite. Speed of response for single compound detection was 0.7 s.

The advantage of the FAIMS or DMS technology is that the ion shutter is eliminated as is the aperture grid that protects the detector from the approaching ion swarm. There are several ramifications on response or drift tube design from the mechanism of ion characterization. The most significant of this is that ions of both polarities can be characterized simultaneously in a single analyzer because ions are transported by gas flow, not electric fields as in traditional IMS drift tubes. Another implication is that drift tubes can be miniaturized without technical limitations from the requirement for a set of small ion shutters. In the late 1990s, a microfabricated planar drift tube was crafted [56] and has led to commercially offered analyzers based on DMS [57]. A DMS analyzer was evaluated for the determination of explosives, and the ionization chemistry was the same as that observed with traditional IMS (Figure 6) where nitro-organic explosives and related compounds exhibited the expected product ions of M^- or $M{\cdot}NO_2^-$ from atmospheric pressure chemical ionization reactions in purified air at 100°C [58]. However, the initial experience with DMS characterization of ions of explosives was unpromising as peaks for product ions were confined to a narrow range of compensation voltages between –3 and –4 V, with little separation or resolution to distinguish among substances. The compression of explosives ions to a narrow analytical band of compensation voltages was understood to be a low field dependence (α parameters ranged from –0.01 to 0.02 at 100 Td) and could be attributed to large product ions or adducts of explosives. The amount of clustering could be enhanced by the addition of organic vapors into the supporting atmosphere and α parameters could be increased to 0.08–0.24 (at 100 Td) when methylene chloride at 1000 ppm was added to the gas flows. Peaks in differential mobility spectra were shifted to compensation voltages of –3 to –21 V improving ion separation by increasing $\Delta K \sim (K_l – K_h)$, where K_l is the mobility coefficient of ions clustered with vapor neutrals during the low-field portion of the separation field waveform and K_h is the mobility coefficient for the same core ion when heated and unclustered during the high-field portion of the waveform.

Previously, the planar micro-fabricated DMS analyzer was characterized as a detector for capillary gas chromatography and performance was comparable directly to that of a flame ionization detector (FID) for the separation of a ketone mixture from butanone to decanone [59]. Effluent from the column was continuously introduced into the detector and DMS scans were obtained throughout the chromatographic analysis. This provided chemical information in DMS scans orthogonal to retention time. For ketones, limits of detection were approximately 1 ng with positive ions and such limits of detection were comparable to or slightly better than those for the FID. A concentration dependence of the DMS scans was seen in the proportional relationship between ion intensity and sample vapor concentration and the inverse relationship between reactant ions and product ions as seen in other API technologies. The extra-column broadening from the micro-fabricated analyzer was calculated as 36% increase in peak broadening versus the FID. The DMS analyzer was found to be an information-rich detector for gas chromatographs. In the years since these studies, a high-speed GC-DMS analyzer for explosives has become available commercially as the EGIS Defender [60]. The EGIS Defender (Figure 11) is a continuation of analyzers produced by Thermo Electron Corporation, beginning with the EGIS and continuing with the EGIS II and III. These were based on high-speed GC [61] with a chemiluminescence detector and have been superseded by the EGIS Defender. The advantage of detecting ions of both polarities in a single drift tube expands the range of explosives detectable with the EGIS Defender and is illustrated in the next section. The speed of analysis and range of explosives detected by the EGIS Defender are

Figure 11 A commercial configuration of high speed GC-DMS is the EGIS Defender, which is a successor of the EGIS and EGIS II explosives analyzers.

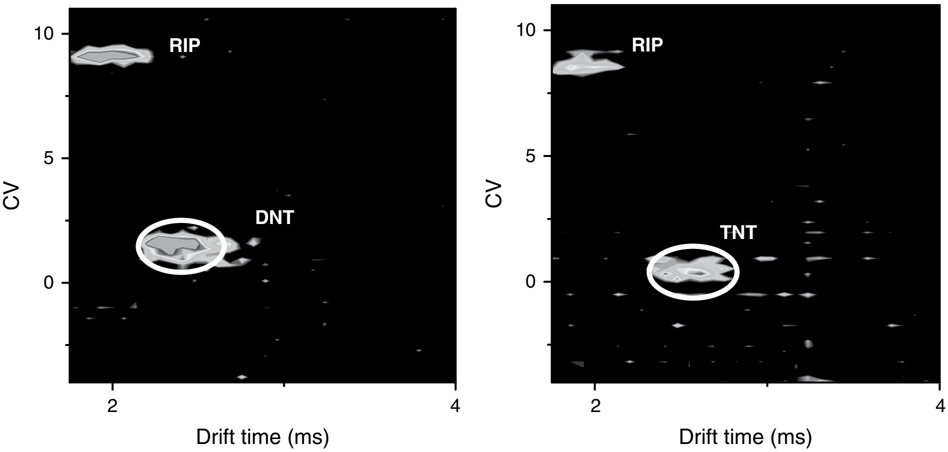

Figure 12 Topographic plots of a DMS-IMS^2 analyzer response to 2,4-DNT (left frame) and 2,4,6-trinitrotoluene (right frame). Positions of ions in plots are circled; the reactant ion peak is seen at compensation voltage of 8 V and drift time of 2 ms. *Source*: (C.R. White et al., unpublished data, New Mexico State University, September 2005.)

unprecedented with determination of nitrates (EGDN/AN), NG, DNT/TNT, PETN, RDX, TATP, HMTD, HMX, and Tetryl in 10–12 s.

A new analyzer based on ion mobility has been introduced in 2005 and combines DMS and IMS analyzers in tandem, hence ions are first separated in a DMS drift tube and then characterized by twin IMS drift tubes [62]. Because the DMS is comparatively slow (0.1–1 Hz) and the mobility spectrometer operates at 30 Hz, mobility spectra can be obtained throughout a DMS sweep of compensation voltage, creating a three-dimensional plot as shown in Figure 12 for DNT and TNT (unpublished experimental results provided by C.R. White et al. at New Mexico State University, September 2005). As shown in the topographic plots of Figure 12, a benefit of ion characterization for K and ΔK is seen in the improved separation of peaks over DMS and IMS alone. The tandem DMS-IMS^2 was described at the 2005 International Symposium on IMS and is under development requiring detailed evaluation as drift tube improvements are made.

6. PRE-SEPARATION WITH IMS

An unavoidable consequence of forming ions in air at ambient pressure is the competition for charge that occurs through collisions of ions and neutrals, including those from the sample matrix. An original attraction of IMS for explosives detection was the intrinsic advantage from properties of ionization for explosives, with negative reactant ions, over other substances such as alkanes, ketones, and matrix constituents. These others do not exhibit substantial binding energies with the reactant ion, the anion (O_2^- or Cl^-), and their product ions consequently have short lifetimes (poor detection) in an IMS analyzer. Although this is generally observed, there is no absolute guarantee that matrix interferences will not occur and, indeed, some interferences can be observed at elevated concentrations of matrix vapors. Eventually, ionization will be affected qualitatively or quantitatively as concentrations of interferences are increased even though ionization may favor explosives over interferents. One solution to matrix interferences in IMS is the adjustment of gas phase ionization reactions through the addition of a reagent gas to suppress the ionization of matrix constituents. This is effective partially with matrices of poor ionization properties; however, the effective suppression of matrix by the control of gas phase reactions diminishes when the matrix contains molecules of comparable ionization properties, or electron affinity in the instance of explosives. In circumstances where matrix effects are effective in interfering with response, only some form of pre-fractionation of samples can simplify the reaction chemistry and provide reduced susceptibility to false response.

Apart from Buryakov's extensive use of multi-capillary columns with FAIMS type drift tubes and the introduction of the EGIS Defender (a GC-DMS analyzer), only a few examples of explosive determination by IMS or DMS with pre-fractionation were described in recent years. Garofolo et al. [63] used liquid chromatography to pre-fractionate a sample and the fractions containing explosives were characterized off-line using an IMS analyzer. Samples collected at scenes of actual detonations were extracted with solvents, purified by solid phase extraction (SPE), and finally pre-fractionated by HPLC. Detection limits were a few hundred picograms, which was better than those for a ultraviolet detector. More importantly, these methods removed interfering substances from the IMS determination with a sample of complex chemical composition. A commercial GC-IMS became available briefly in the early 2000s and was built upon the familiar Barringer model 400 Ionscan [64]. This flexible instrument, allowing either IMS or GC-IMS determinations, demonstrated the advantage of pre-fractionation and the difficulty of commercializing an instrument with higher costs and complexity compared to ordinary IMS analyzers. When the benefits of pre-fractionation may not be needed on every sample and with added delays in a measurement, such instrumentation is not commercially viable in the competitive marketplace of explosives detectors; the GC-IONSCAN is no longer sold by the manufacturer, now Smiths Detection.

Examples of high-speed GC under laboratory conditions can be seen in Figure 13 where high-speed GC-DMS determination of a mixture of explosives shows the benefit of separation and compensation voltage (A. Cagan, H. Schmidt and G.A. Eiceman, unpublished data, New Mexico State University, August 2005). In this plot, the chromatographic separation on the retention time axis illustrates the separation of explosives, providing one dimension of selectivity. Additional selectivity is present with the DMS characterization of ions seen in the compensation voltage scale and, finally, a third level of selectivity is seen with ion polarity with the top frame for positive ions and the bottom frame for negative ions. For example, TNT shows response only in the negative polarity at a retention time of 2.6 min with a compensation voltage of 0.5 V. In contrast, mononitrotoluenes are detected only in the positive polarity with retention times from 0.7 to 0.9 min and compensation voltages of −1 to −1.5 V. Response for TATP was in the positive polarity only whereas HMTD exhibited response in both polarities. These

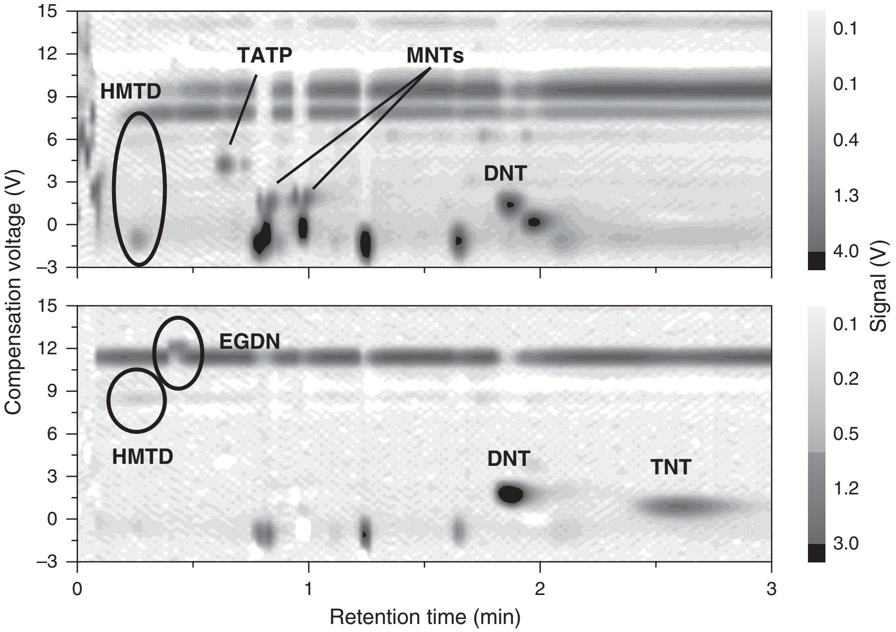

Figure 13 Topographic plot of results from GC-DMS characterization of a mixture of explosives using a 2 m long capillary column with a fast temperature ramp. *Source*: (A. Cagan, H. Schmidt, and G.A. Eiceman, NMSU, August 2005 unpublished results.)

characteristic properties of compensation voltage, retention time, and ion polarity are complementary in analytical value and supplemented still by another aspect of the pre-fractionation step. A feature of pre-fractionation that can be overlooked in assessment of the technology is that pre-fractionation simplifies the ionization reactions in the DMS analyzer, lessening demands on the DMS for resolution of ion mixtures.

7. CALIBRATIONS AND VAPOR SOURCES

Mobility spectrometers are based on principles and technology with responses stable enough so that calibration of analyzers can be regarded as a minor question in view of other analytical requirements of a field instrument. Moreover, mobility analyzers are often used as a threshold analyzer where precise calibrations are not essential. Nonetheless, users of instruments need some level of confidence that an analyzer is functioning, is suitable for use on a daily or regular basis, and meets a certain level of performance, notably a limit of detection. Field methods for calibration were described in the 1990s and patented in 2003 with filter disks that were impregnated with known amounts of analytes and chromatographic stationary phase material, large non-volatile polymers [65]. These polymers aid the retention of explosive during the storage of the disks and do not interfere with the volatilization or detection of the explosives when the disk is analyzed. Disks are analyzed by thermal desorption, and vapors, containing a calibrated amount of explosive, are swept into the analyzer. This method or variations of it can be found in use with explosives monitors in airports.

The disadvantage of this method is that there may be several steps between a NIST reference and determination of the level of explosive delivered to the IMS. Eiceman et al. [66] evaluated a vapor generator based on the diffusion of vapors above a thermostated reservoir of solid explosives into a flowing stream of an inert gas. The amount of explosive in the vapor stream was calculated by gravimetric determination of changes in the mass of the tube containing the explosive. The levels of loss were low but measurable using a micro-balance, which could be referenced directly to standard weights from the US National Institute for Standards and Technology. Rates of mass output were obtained for TNT, RDX, and PETN at three or more temperatures between 79 and 150°C, and were found to be stable over hundreds of hours of continuous operation. The output rate for mass was adjustable from a few picograms per second to several nanograms per second by changing the temperature of the sample. This gravimetric calibration of the vapor generator for TNT at 79°C matched exactly that obtained through independent calibrations using a mobility spectrometer as a measure of mass flux. In contrast, increases in temperature for PETN caused exaggerated losses of mass, which were attributed to decomposition of the solid PETN. The decomposition was observed in both mobility spectra and mass spectra with an API mass spectrometer [66].

Another approach to a source of vapors to calibration of instruments, and similar to that described above, was that of Davies et al. [67] who used a computer-controlled pulsed vapor generator with TNT, RDX, and PETN. The explosive solid was coated on quartz beads, which were then packed into a stainless steel tube. The tube was coiled and placed into a temperature-controlled chamber. Ultrapure air was passed through the coil at temperature and vapors of explosives were vented from the coil at rates or concentrations governed by coil temperature, airflow rate, and pulse width. Calibrations could reach the picogram to nanogram range when an IMS analyzer was used as the calibrating instrument.

8. APPLICATIONS OF IMS FOR EXPLOSIVES DETERMINATIONS

A first approach to determining explosives on-site might include a combination of specialized sample-collection techniques and subsequent analysis using established IMS technologies or instruments. A second level of development could involve the fabrication of analyzers or analytical systems for an on-site operation and real-time analysis of samples. During the past several years, the first step of development has been demonstrated for explosives in water, in soils, and in a few unique uses.

Buxton and Harrington [68] used SPE to pre-concentrate explosives and remove matrices. Water samples were passed through commercially available SPE disks. After the extraction step, the SPE disk containing explosives was inserted into the heated anvil of a commercially available IMS analyzer (a Barringer Ionscan 350) where the explosives were thermally desorbed from the disk and swept into the analyzer. Concentrations of explosives in water were detected at levels as low as one part per trillion. A next step of sophistication and effort involved actual on-site studies of aquatic environments for explosives as described by Rodacy et al. [69] who developed an underwater sample-collection system. This was applied with artificial samples at San Clemente Island (CA, USA), with actual explosive targets in Panama City (FL, USA), and with munitions on the seabed in Bedford Basin (Halifax, Nova Scotia, Canada) (cf. Table 2). A manually operated IMS-based system was able to detect TNT in seawater at a concentration of 0.010 parts per trillion in less than 5 min. Even at a sampling distance of 1 m away from the shell, explosives were detected using a combination of solid phase microextraction for sample enrichment and an IMS analyzer for detection (GC was used for supporting analyses). The process of detecting explosive signatures in water included three basic steps. The first step involved sampling water or sediment near a suspected target (Figure 14) because the sampling location had been shown to be critical in obtaining accurate analytical results. The second step involved separating and concentrating the explosive molecules from the water and, finally, the third step involved transferring the explosive analyte to a detector for processing. In this arrangement of diver, sampler, and analyzer, a pump was used to pass a sample of water (sampling directed by a diver, Figure 14) through the concentrator. This could remove the explosive molecules from the water stream and concentrate them for subsequent desorption into the mobility spectrometer.

The determination of explosives in soils has been mostly commonly associated with the detection of unexploded ordnance such as land mines (both anti-personnel and anti-tank). Chambers et al. [70] designed sampling subsystems for soil/vapor sampling. A probe was used to extract and concentrate vapors of explosives in the pore volume of soil in the vicinity of land mines with sub-part-per-billion detection limits for TNT and related explosive munitions compounds [70]. As an

Table 2 Results from testing of waters near munitions in Halifax Harbor

Summary of method and detection				
Method	**0.3 m from shell**	**1 m from shell**	**2 m from shell**	**3 m from shell**
Underwater grab, GC analysis	Positive detection	Positive detection	ND	No sample collected
Surface grab, GC analysis	Positive detection	Positive detection	ND	No sample collected
Underwater SPME, MityVac	Positive detection	Positive detection	ND	No sample collected
Surface SPME, flow-through	Positive detection	Positive detection	ND	ND
Sediment samples, GC analysis	ND	ND	Positive detection	Positive detection

Source: [71]

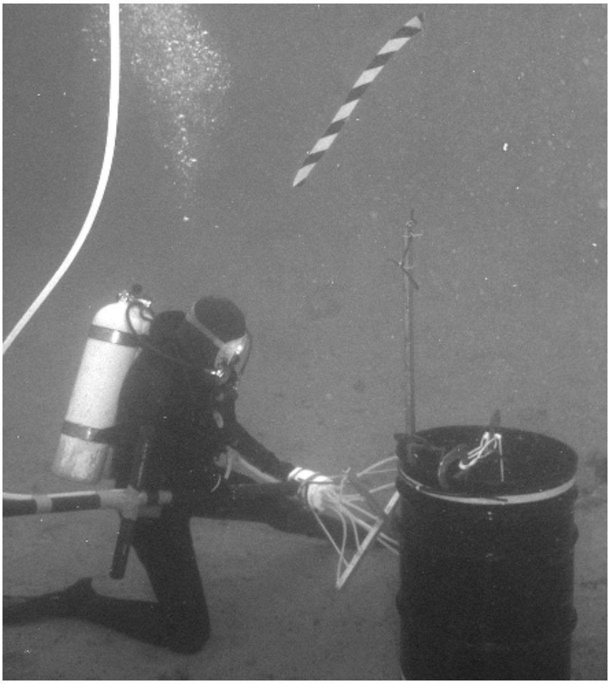

Figure 14 Photograph of diver collecting water samples during early studies on dissolved explosives in simulated ordnance in waters off San Clemente Island. Water is drawn by a pump over a solid phase microextraction fiber (not seen in photo) where explosives are retained and enriched. The SPME fiber was then presented to an IMS analyzer for the determination of explosives. Full application of these methods was made in Halifax Harbor. *Source*: [72]

example of a different approach to preparing samples, environmental samples were treated by solvent extraction to isolate explosives from soils; extracts were subsequently analyzed by IMS [73]. This method provided detection limits of 0.4 ppb for TNT and 7.4 ppb for RDX and was applied to a minefield composed of 51 sites. Freshly buried mines were not detected; however, explosive levels in the soil increased to a level of 2–8 ppb for TNT 10 months after a land mine was buried. A surprising observation was that handling land mines will contaminate hands and this contamination could be transferred by hands to the soil at levels of <0.1 ppb for TNT and at ~ 0.8 ppb for RDX.

An application well-suited for IMS is the decommissioning and cleanup of sites where extensive manufacturing of explosives has taken place in the last century and where widespread contamination of soils and waters has occurred [74]. Decontamination of model metal scrap artificially contaminated with TNT and of decommissioned mortar rounds still containing explosives residue was followed by sampling surfaces with analysis by a portable mobility spectrometer. Mixed anaerobic microbial populations of bioslurries were employed in decontamination of scrap and the mortar rounds, and the IMS analyzer was seen as a sensitive field screening method for assessing decontamination with a high level of certainty provided by minimally trained personnel.

With a focus on trace forensic detection of explosives, especially for use in counterterrorism and to counter narcotics investigations, Fetterolf et al. [75] evaluated the use of ion mobility-mass spectrometry for explosives determinations. In this, explosives residues were collected on a membrane filter by a special attachment on a household vacuum cleaner. Although subsequent thermal desorption and analysis required only 5 s, limits of detection for most common explosives were as low as 200 pg. The persistence of explosives on hands and transfer to other surfaces were also examined as were post-blast residues of NG on fragments of improvised explosive devices constructed with double-based smokeless powder. Finally, post-blast residue from C-4, Semtex, and other explosives was found by IMS analyses on items of forensic and evidentiary value. These few out of many examples demonstrate that mobility spectrometers are well suited tools for laboratory and on-site investigations, before and after the use of explosives.

9. FUTURE

The advantages of point analyzers include a high level of analytical performance and a record of service that is unparalleled in some facets. Still, the record or evidence is that drift tube refinements or developments of fast analytical devices based on IMS or DMS will be continued into the foreseeable future. The need for improvements in minimization of false positives, false negatives, and matrix interferences is a significant concern and innovations in inlet methods or improved analytical separation can be anticipated. Several questions about IMS loom on the horizon of application-technology as seen by the authors and these include:

1. How is the sample brought to the analyzer and can this be improved? This question includes a range of topics from an understanding of the persistence of explosives on surfaces to the collection of samples [76].
2. Can analyzers be developed with lower human involvement than the current generation of instruments? That is, can a new generation of nearly autonomous analyzers be developed? and finally,
3. Do explosives provide vapors other than parent substances that could be useful in chemical determinations? [77, 78]

The record from the past decade suggests that trace analyzers can provide a benefit for commercial aviation security and that the challenges faced today center on the interface between a sample and an analyzer. Contributions of IMS in filling current needs in the determination of explosives, in various venues and with the range of security challenges faced by civilian and military populations, may hang on the next generation of instruments. In these instruments, each of the questions posed above will need development or advancement.

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CHAPTER 10

DETECTION OF EXPLOSIVES USING AMPLIFIED FLUORESCENT POLYMERS

S.W. Thomas III *and* T.M. Swager

Contents

1. INTRODUCTION TO CONJUGATED POLYMERS

A conjugated polymer can be defined as a macromolecule made up of repeating units in which the entire main chain of the polymer is bound together not only by saturated sigma bonds, but also by unsaturated π bonds. In contrast to the more traditional vinyl or condensation polymers, such as polystyrene or polyesters, each repeat unit in the polymer chain is electronically coupled to those units adjacent to it, effectively creating a "molecular wire." This large degree of conjugation in the main chain leads to coalescing of individual molecular orbitals, resulting in the creation of a semiconductor with a valence band (filled with electrons) and conduction band (devoid of electrons). As a result of these extended electronic states, these organic semiconductors often have interesting and useful optical, optoelectronic, and electrochemical properties.

Numerous discoveries in synthetic organic and organometallic chemistry have spawned the development of a whole host of semiconducting fluorescent polymer structural classes, some of which are illustrated in Figure 1. In addition to differences between structural classes of polymers, the properties of these systems can also

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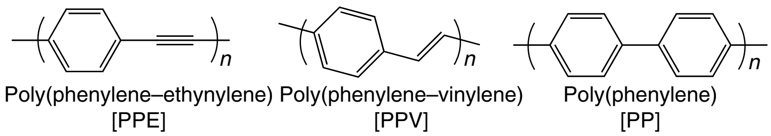


Figure 1 Several structural classes of semiconducting fluorescent polymers.

be more finely tuned by introducing different side groups on the conjugated polymers. Groups can be introduced to enhance solubility in particular solvents, interact with the main chain to perturb the energetics of the valence and conduction bands, or for other reasons depending on the desired application.

Conjugated polymers, however, offer more than just tunability through structural modification as a benefit relative to inorganic semiconductors. Organic materials can also be solution processable and flexible. These unique advantages, combined with their semiconducting properties, have led to widespread research in the field of conjugated polymers, particularly relating to their potential utility in various devices. These devices include organic field effect transistors, organic light-emitting diodes, and chemical sensors based on conductivity or optical events. Various devices containing these materials have been commercially available to consumers for several years.

2. AMPLIFIED FLUORESCENT CONJUGATED POLYMERS AS SENSORS

Conjugated polymers designed and used for explosive detection rely on fluorescence signals and events to indicate presence of an analyte of interest [1, 2]. Fluorescence spectroscopy is inherently a very sensitive technique, and very small changes in fluorescence intensity can be reliably detected. To induce fluorescence, the material is typically irradiated with a frequency of ultraviolet or visible light that it can absorb. This promotes an electron from the valence band into the conduction band, forming a bound electron–hole pair known as an exciton. Some of these excitons relax to the ground state in a radiative fashion by emitting light as fluorescence, whereas the rest of them release their energy non-radiatively as heat in the form of molecular motion. In between these two events, absorption and emission, is a very short (typically about 1 ns) but important time during which the “molecular wire” nature of conjugated polymers plays a critical role.

Consider the two hypothetical situations illustrated in Figure 2. On the top is pictured a collection of individual fluorescent receptors, while on the bottom is pictured the same number of receptors, yet they are connected via a “molecular wire” conjugated polymer. In addition, suppose it is known that binding of the analyte paraquat (PQ) into a receptor causes a complete quenching of its fluorescence. In the case of individual receptors, the binding of one analyte gives only a small diminution in the total intensity of emission observed. This is because each exciton is fixed on one molecule and cannot communicate with other receptor sites.

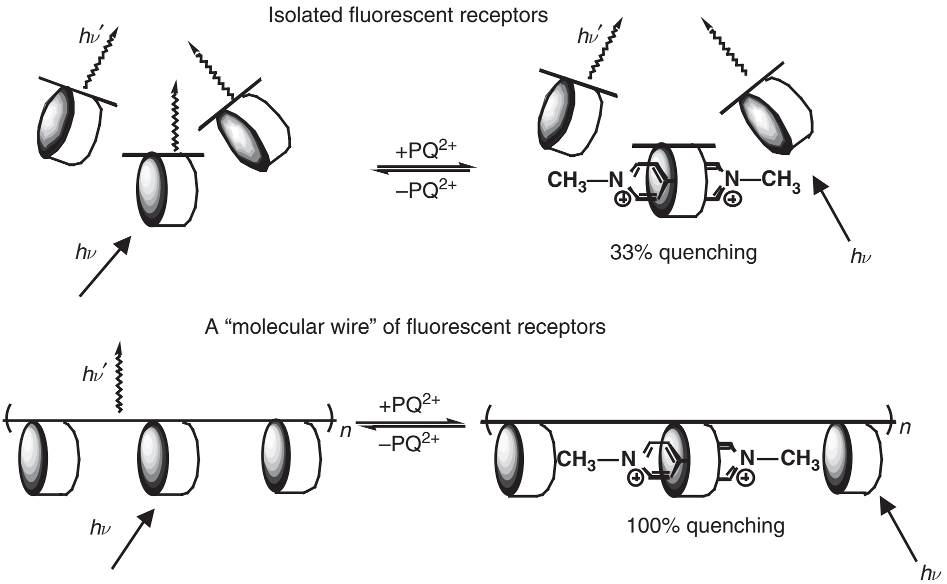


Figure 2 Contrasting monomeric fluorescent receptors and those "wired in series." (Reprinted with permission from Ref. [3]. Copyright 1995 American Chemical Society.)

If the receptors are connected via a molecular wire, the exciton has the ability to travel throughout the conjugated polymer backbone, sampling every receptor site that it passes. If during its excited state lifetime it encounters a bound analyte, its emission will be quenched. This mechanism of exciton transport can result in a large degree of amplification, because with one binding event an entire polymer chain that contains many receptor sites is quenched. This scenario can be correlated with light bulbs wired in series, in which the extinguishing of one bulb turns off the entire network of lights. This approach of amplified fluorescent chemosensing was first demonstrated using a poly(phenylene–ethynylene) containing cyclophane-based receptors and PQ as an analyte as depicted in Figure 2 [3]. Large amplifications of fluorescence quenching (FQ) were observed in the conjugated polymer relative to individual fluorescent receptors.

To summarize, absorption of a photon by a conjugated polymer creates an exciton that can then sample many potential binding sites within its lifetime. Emission from the excited state is observed only if there is no bound analyte encountered by the migrating exciton. If the analyte is encountered there is quenching of the emission, and it is this amplified dimunition in emission intensity that serves as an indication (signal transduction) that the analyte is present.

The signal transduction is obviously a very important aspect of the chemosensing scheme. Even if one exciton could sample an almost infinite number of binding sites, that would be of no benefit if the analyte was not able to alter its fluorescence. In other words, in order for there to be amplification, a signal must be present that can be amplified. There are several mechanisms by which signal transduction is designed into conjugated polymer sensors. Popular especially in biochemical systems is fluorescence resonance energy transfer (FRET) [4, 5]. In this mechanism, excitation energy is transferred from the photoexcited conjugated polymer to a bound dye-labeled analyte resulting in a polymer ground state and a lower energy dye excited state. The dye then emits at a red-shifted wavelength relative to the polymer, the observation of which indicates presence of the analyte of interest. There are several conditions that must be met for FRET to be efficient, but will not be discussed here because this is not an efficient transduction scheme for explosive detection.

3. ELECTRON TRANSFER FLUORESCENCE QUENCHING

Electron-transfer-induced FQ is the most practical and efficient mechanism of signal transduction for the detection of explosives. This is because explosives, especially 2,4,6-trinitrotoluene (TNT), are often highly electron-deficient molecules that readily accept electrons from excited fluorophores. In addition, explosive devices that contain TNT also usually contain a synthetic by-product, 2,4-dinitrotoluene (DNT), which is also highly electron deficient. A basic frontier molecular orbital-based mechanism for electron transfer FQ is illustrated in Figure 3.

In this simplified diagram, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of both the electron donor and acceptor are illustrated. In this case, when both molecules are in their ground state, there is no energetic driving force for any electron transfer reaction to occur. If, however, the donor (D) is irradiated with a photon and brought to its excited state, one of the electrons is now in the LUMO of D, and is of much higher energy. Because of the LUMO of the acceptor (A) is lower in energy than the LUMO of D, there is a significant energetic driving force to lower the energy of the system via an electron transfer from D to A, resulting in oxidation of D and concomitant reduction of A, giving an ion–radical pair. Because the singlet excited state of D has been destroyed in this reaction, it can no longer emit, and typically the fastest process is simple reverse-electron transfer from the LUMO of A to the singly occupied HOMO of D, which is non-radiative in nature.

In addition, it is worth noting that the quenching process can also work with a fluorescent electron acceptor. Irradiation of the acceptor results in the creation of its excited state, and in this scenario it is energetically favorable for an electron from

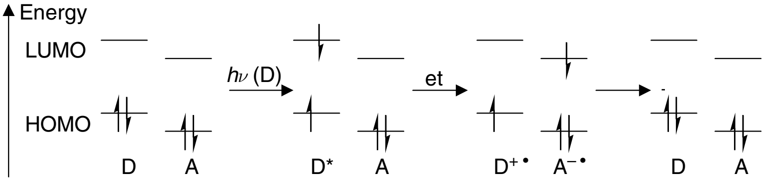


Figure 3 A molecular orbital diagram for photoinduced charge transfer.

the HOMO of D to transfer to the HOMO of A, resulting in the same ion–radical pair that very quickly relaxes via back electron transfer. This, however, is not observed in explosive detection for several reasons, including the fact that most fluorescent conjugated polymers are relatively electron rich and most explosives are electron deficient. It is almost always the scenario in Figure 3 that is relevant.

Overall, contact between a good electron acceptor and a fluorescent electron donor D gives quenched fluorescence. If the LUMO energy of A had not been below the LUMO of D, the electron transfer would be an energetically unfavorable process and quenching would not be observed. This rather qualitative relationship can be more quantitatively summarized simply by analysis of the participating energy levels [6, 7]. Because the electron transfer involves oxidation of the donor and reduction of the acceptor, the corresponding redox potentials determine the ground state driving force of electron transfer, as follows:

$$\Delta G(\mathrm{et}) = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - \Delta \tag{1}$$

In this equation, $\Delta G(\mathrm{et})$ is the driving force of the ground state electron transfer reaction, whereas $E_{\mathrm{ox}}(\mathrm{D})$ and $E_{\mathrm{red}}(\mathrm{A})$ refer to the oxidation potential of the donor and the reduction potential of the acceptor, respectively. Δ stands for any stabilization of the highly charged ion–radical pair by solvent reorganization. This can vary from solvent to solvent and correlates with the dielectric constant of the solvent. Most organic molecules have positive oxidation potentials and negative reduction potentials (versus saturated calomel electrode (SCE)). Therefore, only very powerful electron donors and/or acceptors can participate in ground state charge-transfer complexes, even in highly polar solvents.

However, when quantitatively describing Figure 3, the emission energy of the donor, $E_{\mathrm{ex}}(0,0)$, makes a contribution to Eq. (1) to yield

$$\Delta G(\mathrm{et})^* = E_{\mathrm{ox}}(\mathrm{D}) - E_{\mathrm{red}}(\mathrm{A}) - E_{\mathrm{ex}}(0,0) - \Delta \tag{2}$$

in which $E_{\mathrm{ex}}(0,0)$ indicates the energy associated with the transition of an electron from the $v = 0$ vibrational level in the excited electronic state to the $v = 0$ vibrational level in the ground electronic state of the donor. For a typical poly(phenylene–ethynylene) (PPE) that emits at about 460 nm, this an additional contribution to the electron transfer driving force of nearly 2.7 eV, or approximately the same as the bond energy from the π bond in an alkene. Therefore, many electron transfer reactions that are highly unfavorable in the ground state are made facile by irradiation of the donor (or acceptor). This lends the process its name of FQ by photoinduced electron transfer.

This relationship also conveys one of the reasons why the sensing of explosives can be so effective with this method. Most explosives, especially TNT and other nitroaromatic compounds, are highly electron deficient and have favorable reduction potentials. For instance, the reduction potential of TNT and DNT are only –0.7 and –1.0 V (versus SCE) respectively, quite favorable when compared with other electron acceptors, such as 1,4-dicyanobenzene (−1.7 V versus SCE). This means that if the sensory material emits light, for example, at 460 nm, the oxidation potential of the sensing polymer can approach close to 2.0 V versus SCE and still give a negative change in free energy for photoinduced electron transfer, theoretically allowing for amplified FQ and detection of TNT.

4. POLYMER DESIGN PRINCIPLES FOR SOLID-STATE SENSORS

4.1. Thin-film conjugated polymer sensors and aggregation

Designing a conjugated polymer sensor based on FQ, however, is not only a matter of making a fluorescent polymer for which the photoinduced electron transfer reaction is energetically favorable. There are other important factors that must be considered and requirements that must be met to reliably detect any analyte of interest, including TNT, from the vapor phase. In the broadest sense, these considerations distill to the two primary considerations for any sensing system, sensitivity and selectivity.

By nature, detection of TNT vapor can only be reliably achieved through a highly sensitive process. This comes from a combination of TNT's naturally low vapor pressure (parts per billion range) and the fact that explosive threats are designed to be difficult to detect. As discussed earlier, fluorescent conjugated polymers in solution can offer significant amplification relative to small molecule fluorescent receptors. Under these solution-state conditions, however, this property is primarily limited by the molecular weight of the polymer, because in dilute solution the amount of inter-chain electronic communication is very small. This gives only a one-dimensional amplification, which means that each exciton is confined to the polymer chain on which it was created by absorption, and can therefore can only sample as many binding sites as the individual polymer chain presents.

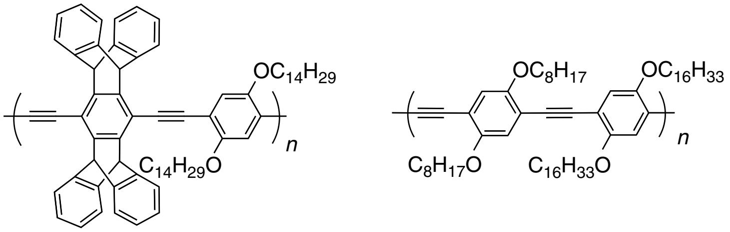
Another disadvantage for explosive detection using a solution-state sensor is that unless there is very strong binding of the analyte to the fluorescent polymer, the efficiency of quenching is limited by the rate of diffusion of the analyte and polymer in solution. Achieving strong solution-state static binding is especially difficult because of competitive solvation of the analyte molecule. Finally, solution-state sensors also do not make easily operated devices for security personnel and other non-technical operators. A solution-state sensor would require frequent handling of toxic solvents and careful solution preparation.

On the contrary, the ability to produce a thin-film conjugated polymer sensor brings with it many important advantages. It simplifies the operation of a sensory device for non-technical users, as well as eliminating competitive solvation of analyte molecules and the accompanying limitation of diffusion, allowing for potentially tight polymer–analyte binding. Most importantly, it extends the dimensionality of the amplification from one dimension to three dimensions. Instead of highly isolated individual polymer chains, being in the solid state brings polymer chains into very close proximity with each other, allowing for excitons to not only travel along one polymer chain, but to also "jump" to other nearby polymer chains. Instead of performing a one-dimensional random walk, excitons can execute a more three-dimensional random walk, allowing for the sampling of more binding sites within one excited state lifetime [8, 9]. This multidimensional nature of exciton transport can therefore give large additional amplification to chemosensing via photoinduced electron transfer.

There are, however, serious complications that arise upon making thin films of conjugated polymers. The conjugated nature of these rigid rod-type polymers often forces them into a highly planarized geometry. This does not have detrimental consequences in solution. In the solid state, however, this largely planar geometry often induces aggregation of the polymeric chains, where the planar chains tend to stack on each other with π orbitals from adjacent chains interacting [10–12]. Aggregation typically lowers the energy of the system, and this phenomenon is often observable in UV/vis spectroscopy as the appearance of a red-shifted absorbance signal.

Efficient intra- and inter-chain exciton migration in thin film, combined with the low-energy traps that areas of aggregation present, results in a large amount of the initial excitation energy transferred to aggregates. Conjugated polymer aggregates formed from π-stacking are typically very weakly emissive. A much weaker fluorescence signal would mean that more TNT must be bound to the sensing material to give a reliable FQ response, which indicates to the device user that TNT is present. Therefore, this drastic reduction in fluorescence intensity observed in most solid-state aggregates of conjugated polymers results in a dramatically less sensitive material. In addition, the optical properties of strongly aggregating polymer films are often difficult to reproduce from sample to sample. As a result of these considerations, an important design principle for highly sensitive fluorescent conjugated polymer sensors is to be able to process thin films while avoiding the creation of non-fluorescent aggregates in the solid state.

There have been extensive efforts in field of conjugated polymer research to control and prevent aggregation in thin films. These have primarily centered on attaching large, sterically demanding groups to the polymer backbone to dissuade the polymer chains from coming so close in the thin film as to form aggregates. One particularly effective group for accomplishing this goal is the pentiptycene group, shown as part of the TNT sensory material **1** in Figure 4 [13–15]. The pentiptycene moiety is a relatively large and very rigid three-dimensional side group that sweeps out a well-defined volume of space adjacent to the polymer backbone. Repulsive interactions between these sterically demanding units prevent π–π stacking in solid thin films of polymer **1**, yet still allow close enough proximity as to allow efficient



1 **2**

Figure 4 Chemical structures of polymers 1 and 2.

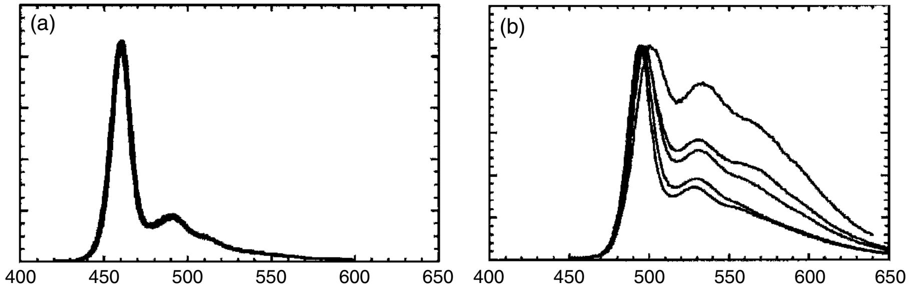


Figure 5 Fluorescence spectra of polymers 1 (A) and 2 (B) in five different spun-cast films. (Reprinted with permission from Ref. [14]. Copyright 1998 American Chemical Society.)

three-dimensional exciton transport. Consequently, spun-cast thin films of polymer **1** give strong, highly reproducible solution-like emission spectra, but display highly amplified sensitivity toward electron-deficient analytes. In contrast, thin films of a more traditional polymer, **2**, contain unacceptable amounts of aggregates, in that they are strongly self-quenched and give unsatisfactory reproducibility of solid-state optical properties, as displayed in Figure 5.

4.2. Other important design parameters for sensitivity and selectivity – polymer 1 as a model

Polymer **1** displays highly sensitive and selective sensing behavior for TNT in particular. Figure 6 displays the response of the polymer's solid-state fluorescence to short duration exposures to TNT equilibrium vapor. After only a matter of seconds, significant FQ is observed. This sensitivity is primarily derived from the exciton transport previously described, but as previously mentioned, more is required of a conjugated polymer sensor than simple amplification. Given a certain degree of amplification, there are several other factors that factor into the efficiency of vapor phase detection by FQ. These are the vapor pressure (VP) of the analyte, the binding constant of the analyte to the polymer film (K_b), and the rate of

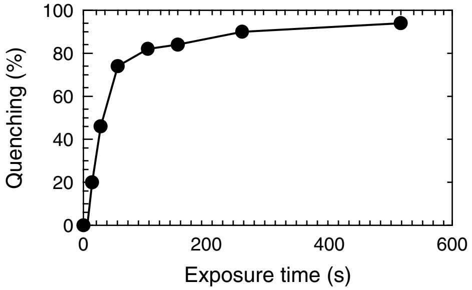


Figure 6 Fluorescence response of a polymer film of 1 to equilibrium TNT vapor. (Reprinted with permission from Ref. [14]. Copyright 1998 American Chemical Society.)

photoinduced electron transfer, which depends strongly on the previously described driving force (Eq. (2)). These three parameters can be more simply represented by the following relationship

$$\mathrm{FQ} \propto (K_\mathrm{b})(-\Delta G_\mathrm{et})(\mathrm{VP}) \tag{3}$$

As previously illustrated, the photoinduced electron transfer reaction must be energetically favorable to induce FQ of the conjugated polymer film by TNT or DNT. An analysis of the energetic profile of the electron transfer reaction between polymer **1** ($E_\mathrm{ox} = 1.22\,\mathrm{eV}$, $E_\mathrm{ex}(0,0) = 2.74\,\mathrm{eV}$) and TNT ($E_\mathrm{red} = -0.7\,\mathrm{eV}$) using Eq. (2) shows that the reaction has a driving force ($-\Delta G$) of 0.82 eV (~19 kcal/mol), large enough to make FQ of polymer **1** by TNT a very facile process [14]. A similar analysis with DNT gives a driving force of 0.52 eV. Note that in the solid state, the reorganization energy Δ is negligible because of restricted polymer mobility and lack of any potential solvent reorganization.

As a compliment to this strong driving force and efficient rate for reduction of nitroaromatics by excited **1** is the way that this scheme also builds selectivity into the sensory material. Only molecules that have a very favorable reduction potential will efficiently quench the polymer's fluorescence. According to Eq. (2), only if the reduction potential of the analyte is greater than $-1.52\,\mathrm{eV}$ will there be a negative free energy change for quenching, resulting in no quenching response, regardless of analyte vapor pressure or binding constant. This leaves only a very small family of organic molecules, basically limited to nitroaromatics and quinones. Even benzophenone, 1,4-dicyanobenzene, and 1,4-dichlorobenzene, all relatively electron-deficient molecules on an absolute scale, do not quench the emission of polymer **1** as a result of the electron transfer being energetically unfavorable [14]. Molecular oxygen is capable of quenching the polymer; however, oxygen does not bind effectively to the polymer and its quenching is diffusion limited. Therefore, the quenching by oxygen is greatly limited by the short lifetimes of the excitons in conjugated polymers.

The other important parameters, analyte vapor pressure and binding constant, also provide other means of selectivity. All other things being equal, those analytes with a higher vapor pressure than TNT should be easier to detect, as larger amounts of the analyte can be sampled and collected onto and into the polymer film. A small vapor pressure is typically seen as a sensitivity limit. However, with the large amplification this technique gives, differences in vapor pressure can lead to different temporal responses that provide an additional mechanism to obtain selectivity.

In fields such as biosensing, "analyte binding" often relies on very specific molecular recognition interactions that nature has supplied, such as antibody–antigen interactions or strands of complimentary DNA forming double helices. Unfortunately, because versatile and highly selective receptors for TNT or other explosive molecules are not available, chemists are left to rely on less specific interactions.

For this purpose, TNT and DNT are quite uniquely suited, in that they are aromatic with multiple fully conjugated, strongly electron withdrawing nitro groups. This gives TNT and DNT strong π-acid properties, meaning that the electron affinity of its π system is very large. Because of this, these molecules can form very strong ground state complexes based on electrostatic attraction with even moderately electron-rich aromatic systems. Pentiptycene PPE **1** consequently binds well with TNT. The two alkoxy groups on each repeat unit have significant electron donating properties, and serve to make the polymer backbone more electron rich, therefore creating a larger attractive force for TNT. Molecules without this strong π-acid quality do not bind in as nearly as strong a fashion.

In addition to selectivity based on electrostatic attraction, polymer **1** also displays size-exclusion properties. Because even very thin films of these polymers are made up of multiple layers of polymer, diffusion of the analyte into the bulk of the polymer film is an important part of achieving efficient FQ. If the analyte is not able to diffuse into the film at all, only quenching of the surface of the film is possible, thereby limiting the amount of emission quenching observable. As previously mentioned, incorporation of the pentiptycene moiety into **1** prevents the polymer chains from closely approaching each other. The large amount of internal free volume defined by the pentiptycenes creates cavities throughout the polymer film (Figure 7). These cavities then allow for small organic molecules, including TNT, to intercalate deeper into the polymer film than would otherwise be possible. In contrast, larger molecules are excluded from interacting with the bulk of the film. The importance of this concept is highlighted by the fact that polymer **2**, which is more electron-rich but lacks iptycene groups to facilitate cavity formation, shows a much smaller quenching response to TNT or DNT vapor than **1** [14].

Therefore, there are many considerations that must be taken into account in the design and synthesis of conjugated polymer sensors for explosive detection. Not only must the electron transfer process be efficient, but solid-state aggregation must also be avoided to retain maximum sensitivity. Strong binding of analyte to the polymer is necessary, which the π-acidic nature of TNT and DNT facilitate via

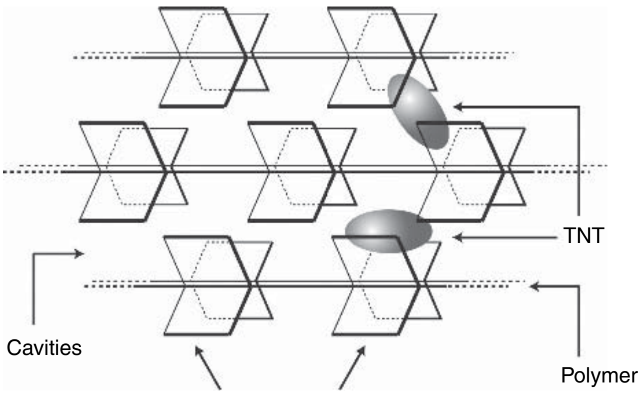


Figure 7 Conceptual depiction of film porosity induced by pentiptycene groups in polymer 1.

electrostatic attraction. It must also be possible for the analyte to readily diffuse into the polymer film to maximize the amount of FQ possible. Polymer **1** embodies an excellent balance of all these properties for nitroaromatic analytes, and as a result is a highly specific and sensitive chemosensor for TNT and DNT.

5. ULTRA-TRACE TNT DETECTION WITH OPERABLE DEVICES

As is the case with any explosive detection technology, the true test of this method's merit is how it performs as part of an operable device in the field. Amplified fluorescent polymer technology can afford excellent results, as previously described, for the detection of TNT in a laboratory setting. Fabricating any laboratory-based technology into an operable device, however, is always an important challenge. In addition to this are the many potential complications that can arise when exposing a technology to field-test conditions.

The unique simplicity of TNT detection by this method renders the fabrication of an operable device built around amplified fluorescent polymer technology a relatively simple proposition in comparison to other technological platforms. The method relies purely on changes in fluorescence intensity. All that is theoretically required is a means of introducing vapor samples to a conjugated polymer film, a light source to excite the polymer film, and a photodetector to measure the emission intensity as a function of time.

Several different types of operable devices based on this simple design schematic have been successfully fabricated by ICx Technologies. under the name Fido. The simplicity of the method allows for the use of a small amount of associated optics and electronics. As a result, complete, portable handheld devices weighing less than 2 lb (Figure 8) have been developed and successfully tested for personnel, vehicle,

Figure 8 ICx Technologies' Fido handheld explosive detector based on AFP technology. Illustration Courtesy of ICx Technologies.

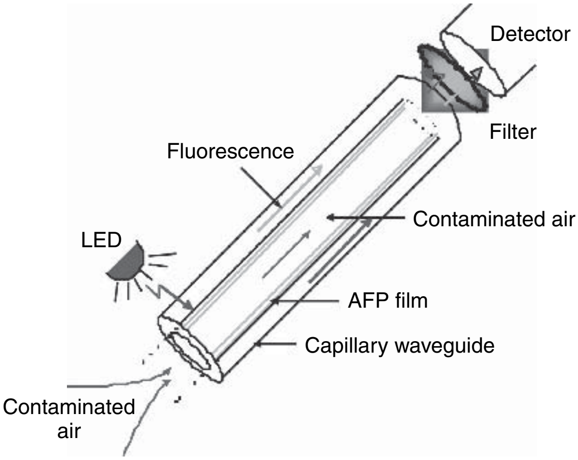


Figure 9 Architecture of Fido sensor based on AFP technology. Illustration courtesy of ICx Technologies.

and container screening. The sensor architecture is illustrated in Figure 9. The fluorescence intensity is monitored as a function of time so that the instrument can be continuously sampling the environment, or concentrated samples can be introduced to the air intake for analysis.

The ability of this technology to support small, lightweight, and portable devices has in part led it to be especially successful in the detection of land mines [16], the principal explosive component of which is TNT. Land mines very often contain DNT as a synthetic by-product as well. Screening of this type requires ultra-trace sensitivity, because the low vapor pressure explosives are buried underground. Equally important is very high selectivity and durability, given the complex environments in which it must operate. These include, but are not limited to, changes in temperature and humidity, environmental pollutants, and other potential chemical interferents (Figure 10).

In addition, the conjugated polymer used must be photochemically stable for long periods of time and under potentially extreme conditions. Whereas most conjugated polymers readily photobleach over even short durations under ambient conditions, well-engineered polymers such as **1** give consistent fluorescence intensities even after long periods of irradiation. This is attributed to the pentiptycene moieties preventing intermolecular photochemical reactions and self-quenching. As a result, these devices are stable and operable even under extreme environmental conditions.

The selectivity inherent to TNT detection by amplified fluorescent polymers, as described in Section 4, helps to minimize false-positives in land mine detection. These sensor devices respond only to nitroaromatics and similarly small, electron-deficient analytes, which are found typically only in or close to explosives and explosive devices. Field-tests to date have demonstrated that these devices are at least as reliable as trained dogs in detecting explosives that contain nitroaromatics. There is still uncertainty concerning what chemical that dogs actually detect when searching for explosives [17]. This

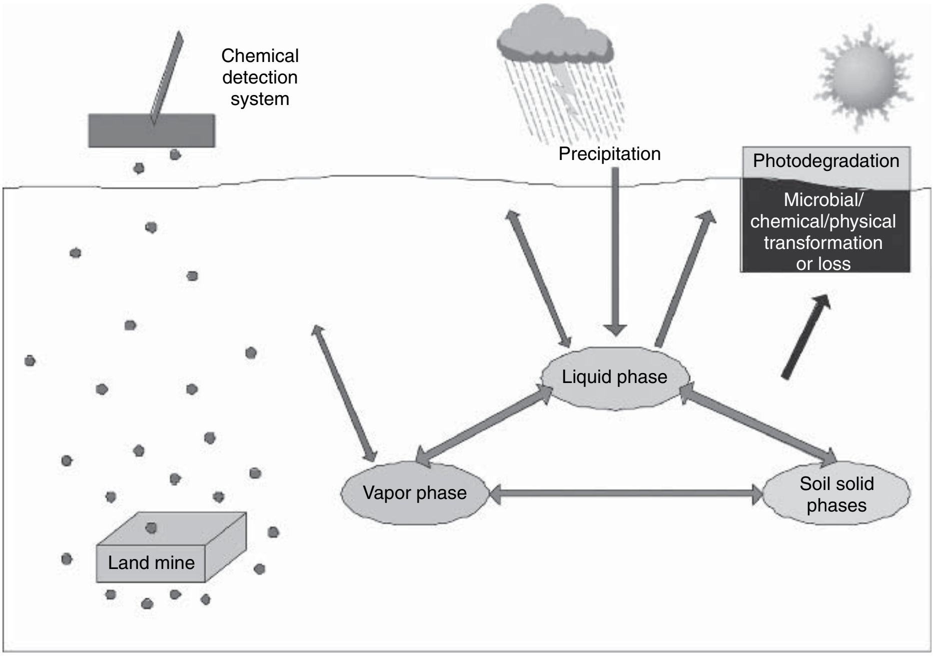


Figure 10 Factors affecting land mine detection using chemical-based methods. Illustration courtesy of ICxTechnologies.

is particularly important for plastic explosives, because the active explosives RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), and PETN (Pentaerythritol tetranitrate) all have vapor pressures in the sub-ppb range. In many cases, dogs may detect TNT and other nitroaromatic molecules, or synthetic by-products or contaminants such as cyclohexanone. In contrast, the mechanism for sensing TNT with conjugated polymer sensors is well understood. This brings the advantage that the actual explosive molecules induce a positive "hit" indicating the presence of an explosive. In addition, the use of sensors avoids the expensive and time-consuming process of training dogs, as well as feeding and caring for live animals.

The simplicity of detecting TNT with conjugated polymer sensors allows for the fabrication of relatively simple, portable, and easily operable devices. The inherent sensitivity of the technique results in the ability of these devices to detect ultra-trace levels of vapor-phase TNT, whereas the selectivity and stability allow them to operate reliably in the complex environmental conditions found in battle-field settings. The resulting versatility has led to their successful application to explosive detection in a variety of situations, including the searching of people, vehicles, large areas of land, and even underwater environments for explosives (Figure 11) [18]. Field-tests have shown these instruments to have sensitivity comparable to trained dogs. Most importantly, Fido devices have recently been taken beyond field-tests and are currently being evaluated by soldiers for the detection of hidden explosives in truly dangerous situations.

Figure 11 ICx Technologies' SeaDog underwater explosives detection sensor mounted on an autonomous underwater vehicle. Figure courtesy of ICx Technologies.

6. FUTURE RESEARCH DIRECTIONS:SELECTED EXAMPLES

The last 10 years has seen both an enormous growth in research interest in conjugated polymer sensors, as well as equally impressive advances in the chemistry, physics, and engineering required to transform this technology into reliable, working devices. Because of the vital importance of reliable, fast, and versatile explosive detection, the pace of research continues to intensify. Researchers are currently exploring developments in both the chemistry and physics of new amplified fluorescent polymeric materials, as well as in the design and fabrication of more efficient devices capable of enhancing sensitivity and selectivity. Some of these are highlighted in the following sections.

6.1. Future device improvements:chromatographic effects

As is the case with any recently established technology, improvements in device architecture are consistently being sought to make advances in size and weight reduction, adaptability, and ease of use for non-technical personnel. In addition to these types of general improvements, advances in critical aspects more specific to explosive detection are fervently being investigated. These issues are the same as they are for any sensor technology, sensitivity, and selectivity.

As discussed in Section 4.2, conjugated polymer sensors utilizing polymers like **1** are highly selective for only very electron-deficient small molecules, especially nitroaromatics and quinones. Because most molecules in either of these two classes induce efficient FQ, however, more precisely identifying what analyte the sensor has "hit" on is impossible based purely on emission intensity. This is because the molecules in these classes have sufficiently favorable reduction potentials to render the photoinduced electron transfer reaction strongly exergonic (see Eq. (3)). There is, however, an additional important and distinguishing parameter for determining quenching efficiency, the analyte vapor pressure. In the field of chemical sensing, it is typically viewed as a disadvantage if an analyte of great interest has a low vapor pressure. With the high sensitivity that amplified fluorescent polymer sensors offer, however, the low vapor pressure of TNT does not preclude its detection even at sub-ppb levels. Not surprisingly, analytes with lower vapor pressures tend to be more "sticky" in that they desorb from surfaces slowly, whereas analytes with higher vapor pressures spend more time in the vapor phase and more easily desorb. Differences in affinity for surfaces can be used to discriminate one analyte from another.

Because the binding of TNT and DNT is dependent on the structure of the polymer film, using two different polymers in series can assist in further discriminating the two similar analytes. This device architecture is shown in Figure 12. Figure 13 illustrates this effect in comparing the temporal response of TNT vapor

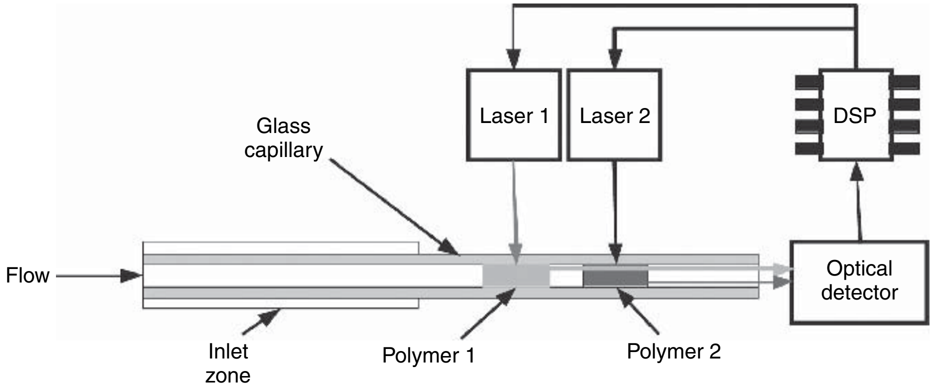


Figure 12 Schematic of dual-channel Fido for the reduction of false positives. Illustration courtesy of ICx Technologies.

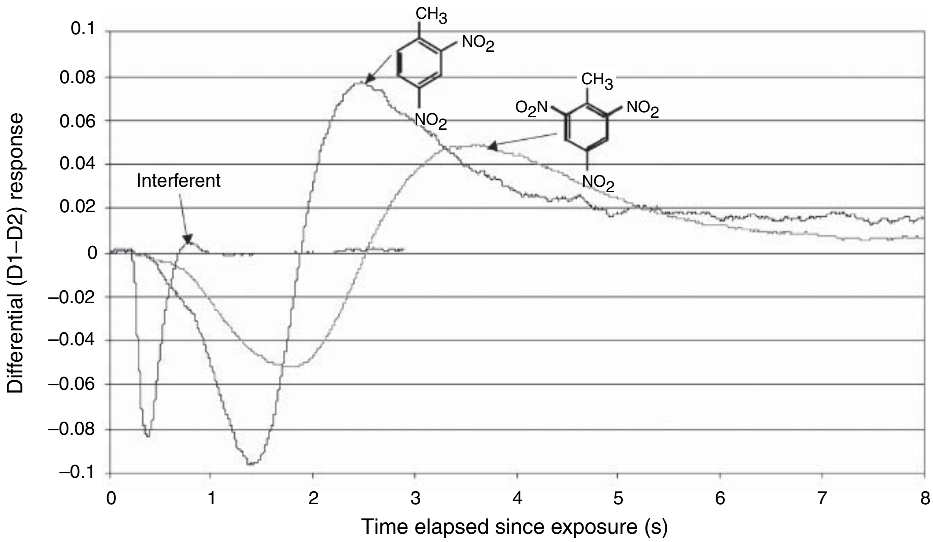


Figure 13 Differential Responses of TNT and DNT, and a volatile interferent, in a dual-channel Fido sensor based on AFP technology. Figure courtesy of ICx Technologies.

relative to DNT vapor in a Fido unit. The vapor is passed over a serial arrangement of two polymer films. The significantly lower vapor pressure and stronger binding of TNT causes it to progress along the length of the films more slowly than DNT. The differential response as a function of time between channels 1 and 2 is representative of a given quencher. The different peak-to-peak times between TNT and DNT, as well as different band shapes in the differential response provide indications of the quencher's nature. This effect therefore allows for the discrimination between two very similar nitroaromatic molecules and introduces a novel mechanism for additional selectivity [19].

This concept is in essence a chromatographic effect similar to that observed in gas chromatography (GC), with the conjugated polymer film acting as the stationary phase. It is possible that like in GC and other candidate technologies for explosive detection, these responses could be empirically standardized for expected analytes of interest and sensory devices calibrated to deconvolute temporal quenching signals to determine which analytes are present. This would further enhance the selectivity of what is already a very selective sensor for TNT and related compounds.

6.2. Future material and transduction improvements – lasing sensors

As is the case with device design and fabrication, there are seemingly endless incremental enhancements that could be developed and incorporated into conjugated polymer design for explosive detection. These include the design of systems that are sensitive to a wider variety of dangerous analytes, the inclusion of specific binding sites for molecular recognition and enhanced selectivity, and various schemes for increasing the diffusion length of excitons for improved amplification. One recent laboratory development that holds great promise for sensitivity improvements of several orders of magnitude is the development of lasing conjugated polymers for TNT sensing.

In principle, any organic conjugated polymer that has a high quantum yield for emission can lase [20]. In practice, however, the punishing optical pumping conditions required to induce the population inversion necessary to observe lasing results in rapid photobleaching and degradation of typical conjugated polymers under ambient atmospheric conditions. Therefore, to take advantage of any benefit that stimulated emission from solid-state organic materials can offer, exceptionally stable polymers are necessary. The polymer illustrated as **3** is one such system [21]. This polymer is of the poly (phenylene–vinylene) (PPV) structural class, with the PPV backbone surrounded by aryl rings on each repeat unit and long, branched alkoxy chains. These side groups serve a similar function as the pentiptycenes on **1** by preventing aggregation and interactions between the conjugated polymer chains, preserving a high quantum yield of emission in the solid state (~80%). They also protect the chains from destructive photochemical reactions, giving this system the necessary stability to survive the high optical pumping intensities needed to induce lasing.

Films of this material can be optically pumped to induce amplified spontaneous emission at 535 nm, as shown in Figure 14. The lasing threshold (E_{TH}) is the pump energy at which amplified spontaneous emission is observable, and depends strongly, among other factors, upon the lifetime of the polymer excited state. A longer excited state lifetime allows more emissive excitons to build up in

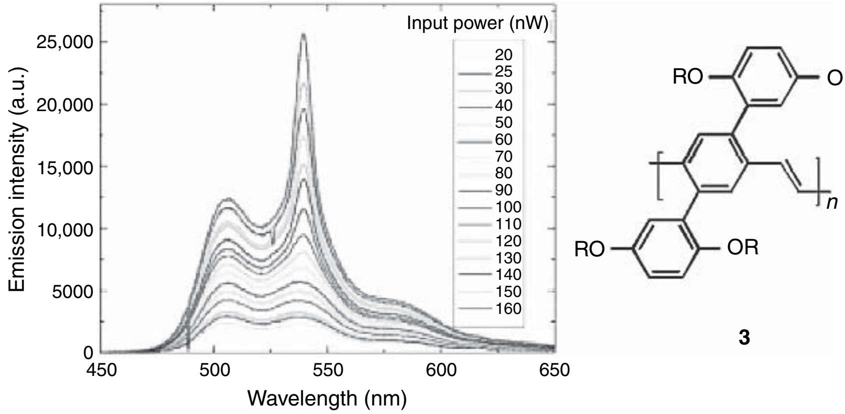


Figure 14 Input power-dependent emission spectrum of a thin film of polymer 3 and its chemical structure (R = 2-ethylhexyl). In this example, the lasing onset, which is apparent from the emergence of a stronger narrower peak at 535 nm, is at 75 nW.

the system, a large amount of which is needed to induce amplified stimulated emission. All else being equal, shorter lifetimes give higher lasing thresholds, whereas longer lifetimes have the opposite effect.

The potential for additional sensitivity is clear upon analysis of the effect of FQ on excited state lifetime (τ), which is merely a representation of all the excited state deactivation processes, as shown in the following equation:

$$\tau = (k_r + k_{nr})^{-1} \tag{4}$$

Here, k_r is the rate constant for radiative decay (fluorescence), while k_{nr} is the combined rate constant for all non-radiative decay processes. k_r is virtually constant and is an inherent property of the material in question, and for this material is significantly greater than k_{nr}, given the high fluorescence efficiency. When a fluorescence quencher, such as TNT, is introduced, k_{nr} increases because an additional efficient non-radiative pathway now exists. This, via Eq. (4), makes τ smaller.

As previously described, a smaller excited-state lifetime can have a dramatic effect upon the lasing threshold and lasing efficiency. The end result is that E_{TH} is increased in the presence of DNT or TNT. This makes the stimulated emission intensity more susceptible to quenching than the spontaneous emission. As illustrated in Figure 15, DNT can significantly quench lasing emission without causing any change to the already sensitive spontaneous emission, giving an additional 30-fold sensitivity enhancement to DNT vapor.

Therefore, the use of lasing conjugated polymer sensors is an exciting approach to improving the sensitivity of a technique that is already strongly amplified by exciton migration. This method relies upon the use of a lasing signal that is more highly dependent upon excited state population than the more traditionally observed spontaneous emission. This, when

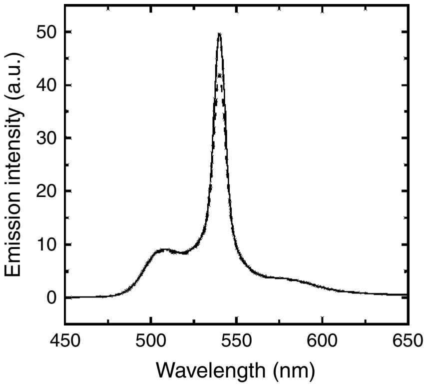


Figure 15 Laser-induced emission spectra of polymer 3 before (solid line) and after (dashed line) a one second exposure to DNT vapor.

combined with the amplification obtained from three-dimensional exciton migration in CP sensors, gives a material with unparalleled sensitivity to vapor-phase nitroaromatics.

7. CONCLUSION

Chemical sensing using FQ of amplified fluorescent conjugated polymers is a powerful technique that can achieve high sensitivity for vapor-phase analytes. The ability of the excited state of conjugated polymers to rapidly diffuse allows for large degrees of amplification, because the exciton in this "molecular wire" samples many binding sites within one excited state lifetime, instead of remaining fixed on one binding site. Well-designed polymers such as **1** and **3** combine critical structural elements to allow for highly emissive, porous polymer films that are readily synthesized, solution processable, and display large sensitivity gains over monomeric or solution-based systems.

The electron transfer nature of the quenching mechanism allows for the sensitive and selective detection of highly electron-deficient molecules, including vapors of the powerful and dangerous explosive TNT and the commonly found synthetic by-product DNT. As a result, this technology has been successfully field tested in many different scenarios, from the screening of vehicles to the detection of land mines and even underwater explosive detection. The effectiveness and applicability of these materials and devices is constantly being improved by research in both industry and academia. With the nearly infinite amount of additional design features and modifications that can be incorporated into the structures of conjugated polymers via chemical synthesis, the expansion of the sensitivity, selectivity, and versatility of explosive detection equipment based on amplified fluorescent polymer technology is an exciting and important goal.

ACKNOWLEDGMENTS

We thank Sandia National Laboratories, The Technical Support Working Group, The Transportation Security Administration, The MIT Institute For Soldier Nanotechnologies, and ICx Technologies. for Support. We also thank M. Fisher and J. Sikes of ICx Technologies for their assistance in the preparation of this chapter and for supplying Figures 8–13.

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CHAPTER 11

POST-BLAST DETECTION ISSUES

M. Marshall

Contents

1. OBJECTIVES

Four broad objectives need to be considered in the scientific investigation of bombing scenes:

(i) Assessment of the efficacy of existing protective measures.

(ii) Collection of technical information to guide the development of improved protective measures.
(iii) Collection of forensic evidence to assist police and judicial investigations.
(iv) The identification of new threats to public safety.

At all times, the potential hazards need to be borne in mind. Bomb scenes are very dangerous places and appropriate precautions need to be identified and taken if investigators are not to be added to the list of the injured.

2. CONTROLLING THE AFTERMATH

2.1. Questions from the media and government leaders

Immediately after an explosion, investigators are likely to be besieged by journalists from various media organisations seeking instant, and supposedly authoritative, answers: “What happened?” “How big was the bomb?” “How many were injured?” “Who was responsible?” “Was this the work of the xyz terrorist group?” It would be very unusual if information was immediately available to answer such enquiries reliably, and experience shows that to do so in an attempt to be helpful is a certain recipe for problems later. It is wise to avoid issuing definitive statements before the facts have been established. To do so may prejudice investigations, adversely affect later judicial proceedings and in some jurisdictions constitute contempt of court.

Nonetheless, the media do have an important and legitimate role in a democratic society and can also be very helpful, for example, in publishing appeals for witnesses. A properly defined plan for handling media enquiries, with well-trained and thoroughly briefed press officers to liaise with journalists, is an essential part of a strategy for dealing with bombing incidents.

Similarly Ministers and senior government officials will be legitimately anxious for information and answers about any major incident. This is entirely appropriate given their responsibility for protection of the public, and particular care needs to be taken to ensure that such requests are answered properly, whilst tactfully deflecting questions from those who are merely curious.

2.2. Scene control

The rescuing of survivors, treatment of casualties, and making the scene safe are all likely to be priority tasks at any bombing incident, and additional potential hazards from fires, damaged buildings in a state of near collapse, unexploded devices, or deliberately placed booby traps must also be borne in mind. A cordon around the scene should be established at the earliest possible moment to control access and ensure the preservation of evidence.

Post-blast incidents are inevitably scenes of devastation; unless control is established quickly they will also be scenes of panic and chaos.

A control point should be set up to act as the gateway through the cordon, and a log kept of all movements in and out, together with a record of where people went and what they did at the scene. As soon as possible safe access pathways into and around the scene should be established to minimise possible disturbance of evidence. This can be as simple as lines of chalk, tapes strung between posts, or by using sections of portable metal walkway on legs to cross debris fields.

Controls should aim to effectively prevent the risk of small items of evidence being unwittingly removed on people's footwear, or conversely confusing items or chemical residues being carried into the scene. For example, the possibility of cross-contamination between crime scenes needs to be rigorously prevented. Thorough cleaning of equipment and wherever possible one-time use of disposable items form part of any effective contamination avoidance strategy. It should also be remembered that casualties can be an important source of physical evidence; for example, their injuries may be due to either blast or bomb fragments. Arrangements need to be made to ensure that any evidence available from victims is identified and recovered.

Not only is it important to take all these steps, but also if evidence obtained from a bombing scene is to have validity for investigational and judicial purposes, then written records need to be kept to prove everything was done correctly.

2.3. Zoning

There is a widespread misapprehension that explosions destroy everything in immediate contact with them. This is incorrect. In reality, bombs shatter and scatter, breaking objects in close proximity into fragments whose size depends on proximity, the properties of the target material, and the properties of the explosive. In very approximate terms explosives having a high velocity of detonation, e.g. trinitrotoluene (TNT) or 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), will tend to cause shattering and brittle fracture of nearby metallic objects, whilst low velocity of detonation explosives, e.g. ammonium nitrate and fuel oil (ANFO), will tend to cause tearing, bending, and ductile failure. However, this generalisation should not be carried too far; there can be no absolute certainty about the identity of an explosive involved without the identification of explosive residues by chemical analysis.

Crime scenes are often divided into zones, and the location of items of evidence within particular zones meticulously recorded. Indeed location may sometimes be of crucial evidential significance, e.g. "the gun was found clutched in the alleged suicide victim's hand". However, precise location may actually be of little significance at a bombing scene, other than the fact that the item was actually at the scene. So many unknown and unknowable factors are involved in the production and projection of fragments from an explosion that recording the precise location of every one of thousands of items may simply be a recipe for confusion and eventually failure to identify the most significant points.

In any investigation that may ultimately lead to judicial proceedings, it is essential to maintain a fully documented chain of evidential continuity. This represents a significant administrative burden, but unless it is done effectively it may be impossible to prove that test results and conclusions actually relate to the specific explosion scene; the work is then essentially useless.

If a bombing scene is divided into an excessive number of zones for evidence recovery, a correspondingly excessive amount of documentation will have to be generated and maintained, with all the attendant risks of errors and omissions.

Experience in the United Kingdom during recent bombing campaigns has been that bombing scenes should be divided into a minimum number of zones for evidence recovery purposes, e.g. "inside the building" and "outside the building".

3. INITIAL SCENE EXAMINATION

3.1. Map the scene

Once control has been established, it is useful to gain an overview of the scene. A sketch plan should be produced showing the location of major items and physical damage.

Photography of the scene and any key features will prove invaluable later, and an imagery plan should be developed at an early stage to ensure that all the essential points are covered [1].

3.2. Was it a bomb?

This is likely to be the first question the investigator is asked, and many will consider it a key question; the answer may not be obvious. However it is also the wrong question, asked at the wrong time.

3.3. The right question(s)

What we actually need is to establish from the evidence what happened, and whether it was an accident or a deliberate criminal act.

We commonly refer to an "explosion", but technically we can discern four cases:

(i) A deflagration in a dispersed phase medium.
(ii) A detonation in a dispersed phase medium.
(iii) A deflagration in a condensed phase medium.
(iv) A detonation in a condensed phase medium.

In accordance with the usual convention, we define a detonation as a reaction travelling faster than the local speed of sound in the unreacted medium, and a deflagration as being a reaction travelling at or slower than the local speed of sound in the unreacted medium. An example of each type of event is given below:

(i) Dispersed phase deflagration: violent combustion of a fuel-rich mixture of methane and air.
(ii) Dispersed phase detonation: the detonation of a balloon filled with acetylene gas.
(iii) Condensed phase deflagration: combustion of a stick of rocket propellant.
(iv) Condensed phase detonation: the detonation of a slab of military plastic explosive.

Each of these different events may progress so violently as to be ordinarily described as an "explosion", and produce serious damage to people and property in the vicinity. However detailed examination of the post-blast scene will reveal key differences. Condensed phase events have a distinct point of origin, commonly referred to as the "seat". Damage patterns will spread out from the seat usually diminishing with distance, and in most cases it should be possible to track back from the damage to the seat. Dispersed phase events tend to exhibit a more uniform damage pattern, without a clearly defined point of origin.

Determination of the nature of the event: dispersed phase or condensed phase, deflagration or detonation, is a first step in answering the questions facing the investigator. If the event was a dispersed phase event then the likelihood of an accident, due for example to a gas leak, increases. However, there have been well-documented examples of deliberately induced dispersed phase explosions, and the key point here for the investigator becomes identification of the means of initiation. Conversely, a condensed phase event is more likely to be the first pointer to a deliberate act, but the possibility of accident must still be considered, and evidence of the means of initiation sought. An essential part of the inquiry will be to establish whether any fuels or chemicals might have been stored at the site whose leakage could have preceded an accidental explosion.

3.4. Damage assessment

If the seat of a condensed phase explosion and an associated crater can be located, this can be quite helpful. Measurement of crater dimensions can enable an approximate estimate of the amount of explosive involved, and also may focus questioning of witnesses or examination of video footage from security cameras. Crater size depends on the mass and nature of the explosive, the nature of the substrate, and the position of the explosive charge relative to the substrate surface. As a first approximation, the diameter of a crater in a uniform substrate varies as the cube root of the explosive mass for a charge on or above the surface. For charges buried just below the surface, the diameter of the crater is proportional to the mass of explosive raised to the power 7/24; this factor allows for the effect of backfilling of the crater by ejected material. Intuitively (and practically), the diameter of the crater in the surface also decreases with distance of the charge above or below the surface.

Even with a condensed phase explosion there may be no crater. For example, no crater and no explosive traces were found after the explosion at the London Stock Exchange in 1990, even though physical damage was characteristic of a small charge of a few kilogrammes of high-velocity military explosive. Warning telephone calls to news media, allegedly on behalf of an Irish Terrorist group, preceded the explosion. The explosion occurred in a toilet. After careful searching of the debris, the toilet door was recovered, and its original position confirmed by the distinctive physical fit between the hinges and the door frame. Examination of the door showed numerous fragment penetrations. Insertion of probes in the fragment holes indicated a point of origin in the false ceiling of the toilet. Moreover a fragment of one of the ceiling struts showed pitting (micro-cratering) characteristic of proximity to a high explosive detonation. In this instance, the bomber had concealed his device by lifting one of the ceiling tiles and hiding the bomb inside the false ceiling.

Objects in the vicinity of an explosion can often serve as useful post-blast witnesses. Thus for large explosions damage to structural elements of buildings, street furniture, motor vehicles, and glazing can all prove informative. A number of authors have published studies that provide guidance on both damage assessment techniques and interpretation of the data [2–7].

3.5. Debris collection

Bombs shatter and scatter: the scene debris will contain fragments of the explosive device, any container in which it was held, and also the remains of items which were in immediate proximity. The size of such fragments will depend on the explosive performance and device size, as will the degree of fragment scatter and the chance of recovery of evidentially significant items. A preliminary search should be made to identify and recover any obvious evidential items. Arrangements should then be made to recover the bomb scene debris for more detailed searching.

Some thought needs to be given to the practical aspects of debris collection. Historically, in the United Kingdom when a large explosion occurred, the police would improvise by buying large numbers of clean garbage containers and then pack them with the relevant scene debris for later laboratory examination. However, a large explosion can generate very large quantities of material which require examination – often tonnes or tens of tonnes. A better solution was found to be the use of standard rectangular plastic boxes of 40 or 50 l capacity which could be stockpiled in advance at strategic locations, and could be cleaned for reuse. Such boxes could be sealed readily with an evidential label, moved on hand trucks, and stacked efficiently both when empty and when full.

3.6. Explosives residues

On occasion a partial detonation may take place, resulting in large visible quantities of explosive being left at the scene; in this event collection and subsequent identification of samples is relatively straightforward. However most explosions only leave invisible residues of unconsumed explosive at the scene. The first problem then is to find the right place from which to take samples. Of course, it will be necessary to have a stock of sampling and packaging materials available, which have been quality assured to ensure they are free from any possible traces of explosive so that the validity of any subsequent tests can be established.

Practical experience has been that the best places to look for such residues are surfaces that were either in contact with or in close proximity to the explosive before the explosion, and also that non-porous substrates such as metals tend to be better prospects than porous surfaces. Having located the seat of the explosion one can then think about where items bearing residues are likely to have been thrown, as well as identifying any items remaining in situ which could have acted as residue collectors. For example, if a small device has exploded inside a building then nearby metal objects such as light fittings, window frames, and door frames may remain and could repay examination. Usually, visual examination of metal surfaces with either the naked eye or a magnifying glass will suffice to reveal the effects of gas wash and micro-cratering, which often occur on surfaces exposed to a nearby explosion. Sometimes the explosive may leave a sooty residue that can be readily identified. If such items are portable, then the best strategy is to seal them in nylon bags and transport them to the laboratory for detailed examination. Items that are too large to send to the laboratory should be swabbed in situ and then the swabs analysed in the laboratory.

Techniques which may be used for collection of trace explosives residues at a scene include swabbing with either dry or solvent wetted swabs, sweeping up dust and small particles into suitable receptacles, vacuum collection, and the use of a contact heater to collect semi-volatile materials. If a bomb crater can be located, then samples of the soil from the crater should be sealed in nylon bags for later laboratory analysis.

Motor vehicles are often involved as the target or as the means for transporting a device, or simply as inanimate witnesses to the event. In each case they are likely to be forensically useful. In general, the best approach is to wrap the vehicle in plastic sheet and transport it to the laboratory for examination.

3.7. Aircraft

Particular issues arise in the forensic examination of aircraft crash scenes. When break-up of the aircraft has taken place at high altitude then wreckage and debris will be dispersed over a very wide area, making recovery difficult. To make matters worse, wreckage often falls into the ocean or other large body of water. This can lead to misleading effects; for example, enclosed sections containing trapped air can burst open after impacting the water at high velocity, giving the appearance that a low-velocity explosion might have occurred in that part of the structure. Microscopic examination of the metal parts to search for the characteristic signs of gas wash and micro-cratering is a good way of eliminating this confusion [8]. Prolonged immersion in water is likely to significantly reduce the chance of recovering chemical traces of explosives residue, even if an evidentially significant piece of debris is found [9].

Aircraft usually contain a plethora of complex mechanical and electronic systems and close collaboration between the forensic scientist and aircraft engineers experienced in crash investigation is essential if there is to be any prospect of reaching meaningful conclusions. Analysis of data from the flight data recorders carried by commercial aircraft can be particularly helpful in ruling out issues such as engine failure, establishing the event time, and whether the flight was proceeding normally before disaster struck. Where a cockpit voice recorder was carried, this can also provide valuable information.

It is common for crash investigators to undertake reconstruction of the aircraft wreckage, and this can be exceptionally useful in establishing the seat of an explosion, if that is what in fact took place. The National Transportation Safety Board in the United States and the United Kingdom Air Accident Investigation Branch have both done some exceptionally fine work of this type.

Post-mortem examination of victims is essential; if a bomb exploded in the passenger cabin then significant evidence is likely to be produced from the bodies of those in the immediate vicinity.

Detailed examination of the aircraft's cargo documents and passenger check-in information should be made; this will usually allow a plan to be made of the location of people, items of luggage, and cargo.

Finally, the position of seats recovered amongst the wreckage can generally be accurately identified and any items of significant debris recovered. Synthetic textiles used in seat covers or carpets can also sometimes display microscopic features characteristic of proximity to an explosion.

3.8. Quality assurance

This is a key issue in every aspect of the forensic examination of explosion scenes, and in subsequent analysis of evidential samples. Unless the results can withstand the meticulous scrutiny properly given to them in a court, they are useless. The requirements include:

(i) A clear chain of custody for evidence to prove its origin and integrity.
(ii) Prevention of contamination.
(iii) Training and competence of persons involved in the forensic process.
(iv) The use of validated test methods which have been subject to peer review.
(v) Production of contemporaneous notes in sufficient detail that they can be effectively reviewed and enable another competent scientist to evaluate the results.

3.9. Bomb scenes and mental stress

As previously mentioned, bomb scenes are dangerous places, and proper attention needs to be paid to the control and avoidance of physical hazards. The mental stresses imposed on people involved in work at a bomb scene also need to be recognised and managed.

Training and the creation of a team spirit are the first steps; work schedules also need to be carefully monitored and controlled with appropriate rest breaks being enforced before people experience mental rather than physical exhaustion. It is useful if staff engaged in this type of work receive awareness training to recognise the symptoms of excessive stress in both themselves and colleagues so that such problems can be contained before becoming unmanageable.

In exceptional cases, there may be a risk of individuals developing post-traumatic stress disorder; in such circumstances early intervention and professional counselling are essential.

Apart from the need to avoid such adverse effects on the people involved in the investigation of an explosion, there is also a need to be aware of possible risks to the quality of the actual work. Good scientific work requires the maintenance of an impartial objective and open-minded attitude to the collection and evaluation of evidence. Moreover, the more horrific the crime, the more important it is to establish the truth rather than some partial or distorted version. However feelings of distress and anger are inevitable in any normal person involved in a scene of carnage. Training for scientists and scene investigators needs to address these issues so that individuals are equipped to recognise and deal with them. Safeguards also need to be built into management systems; the first step being to ensure that, despite the inevitable pressures, sufficient time is built into the process that conclusions are only reached after calm reflection. Finally, all reports should be subject to effective internal peer review before issue.

4. LABORATORY EXAMINATIONS

4.1. Work streams

One can view samples from an explosion scene as belonging to one of two work streams: (i) clean and (ii) dirty. Separation between these work streams needs to be established at the earliest possible moment in the process with appropriate laboratory facilities to handle each. The clean work stream contains items which are to be examined for invisible chemical traces of explosives. Such items need protection from any external contamination to a degree commensurate with the sensitivity of the chemical analysis techniques to be employed. The dirty work stream contains items that do not require trace analysis precautions, e.g., scene debris for physical searching. Nonetheless, such items still need to be handled in a way which protects their evidential integrity. Some items can start in the clean stream and then be transferred to the dirty stream, e.g., damaged motor vehicles may first be examined for explosive traces, and then transferred out of the trace examination area to be searched for physical evidence.

4.2. Functions

For each type of work the laboratory needs facilities for four basic functions:

(i) Safety.
(ii) Receipt.
(iii) Examination.
(iv) Storage and disposal.

4.3. Laboratory safety

Apart from the safety issues normally associated with any chemistry laboratory, there are a number of specific issues associated with explosives and bomb scene examination. An obvious point is the hazards associated with handling and storage of explosives; most countries have strict regulations covering this area, and compliance is mandatory. This is not a trivial matter as it is common to receive unknown and unidentified materials, or items that have been subject to physical abuse.

To minimise risk any explosives or disrupted explosive devices should always be examined by competent explosive ordnance disposal experts before submission to the laboratory.

Less obvious are the biological and toxicological hazards from bomb scene debris. Apart from the possibility that malefactors may deliberately incorporate noxious substances in their devices, hazards can be generated from the scene itself. For example, victims may have been suffering from an infectious disease, and so victims' clothing (which is often soaked in blood) needs to be handled and stored with proper biohazard precautions. Scene debris may also contain dismembered body parts.

Explosions in buildings and urban situations frequently damage sewers and drainage systems, spreading their contents over the scene. Consequently, there is a risk of debris being contaminated by dangerous infectious agents.

A wise precaution is to seek professional medical advice and institute a vaccination programme to protect staff against as wide a range of identified risks as possible.

Toxic substances can also be encountered in debris. For example, hazardous chemicals may have been legitimately stored in a blown up building or there could be lead from the batteries of bomb damaged motor vehicles. Another common hazard is the presence of asbestos in old buildings.

Physical hazards should also be remembered. Debris from bomb scenes generally contains potentially contaminated items with sharp jagged edges, including pieces of broken glass and shards of metal. Bomb-damaged vehicles present particular hazards: apart from leaking fluids and flammable materials, they may also have suffered structural damage, so especial care needs to be taken when lifting or moving them. Fuel tanks should be drained and vented as soon as possible to reduce fire risks. And of course it is essential that adequate supports are in place before any examination underneath the vehicle.

4.4. Receipt

Reception arrangements need to provide for checking the safety of items being submitted, separation of items to prevent cross-contamination, initial identification of submitted material, and the preparation of all the requisite documentation. After items have been received and documented they will need to be transferred to an appropriate storage area, whether this be for trace analysis, biohazard, explosive, flammable, toxic, or bulk debris. It is advisable to have pre-planned quarantine storage for anything whose characteristics or provenance cannot be guaranteed.

4.5. Receipt of items for trace analysis

The first step is to verify the integrity of the packaging, to ensure that there cannot be justification for doubt later about the possibility of contamination of the items by the environment. Particular care needs to be taken with packaging of items for trace analysis because, by definition, what is being sought is invisible to the naked eye. All materials used for packaging of items for trace analysis must be subjected to a rigorous and comprehensive quality assurance regime to ensure that nothing is present which might interfere with, or invalidate, the subsequent analysis. Control levels for different species will depend on the sensitivity of the particular analytical technique and the potential forensic significance of different quantities [10, 11]. Decisions on this will be aided by reference to general environmental surveys for species of potential forensic interest [12–15].

As a general guide items for trace analysis should be enclosed in three layers of packaging; these are removed in sequence as the item is moved from the uncontrolled general environment into the controlled trace laboratory environment. This approach is intended to avoid the possibility of any contamination on the outside of the packaging being transferred into the trace laboratory.

4.6. Trace analysis

4.6.1. Thin-layer chromatography

A good general purpose screening technique for organic explosive traces, albeit often undervalued, is thin-layer chromatography (TLC). The advantages of TLC are that it requires only limited capital equipment, little sample preparation other than dissolution in a suitable solvent, and that it provides rapid results that are easily interpreted and explained [16].

Conversely, it lacks the selectivity and sensitivity of the best instrumental methods of analysis; results from TLC analysis should always be supported with confirmation by other analytical techniques or appropriate supplementary evidence.

Colleagues at the Forensic Explosives Laboratory have found the following procedure suitable: pre-activated silica gel coated plates containing an ultraviolet fluorescent indicator are used. A mixed standard solution is run in one of the channels on the plate, alongside solutions of the samples and blanks. Table 1 shows the recommended eluent systems.

Normally only mixed explosive standards should be taken into, or used in, a trace laboratory: this has the advantage that in the unlikely event of an error the presence of multiple species matching the mixed standard will clearly show what has happened. If circumstances dictate the use of a single standard, it is important to document any extra precautions taken to prevent confusion between samples and standards. It may also be wise to review the cleaning and quality assurance

Table 1 Eluent systems for thin-layer chromatography of explosives

System	Eluent composition	Proportion	Notes
1	Toluene	100%	Former general screen PETN/NG not resolved
2	Petroleum ether 40–60°C	40% (v/v)	Former general screen
	Petroleum ether 60–80°C	40% (v/v)	PETN/NG resolved
	Ethyl acetate	20% (v/v)	RDX/HMX low R_f
3	Chloroform	90% (v/v)	RDX/HMX/NC resolved, especially HMX versus high RDX
	Methanol	10% (v/v)	
4	Toluene	90% (v/v)	Preferred general screen
	Ethyl acetate	10% (v/v)	RDX/HMX/NC resolved

Table 2 Thin-layer chromatography results for various explosives

Explosive	R_f in system				Response to UV	Colour after NaOH and heat	Colour after Griess
	#1	#2	#3	#4			
NC	0.00	0.00	0.00	0.00	None	None	Magenta
HMX	0.01	0.02	0.25	0.06	Absorbs	None	Magenta
RDX	0.07	0.03	0.53	0.13	Absorbs	None	Magenta
Tetryl	0.43	0.18	0.83	0.61	Absorbs	Orange before heat, yellow after	Magenta
NG	0.61	0.32	0.84	0.66	None	None	Magenta
PETN	0.64	0.44	0.88	0.78	None	None	Magenta
TNT	0.74	0.52	0.93	0.88	Absorbs	Brown	Magenta

NG, nitroglycerin; NE, nitrocellulose

procedures employed to ensure that they are adequate if single standards are employed.

In unknown situations, the application of an amount of mixed standard containing approximately 200 ng of each explosive is suggested. This may be adjusted as circumstances dictate.

After elution, the plate is dried and then observed under ultraviolet light. Next, it is sprayed with 1 M sodium hydroxide solution and then heated at 140°C for 10 min. After noting any changes, the plate is left to cool to room temperature and then sprayed with modified Griess reagent. Table 2 summarises the various indications to be expected during the different stages of the visualisation process.

A photographic record showing the various spots and the colours on the TLC plate at the different stages may be useful. However this is not actually essential if proper notes are made. The limitations of photography also need to be borne in mind; it can be difficult to produce photographs that accurately reproduce the colours of pale and fugitive subjects. An alternative can be to have a second scientist view the plates and make confirmatory notes, thereby reducing the scope for later doubt.

Confirmation of TLC results can be readily accomplished by scraping off the spots of interest after visualisation and carrying out further analysis. For example, a small glass capillary tube such as used for melting point determinations or TLC spotting can be used as a sampler. The capillary may be cleaned before use by passing it briefly through the flame of a Bunsen burner to ensure freedom from explosives. The collected material is then extracted with solvent ready for further analysis either using TLC with a different solvent system, or in favourable cases by infrared spectroscopy or mass spectrometry (MS). Such a multi-step approach can allow a very high degree of confidence in the conclusions to be attained, even in laboratories with quite limited facilities.

TLC is also quite readily and quickly applicable to analysis of novel materials. For example, the organic peroxides triacetonetriperoxide (TATP), diacetonediperoxide (DADP), and hexamethylenetriperoxidediamine (HMTD) can be readily determined by TLC on a silica plate using toluene as eluent, and a solution of 1% diphenylamine in concentrated sulphuric acid as visualising agent. Detection of a few microgrammes is possible [17].

4.6.2. Trace analysis scheme

Instrumental methods of analysis generally offer greater sensitivity and selectivity than the TLC approach outlined above. Different techniques are required for inorganic or organic analytes, as well as for compounds having limited volatility or thermal stability. In general, the greater sensitivity offered by instrumental methods is accompanied by a need for some form of sample pre-treatment.

One such scheme is illustrated in Figure 1. A mixture of ethanol and water (1:1 by volume) is used as a general purpose extraction solvent. Although not necessarily the strongest solvent for any particular species, it does act as a reasonable solvent for traces of a very wide range of both organic and inorganic compounds. The extract is then passed through a small column of solid adsorbent that retains the organic explosives while the inorganic species remain in solution in the ethanol/water eluate. The organic explosives are subsequently eluted from the solid adsorbent with ethyl acetate, while the ethanol/water solution is used for determination of the dissolved inorganic substances [18].

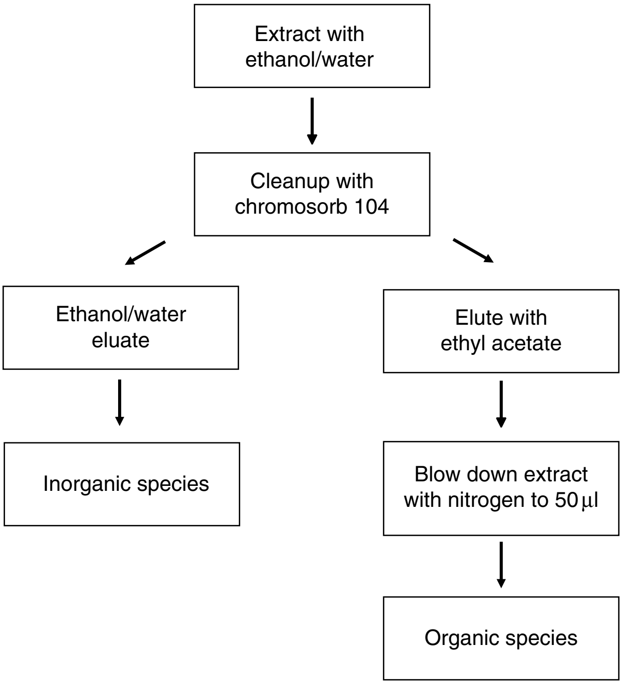

Figure 1 Sample pre-treatment scheme for instrumental analysis.

4.6.3. Capillary gas chromatography–thermal energy analyser

An excellent instrumental method applicable to the detection of a wide range of common nitrogen containing organic explosives is capillary gas chromatography coupled to a selective chemi-luminescence detector, often called a thermal energy analyser, hence the acronym GC–TEA. In the TEA the effluent from the gas chromatograph first enters a pyrolysis chamber where organic explosives containing nitrate ester or nitro groups are broken down to form nitric oxide. The gas stream then flows into a reaction chamber where it is mixed with ozone. The ozone and nitric oxide react to form nitrogen dioxide in an excited state. This then relaxes to the ground state, emitting a photon of characteristic wavelength in the near infrared. The emitted photons are detected by a photomultiplier combined with a filter to select light in the wavelength range 0.6–0.8 μm. Carbon monoxide can also exhibit chemi-luminescence with ozone; the selectivity of the overall analytical system is ensured by (i) use of a high-resolution capillary column and (ii) careful choice of the reaction conditions and the optical filter in the detector. Although for explosives detection such systems are carefully optimised for species containing the NO moiety, they can potentially be set up to detect other types of compounds.

The ethyl acetate solution of organic species from the pre-treatment scheme shown in Figure 1 is suitable for analysis by this method. In order to cover the range of common explosives several chromatography columns with different types of stationary phase are required to allow for different polarities and volatilities. Dimethylsiloxane, phenyl-modified dimethylsiloxane, cyanopropyl- phenyl- vinyl-modified dimethylsiloxane, and polyethylene glycol have been found to represent a useful set of stationary phases. Carefully optimised temperature programming is also needed to obtain the requisite resolution and avoid interferences [19, 20].

4.6.4. Gas chromatography–mass spectrometry

Although generally accepted as one of the most versatile techniques for the analysis of organic compounds, in practice this method does suffer from some limitations for the analysis of explosive traces. In particular, molecular explosives are by definition unstable, and so tend to fragment rather too readily in the mass spectrometer. Nonetheless, with careful optimisation of conditions it is possible to get useful results from many compounds of interest, although the sensitivity of the technique is typically an order of magnitude poorer than GC–TEA when a full scan mass spectrum is sought. When it is possible to use selected ion GC–MS, focussing on one or just a few characteristic ions, then the techniques can be broadly similar in sensitivity. The method is of especial value when new compounds are encountered as it offers one of the best ways of identifying unknown materials. The more complex MS techniques such as negative ion chemical ionisation and coupled MS–MS can be useful in some circumstances, particularly where matrix interference is a problem [21].

4.6.5. Liquid chromatography–mass spectrometry

This technique is generally complementary to GC–MS and is particularly useful for identification of organic compounds that are either involatile or thermally unstable. Development of improved systems for coupling the liquid chromatograph to the mass spectrometer, and transferring the dissolved analytes efficiently has resulted in substantial improvements in performance. Liquid chromatography–mass spectrometry (LC–MS) has proven rather better than GC–MS for identification of traces of the unstable peroxide explosives TATP and HMTD, as well as the involatile HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane) [22–25].

4.6.6. Ion chromatography

Employed as a general screening technique for inorganic ions, for example, where the use of pyrotechnics, blackpowder, or fuel/oxidant mixtures is suspected, ion chromatography (IC) offers much poorer sensitivity and resolution than organic trace techniques such as GC–TEA. However, by using different chromatographic columns and eluent systems, a wide range of anions and cations may be determined, as well as the common sugars. In practice, the lower sensitivity is less of an issue than might first be thought: inorganic species of potential explosives significance such as ammonium, nitrate and chlorate ions are more common in the general environment than are the organic explosives, so higher levels are needed before any forensic significance can be attached to their presence.

4.6.7. Capillary electrophoresis

Complementary to IC, the capillary electrophoresis (CE) technique is useful for both anions and cations. The method is significantly faster than IC for screening and is relatively easy to automate which is advantageous when large numbers of samples require analysis. Although CE is currently similar in terms of sensitivity to IC it is a relatively new technique and significant improvements in both selectivity and sensitivity continue to be made [26].

4.6.8. The significance of trace analysis results

Continuing developments in analytical chemistry enable the detection, identification and quantification of ever smaller masses of substances of potential interest. Three questions need to be answered about every analytical result:

(i) Is the result real and not just because of random noise?
(ii) Has the substance been correctly identified?
(iii) What is the practical significance of the result?

The first two points are best dealt with as part of the process for developing validated analytical methods. Validation should include testing the robustness of a method in repeated use over a period of time; determining the precision and accuracy; and study of potential interferences. As an example, it would be expected that in the capillary GC–TEA method for organic explosives, a peak should be at least three times the baseline noise to be counted as a real signal, and that the relative retention time should be within 1.0% of the standard for volatile compounds and within 0.5% for the rest. The relative retention time is simply the ratio of the analyte's retention time compared with that of an internal standard. Use of relative retention times significantly improves the repeatability of GC analysis compared with the use of absolute retention times. Methods which yield poor repeatability or are susceptible to interference are unsuitable for forensic use, or indeed even general chemical analysis.

The third point about practical significance implies a need for information about background levels in the environment. Scientists at the Forensic Explosives Laboratory have undertaken extensive studies of the occurrence of common organic explosives in Great Britain, and have shown that they are uncommon in the public environment [12, 13]. In contrast, studies of the occurrence of inorganic species have shown them to be more common in the general environment [14, 15]. Any significance attached to a detection of particular species in an evidential sample must take these factors into account, and a proper balance must be struck in any conclusions. In some circumstances it can be helpful to take environmental swabs from sites which are in the general vicinity of an explosion scene, but sufficiently removed to avoid direct contamination from the explosion itself.

4.7. Storage and disposal

Items submitted for examination include many types of hazardous materials, as described above. It is essential to have proper storage arrangements and most importantly safe disposal arrangements before receipt in the laboratory.

5. FACSIMILES AND TESTS

Police investigators and courts sometimes find a facsimile of the explosive device helpful in understanding what is alleged to have happened. Apart from the obvious issue of avoiding providing tutorials for miscreants, careful thought should be given to the evidential certainty and value of such exercises. If most of the component parts of a device are recovered after being partially disrupted by explosive ordnance disposal (EOD) action then it is likely that a truly representative facsimile device can be constructed. Conversely where only a few tiny fragments are recovered, any facsimile is likely to require more imagination in its construction than is appropriate for supposedly objective scientific evidence.

Similar issues arise with practical tests of facsimile devices. Any explosive test can be arranged to horrify; however, is it likely to provide evidence relevant to the issue before the court?

Apart from the use of practical explosive tests to assess damage patterns at a crime scene, it has been suggested that patterns of deposition of explosives residue could be similarly assessed [27]. Practical experience shows that even in a planned scientific experiment there are huge variations in residue deposition patterns because of the difficulty of controlling all the relevant parameters. Events at a crime scene are completely uncontrolled and subject to even greater variations, and to make matters worse the design, placement and performance of the explosive device are at best inferred rather than known. The presence of chemical traces of a particular explosive at a bomb scene is a useful indication of the material used; the drawing of any conclusions beyond that point should be subject to extremely cautious consideration.

6. PREDICTION OF EXPLOSIVE EFFECTS

Both courts and police investigators need to be able to understand the potential effects of a particular explosive or explosive device and to be able to set it into its proper context. For example: was this a mere firework being misused by a naughty schoolboy, or a weapon of mass destruction? That is not, of course, to forget that devices illegally constructed from fireworks can cause horrific injuries.

The nature of the explosive involved in a particular incident may be inferred from statements made by suspects or witnesses, from evidential material seized by investigators, or from chemical analysis. Expert scientific evidence about the likely performance and effect of a suspect explosive will be needed to assist the relevant court in its deliberations. If the explosive is a well-known military or commercial type then this is relatively straightforward. In the case of improvised or home-made explosives the issues can be more complex. This is particularly so where individuals have been experimenting with unusual chemicals. Unless the scientist has previous experience of the materials involved, the first step is likely to be a search of the relevant literature [28–30].

Calculations can also be helpful. The defence departments of various countries have developed sophisticated computer codes for the prediction and analysis of explosive effects. However not only are these not generally published which makes forensic review and scrutiny difficult, but they are also designed for use with military materials and may be less applicable to home-made explosives.

A widely recognised approach uses the modified Kistiakowsky–Wilson rules to predict the chemical products from an explosion, and then the Berthelot approximation to evaluate the explosive output compared with a standard explosive, usually TNT.

The first step is to devise a set of decomposition reactions, assuming the transformation of the reactants (i.e. explosive ingredients) into their constituent elements.

The second step is to write a set of equations to reassemble those constituent elements into simple products, usually the common oxides such as water, carbon monoxide, and carbon dioxide. Nitrogen is assumed to appear as the element in the products, whereas metals appear as their oxides. Various authors have suggested slightly different product formation sequences; all are approximations. In most cases, the product assumptions do not make a huge difference to the final result: the approximations tend to be self-cancelling [31, 32].

The heat of explosion is then calculated as the difference between the sum of the heats of formation of the products, and the sum of the heats of formation of the reactants, using the usual thermodynamic convention that heat evolved is negative.

Next the change in volume is determined. Normally, the starting material is a solid and the products gaseous so the volume change is simply taken as proportional to the number of moles of gas produced, ignoring the effect of temperature and taking the molar gas volume as 22.4 l. Water is assumed to be gaseous for this purpose.

Berthelot's approximation is then employed whereby the explosive output is assumed to be proportional to the product of the heat of explosion and the volume change.

The following worked examples for TNT and pentaerythritol tetranitrate (PETN) illustrate the procedure:

Example 1: TNT

$C_7H_5N_3O_6 = 1.5N_2 + 2.5H_2O + 3.5CO + 3.5C$

ΔHf Products $= 1.5 \times 0 + 2.5 \times (-241.9) + 3.5 \times (-110.5) + 3.5 \times 0 = -991.5$ kJ/mol

ΔHf TNT $= -67.0$ kJ/mol

$\Delta Hd = -991.5 + 67.0 \cong -924$ kJ/mol

Volume increase $= 1.5 + 2.5 + 3.5$ mol (nb: water gaseous) $= 7.5 \times 22.4 = 168$ l/mol at 273°K, 101.3 kPa

Output product $= -924 \times 168 = 155{,}232$ kJ l/mol^2

We then multiply by 1000 to change from kilojoules to joules and divide by the square of the molecular weight to convert to a mass basis:

$$\text{Power index} = 1000 \times 155{,}232/227^2 = 3013\ \text{J l/g}^2$$

Example 2: PETN

$C_5H_8N_4O_{12} = 2N_2 + 4H_2O + 2CO + 3CO_2$

ΔHf Products $= 2 \times 0 + 4 \times (-241.9) + 2 \times (-110.5) + 3 \times (-393.9) = -2370$ kJ/mol

ΔHf PETN $= -538.7$ kJ/mol

$\Delta Hd = -2370 + 538.7 \cong -1831$ kJ/mol

Volume increase $= 2 + 4 + 2 + 3$ mol (nb: water gaseous) $= 11 \times 22.4 = 246$ l/mol

Output product $= -1831 \times 246 = 450{,}426$ kJ l/mol^2

Converting into joules and a mass basis:

$$\text{Power index} = 1000 \times 450{,}426/316^2 = 4511\ \text{J l/g}^2$$

It is common to compare the output of different explosives as their "TNT equivalent", this being the weight of TNT that would produce the same explosive effect in similar circumstances. In the Berthelot method, the TNT equivalent is taken as the ratio of the power index of the explosive divided by the power index of TNT. The result is usually expressed as a percentage.

$$\text{So \%TNT equivalent of PETN} = 100 \times 4511/3013 = 150\%$$

Such calculations can give an approximate estimate of the likely maximum yield of explosives and explosives mixtures, and may readily be transferred to a spreadsheet for ease of use. In practice, small charges, particularly of improvised explosives, tend to produce less than their maximum output, and this needs to be established by experimental measurements. The results of simple calculations such as those above can be particularly helpful in the design of suitable experimental tests of explosives.

Small-scale laboratory tests can also be useful in the evaluation of unusual and unfamiliar mixtures produced by illicit experimenters. Colleagues in the UK's Forensic Explosives Laboratory developed the "cartridge case" test for this purpose (D.P. Lidstone, unpublished work) [33]. In this test use is made of a standard .303 brass cartridge case that has the particular merit that the wall is thicker at the base than the top, so enabling a progressive effect to be obtained. The hole in the cartridge base is closed with a small plug of modelling clay and then a standard amount, usually 2 g, of the test explosive weighed into the cartridge case. A number six detonator is inserted into the open end and held in place by a foam plastic plug. The complete assembly is then placed centrally in a stout metal tank. The empty space in the tank is filled with wood pellets to catch any fragments from the explosion, and a heavy metal lid placed on top. The detonator is then fired remotely and the results observed. First the contents of the tank are sieved through a coarse metal screen to separate the remains of the cartridge case from the surrounding wood pellets, and then the effect is evaluated against comparative results from standard explosives. Boric acid powder may be used as a suitable inert reference to demonstrate the effect of the detonator alone. A series of known explosives may be used to produce photographic standards for comparison purposes, or the remnants of the cartridge case can be weighed, and the mass of the largest fragment used as a comparison against the known standards [34]. This is a very useful test for initial screening of unusual materials to demonstrate in a qualitative or semi-quantitative way their explosive potential.

However, the very small scale of the cartridge case test must be borne in mind. Explosives all have what is known as a critical diameter; this is effectively the diameter of a charge at which the rates of generation and loss of energy from the explosive reaction are in balance, so that a self-sustaining reaction can continue. Charges less than the critical diameter will tend to react incompletely and in extreme cases fail to detonate. The rate of energy loss from the charge is affected by its confinement; thus a small charge confined in a strong metal cylinder will react more than an unconfined charge. Some improvised explosives have large or very large critical diameters. Such explosives are often referred to as non-ideal explosives, whereas military explosives such as RDX with critical diameters of a few millimetres or less are often referred as ideal explosives. Some important practical consequences are as follows:

(i) Large charges of non-ideal explosives react more efficiently than small charges, provided that the initial stimulus is sufficient to fully shock a volume of the charge which encompasses the critical diameter.
(ii) If a material explodes under the conditions of the cartridge case test it is very likely to be explosive in larger quantities.

7. SUMMARY

Every phase of the response to a bomb incident presents challenges. The key to a successful response is planning and training. Inexperienced and untrained people are likely to be so affected by the event that they make mistakes.

The temptation to reach conclusions before all the essential facts have been established must be recognised and avoided.

Events develop too rapidly at the start of an incident to make use of anything other than immediately available resources and methods. Every stage of the process needs to be subject to rigorous quality assurance. Meticulous care and documentation is essential if any investigation is to be useful in bringing malefactors to justice.

ACKNOWLEDGEMENT

I wish to thank my former colleagues in the Forensic Explosives Laboratory for their generous assistance and constructive suggestions and the Ministry of Defence for permission to publish this work.

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CHAPTER 12

EXPLOSIVES AND DANGEROUS CHEMICALS: CONSTITUTIONAL ASPECTS OF SEARCH AND SEIZURE

G.I. Sapir *and* M.G. Giangrande

Contents

1. INTRODUCTION

> The right of the people to be secure in their persons, houses, papers, and effects, against unreasonable searches and seizures, shall not be violated, and no Warrants shall issue, but upon probable cause, supported by Oath or affirmation, and particularly describing the place to be searched, and the persons or things to be seized.
>
> Constitution of the United States: Bill of Rights –
> Fourth Amendment (1791).

Society is both immeasurably enriched and seriously imperiled by the advances in science and technology. These developments have significant impact on the lives of individuals, communities and entire nations. One prominent aspect is social order through law enforcement and constitutional law. The value of liberty is impossible to quantify, but clearly cherished by our society [1]. Vigilance against exploitation of novel developments that endanger the core of our constitutional system, freedoms, and liberty is essential. A delicate balance must be defined and maintained between liberty and social order. The ensuing question is what does the Fourth Amendment protect – property, privacy, or security?

This chapter will focus on (1) basic principles of search and seizure law; (2) the balance between law enforcement's use of science and technological advances to the Fourth Amendment; (3) when exploitation of technology should be governed by the Fourth Amendment constraints of unreasonable searches as it pertains to explosives and dangerous chemicals; and (4) effect of the USA Patriot Act and related legislation on the Fourth Amendment. The question of what constitutionally determines a reasonable search is simple, its answer and application are not.

A right to be free from unreasonable searches and seizures is declared by the Fourth Amendment, but how this right translates into substantive actual terms is not specified. Traditional constitutional and statutory legal analyses of the Fourth Amendment are heavily affected by rapidly changing societal values, fears, and security interests after the World Trade Center and Pentagon terrorist attacks of September 11, 2001.

2. THE FOURTH AMENDMENT

The Fourth Amendment is 54 words long. It is divided into two general parts. The first 24 words are important. It pertains to what the amendment prohibits. It states who is covered ("the people"), what is covered ("persons, houses, papers, and effects") and nature of protection ("to be secure... against unreasonable searches and seizures"). This part of the Fourth Amendment is usually described as the "Reasonableness Clause" or reasonableness requirement.

The second part defines the scope of police powers in that, no Warrants shall issue, but upon probable cause, supported by Oath or affirmation, particularly describing the place to be searched, and the persons or things to be seized. This is the "Warrant Clause." The warrant clause's requirements are stated in general terms which are not self-defining, except that they must issue upon probable cause. This clause reflects the inherent difficulties in developing a cogent and stable body of Fourth Amendment jurisprudence. The Supreme Court has expanded its interpretation and scope of the Fourth Amendment to keep pace with advances in communication and surveillance technology. Proliferation of technology and sophistication of information have a cause and effect relationship. The mobility of society contributes to the dilution of rights or increased protection of rights. Congress has enacted legislation to protect privacy and enable legitimate enforcement of the law. The government however, continually seeks to exploit state of the art technology for law enforcement and intelligence purposes, thereby redefining privacy rights. Yet, what is constitutionally required and allowable under the Fourth Amendment is not always free from ambiguity, if not controversy.

The relationship, if any, between these two clauses is a "syntactical mystery" and matter of continual controversy. The Supreme Court's jurisprudence is between a categorical warrant requirement and looking to reasonableness alone. The late twentieth century trend in Fourth Amendment law is toward the Reasonableness Clause [2]. Only unreasonable search and seizures are prohibited, but unreasonableness cannot be stated in rigid and absolute terms. However, the clarity of the language of the Fourth Amendment suggests it has wide spread application. An examination of jurisprudence will show it does not.

Fourth Amendment has a uniquely American heritage [3]. "The Fourth Amendment was in large part a reaction to the general warrants and warrantless searches that has so alienated the colonist and helped speed the movement for independence. In the scheme of the Amendment, therefore, the requirement that 'no Warrants shall issue, but upon probable cause,' plays a crucial part" [4]. Therefore, "the police must, whenever practicable, obtain advance judicial approval of searches and seizures through a warrant procedure." [5]. Thus, what is "reasonable" in terms of a search and seizure derives content and meaning through reference to the Warrant Clause [6]. The Fourth Amendment is also viewed as the weakest amendment of the Bill of Rights because of being riddled with exceptions. The Bill of Rights is applicable to the States through the Fourteenth Amendment [7].

2.1. Elements of Fourth Amendment

A basic understanding of search and seizure is necessary before it can be applied to explosives and dangerous chemicals. Accordingly, elemental parts of the Fourth Amendment are presented and then the applicable law.

2.1.1. People and persons

" 'The people' refers to a class of persons who are part of a national community or who have otherwise developed sufficient connection with the United States to be considered part of that community" [8]. The Fourth Amendment does not apply to the search and seizure of property by US agents that is owned by a nonresident alien and located in a foreign country. The class of protected people includes US citizens who are abroad, as well as aliens who have voluntarily entered the US territory and developed substantial connections with this country. The United States Supreme Court has consistently ruled the First (free speech), Fourth (search and seizure) and Fifth Amendments (self-incrimination and due process) directly apply to "the people" – all people on American soil, not just citizens.

2.1.2. Houses

Houses is broadly construed to include all types of structures people commonly use on either a long - or short - term basis for a residence. (e.g., houses, apartments, hotel rooms) It encompasses the curtilage, attached and detached structures if related to intimate activities of the home. Curtilage is the land immediately surrounding and associated with the home. "At common law, it is the area which extends the intimate activity associated with the sanctity of a man's home and the privacies of life" [9]. Factors relevant in determining curtilage are (1) proximity of land to home; (2) whether area contained by enclosures surrounding the house; (3) nature of use; and (4) steps taken to protect land in question from observation [10]. The term "house" constitutionally includes offices, stores and commercial buildings. However, commercial property is treated differently due to a lesser expectation of privacy than in a home. Open fields or unoccupied and undeveloped real property outside of the curtilage and home are excluded.

2.1.3. Papers and effects

"Papers" encompasses personal documentary items, letters, diaries and impersonal business records. "Effects" is less inclusive than property. It does include automobiles, luggage and containers, clothing, weapons, and even fruits of a crime [11]. However, a house and open field are not an effect [12].

2.1.4. Reasonable

Reasonableness depends on circumstances – it is fact dependent. Evidence determined as unreliable, whether by experience or other means, will not justify a search as reasonable. Once a practice is determined to be reasonable, the court is unlikely to retract it [13].

2.1.5. Searches and seizures

A search consists of a governmental intrusion into an area where a person has a justifiable and reasonable expectation of privacy. Seizure occurs "when there is a governmental termination of freedom of movement through means intentionally applied" [14].

2.1.6. Warrants

Warrants are documents giving authority to a person to do something, which he otherwise has, no right to do and this secures him from loss or damage. "A precept or writ issued by a competent officer or magistrate authorizing an officer to make an arrest, a seizure, or a search or to do other acts incident to the administration of justice" [15].

Requisites for a valid warrant are (1) issued by a neutral and impartial magistrate; (2) based on probable cause; and (3) describe with particularity the place to be searched and items to be seized.

Without impartial controls, investigators even when acting in good faith, too often and too quickly (self-serving) find probable cause, because of the competitive enterprise and predisposition of investigating crime. Therefore, it is the neutral and detached magistrate who narrowly defines the permissible scope of a search before it occurs [16].

Application for a warrant must demonstrate "necessity," which is defined as showing other means of investigation have been tried and have failed to meet the investigation's objectives, or are not likely to succeed, or are too dangerous to employ. Warrants can only authorize the seizure of goods, effects, and papers – they cannot be used to compel testimony [17]. Compliance with the warrant's notice provision is usually provided by giving the person, or leaving at the premises, a copy of the warrant and a receipt of any property taken [18, 19]. However, situations occur when law enforcement prefers not to notify the individual of a search and seizure. In these instances, the issue is whether officers may search the premises but delay notifying the occupant of the covert search. Contrary to established constitutional law, the Patriot Act permits such conduct through "sneak-and-peak" warrants [20].

Warrants are not to be confused with subpoenas. A subpoena is a judicial writ compelling the appearance of a witness in court under penalty of law. Subpoena comes from the Latin meaning "under penalty." Subpoenas are used in all stages of the judicial process where testimony or production of material is sought, including pretrial hearings and grand jury appearances. There are two types of subpoenas, the subpoena ad testificandum and the subpoena duces tecum. The first is for the person and second is for production of documents and records. The subpoenaed party can contest the subpoena before compliance, whereas with a warrant any objections to it are after the fact.

There are generally two categories of warrants, the arrest warrant and the search warrant, the latter having several variants:

(a) Arrest Warrant – A warrant issued only on probable cause, directing a law enforcement officer to arrest and bring a person to court [21]. It can be used to enter a suspect's home and arrest them. Police must have a warrant for a nonemergency arrest of a person in their home [22]. An arrest occurs when a person is taken into custody, against their will, for purposes of interrogation or criminal prosecution. A person can be arrested in a public place without an arrest warrant, even if police have time to obtain a warrant. A person may also be arrested without a warrant when the police officer has reasonable grounds to believe a felony has been committed and that person committed it. For a warrantless misdemeanor arrest to occur, the crime must be committed in the presence of the arresting police officer.

(b) Search Warrant (generic) – A judge's written authorization for a law enforcement officer to conduct a search of a specified place and to seize evidence [21].

(c) Administrative Search Warrant – A warrant issued by a judge at the request of an administrative agency, this type of warrant is sought to conduct an administrative search [21].
(d) Covert Search Warrant – A warrant authorizing law enforcement officers to clandestinely enter (whether physically or virtually) private premises in the absence of the owner or occupant without prior notice, and to search the premises and collect intangible evidence, especially, photographs and eyewitness information, without leaving notice of their presence or to be surreptitious, a.k.a. "sneak and peak" [21, 23].
(e) No-Knock Search Warrant – A search warrant that authorizes the police to enter premises without knocking and announcing their presence and purpose before entry, because a prior announcement would lead to the destruction of the objects searched for, or would endanger the safety of the police, or another person [21].

Application for a search warrant must demonstrate "necessity," which is defined as showing other means of investigation have been tried and have failed to meet the investigation's objectives, or are not likely to succeed, or are too dangerous to employ.

The search warrant must describe with particularity what is to be seized, when it is to be seized and location, so nothing is left to the discretion of the officer executing the warrant. This requirement limits the scope and duration of the search. Warrants are routinely issued for contraband, fruits and instrumentalities of crimes and evidentiary items such as, DNA, blood and urine samples, fingernail and skin scrapings, voice and handwriting exemplars, computer data, and electronic media. Information gained from valid warrantless searches may be used to obtain other warrants.

Because privacy of the home is the essence, the Fourth Amendment, police actions must relate to the authorized intrusion. All searches outside the judicial process, without prior approval of a judge, is per se unreasonable [24]. The police must establish exigent circumstances to overcome this presumption. Only police can serve a warrant. Furthermore, members of the media and third parties cannot be present during execution of a search warrant [25, 26]. It is noteworthy that a valid arrest warrant cannot be used to enter the home of a third party named in the warrant. There must be a search warrant based on probable cause if the named person is on the premises [27]. Upon execution of a valid search warrant, police may detain its occupants while conducting the search [28]. Also, during the search of the premises, the police may not automatically search someone else found at that location. The third party may be subjected to a safety "pat down" search based on a reasonable articuable basis for their safety and then temporarily detained, but nothing more.

2.1.7. Probable cause

Probable cause is integral to Warrant Clause. It is required to keep the state out of constitutionally protected areas. Probable cause is the standard which must be met in order for there to be a valid search and seizure or arrest. It includes the showing of facts and circumstances reasonably sufficient and credible to permit the police to obtain a warrant within the officer's personal knowledge. This is an objective standard [29]. As a guiding principal, the doctrine has evolved with police technology in defining limitations. The courts now look at each new technology to determine if expectations of privacy are reasonable.

Probable cause is commonly defined as: A reasonable ground to suspect that a person has committed, or is committing a crime, or that a place contains specific items connected with a crime. Under the Fourth Amendment, probable cause – which amounts to more than a bare suspicion, but less than evidence that would justify a conviction – must be shown before an arrest warrant or search warrant may be issued by a neutral judge [21].

3. THE BILL OF RIGHTS

The Bill of Rights consists of the first 10 amendments to the US Constitution. They were adopted shortly after the main text of the Constitution. The Bill of Rights was conceived to limit the federal government's powers, including those of the President. It codifies a person's civil and legal rights. These provisions were also designed to prevent governmental intrusion especially when a person had done nothing "wrong." If the Bill of Rights did not exist, then people may be, for example, subjected to unreasonable searches and seizures, coercive interrogation techniques, self-incrimination, excessive bail, felony trials without the assistance of counsel, and cruel and unusual punishment.

4. THE FOURTEENTH AMENDMENT

The freedom from unreasonable searches and seizures is a fundamental right protected by the due process clause of the Fourteenth Amendment. The Fourth Amendment, as part of the Bill of Rights, is applicable to the states through the due process clause of the Fourteenth Amendment. The Bill of Rights is "fundamental to our concept of ordered liberty" [30] and governs conduct of state and federal governmental agents (police, government employees, and private persons acting at the direction or request of the government). The same standards or reasonableness and probable cause apply to both federal and state activities.

5. THE LAW ON SEARCH AND SEIZURE

A complex mixture of constitutional limits, detailed statutory regulations, and social values provide a legal regime that governs searches, surveillance, and seizures. These legal and statutory principles are briefly presented using federal law.

5.1. Background: Fourth Amendment jurisprudence

The Fourth Amendment protects property as well as privacy, and applies in the civil as well as criminal context. Seizures are covered even if there is no search [31].

Most of Fourth Amendment jurisprudence is fact orientated. Even subtle factual differences may affect application of the search and seizure doctrine in an infinite variety of circumstances. The preservation of civil liberties and protections is largely determined by the courts.

The Fourth Amendment protects people, not places, from unreasonable searches and seizures. “No right is held more sacred, or is more carefully guarded, by the common law, than the right of every individual to the possession and control of his own person, free from all restraint or interference of others, unless by clear and unquestionable authority of law” [32]. This is a protected, not absolute right. Only unreasonable searches are forbidden. The United States Supreme Court has preferred to develop the doctrine of reasonableness based upon the facts of each case, rather than adopting “bright-line rules” [33]. “Articulating precisely what ‘reasonable suspicion’ and ‘probable cause’ mean is not possible, they are common sense, nontechnical conceptions that deal with the factual and practical considerations of everyday life on which reasonable and prudent men, not legal technicians, act . . . the standards are not readily, or even usefully, reduced to a neat set of legal rules. . . They are fluid concepts that take their substantive content from the particular contexts in which the standards are being assessed. . . Each case is to be decided on its own facts and circumstances” [34]. Simply, Fourth Amendment rights are normally measured in qualitative and not quantitative terms [35].

5.2. Evidentiary search and seizure

All of the following predicate preconditions are required:

- Standing under the Fourth Amendment.
- Was there government conduct?
- Was there a reasonable expectation of privacy by defendant?
- Existence of valid warrant.
- Absent a valid warrant, basis for warrantless search.

“Search and seizure” is generally defined as the search by law enforcement officials, or their agents, of a person or place to seize evidence to be used in the investigation and prosecution of a crime. The security of one’s privacy against arbitrary intrusion by the police, which is the core of the Fourth Amendment, is basic to a free society, and therefore, implicit in “the concept of ordered liberty” [36].

The general types of searches normally encountered are: emergency, exigent, inventory, no-knock, private, protective, regulatory, administrative, special needs, shakedown (prison) strip, voluntary, warrantless, and zone.

Under the Fourth Amendment, several general search categories exempt from the warrant-and-probable cause requirement include: suspicionless searches conducted at the border; in prisons; at airports; entrances to government buildings; administrative searches; inspections of closely regulated businesses; routine regulatory investigations; and special needs searches. These warrantless situations predominantly involve searches conducted for important nonlaw enforcement purposes where adherence to the warrant-and-probable cause requirement would be impracticable.

A preliminary overview of the Fourth Amendment's application and exceptions include the search, seizure, protective stop, and frisk (Terry Stop) exception, search incident to arrest, administrative search exception, and consent exception.

5.2.1. Search

In modern society, a search is premised upon a person's right to privacy, rather than traditional physical trespass. The Amendment protects people, not places. In *Katz v. United States* [24] the Court rejected the property approach in favor of a privacy approach. The Supreme Court held a nontresspassory eavesdropping into a public telephone booth constituted a search. The Court focused on the privacy aspect of the amendment, rather than applying it to specific location. The Court declined to characterize a telephone booth as a "constitutionally protected area." A search occurs when (1) a person's subjective expectation of privacy is invaded; providing (2) society is prepared to recognize that expectation is reasonable. The definition of reasonableness is itself determined on a case by case basis [37].

5.2.2. Seizures

A seizure of property occurs when "there is some meaningful interference with an individual's possessory interest in that property" [38]. Seizure of a person can occur "when a police officer, by means of physical force or show of authority, has in some way restrained the liberty of a citizen." However, "not all personal intercourse between policemen and citizens involves 'seizures' of persons" [39].

Once a court determines a seizure has occurred, a factual analysis of the circumstances is conducted to objectively decide if the particular seizure was reasonable.

5.2.3. Investigatory detentions – stop and frisk (Terry Stop)

The investigative stop is predicated upon a reasonable suspicion, supported by articulable facts of past or present criminal activity, and based on all of the circumstances. Probable cause is not required. Officers may stop, and briefly detain the person and their property. A pat down search of the person's outer clothing for weapons, to protect the officers and those in the immediate vicinity, may be conducted if the officer believes the person is armed and dangerous. Courts look to see if the good faith search was necessary and reasonable to insure the safety of others [40, 41]. Reasonable suspicion is more than a vague suspicion and is based on the totality of the circumstances [42]. If probable cause is developed, the detention becomes an arrest. This doctrine has been applied to validate searches of airline passengers.

5.2.4. Search incident to arrest

Under the Fourth Amendment, police may execute warrantless searches incident to a lawful arrest, as it is reasonable for authorities to search an arrestee for weapons that might threaten their safety, or for evidence, which might be destroyed.

5.2.5. Administrative search exception

Administrative searches are conducted by the government, or its agents through state action, to supervise a highly regulated activity. Warrants are not required for highly regulated businesses and industries, due to urgent public interest and implied consent to participate in the operation. These industries include liquor, weapons, strip mining, automobile junkyards, and explosive manufacturing for report and record compliance [43]. The suspicionless search may occur without probable cause or a warrant, and must be "conducted in good faith." The search is limited by its intrusiveness based upon its need and notice to those people being searched. Administrative searches are routinely conducted as a comprehensive scheme at airports during pre-boarding procedures to screen for weapons and explosives, thereby protecting the public and airline industry.

Administrative searches in the mass transportation industry are designed and intended for safety and security through compliance with the following objectives: (1) keep unauthorized persons with deadly weapons off the transporter; (2) prevent sabotage devices from being carried or placed on the transporter; and (3) to maintain a proper level of security in operational areas [44]. These searches are valid when they are (1) conducted in good faith to prevent harm to the persons or property; (2) limited to a reasonable scope; and (3) passengers have the option of choosing not to use that transportation [45, 46]. All persons are required to produce valid personal photographic identification on request, or be subjected to a "more exacting" search, or be barred from boarding the aircraft if they refuse to show the requested identification [47].

5.2.6. Special needs (Governmental) exception

These are suspicionless searches conducted for important nonlaw enforcement purposes where adherence to the warrant-and-probable cause requirement would be impracticable, yet governed by its reasonableness (i.e., highway check points, border searches, public school students, public employees, probationers, limited drug and alcohol testing) [48, 49]. The special needs doctrine does not apply when the immediate objective of the search is to generate evidence for law enforcement purposes, even if the ultimate goal is to promote some value other than crime control. Extensive entanglement of law enforcement will jeopardize this exception. An example of the Special Needs Doctrine is the search of prison cells by prison administrators. Another example is an administrative search of a probationer's home. Probation, as incarceration, is a form of criminal sanction imposed by a court upon a guilty offender. Probationers and parolees enjoy only conditional liberty that is dependent on observance of special probation restrictions.

5.2.7. Consent exception (waiver of rights)

A person may voluntarily waive their Fourth Amendment rights. Upon doing so, the police may search or seize the person and property. Questions of voluntary relinquishment are reviewed and scrutinized by the courts based on the totality of all the circumstances. Factors to be considered are as follows: whether the person had knowledge of his right to refuse consent; whether the waiver was knowingly and voluntarily made; whether consent was actual or implied by their actions and; whether the person was actually free to leave. Police officers may approach and question anyone in public at any time. The approached person decides whether or not to speak or cooperate with the officer. Consent must be free of "duress or coercion, express or implied" [50], and distinguishable from "mere acquiescence to apparent lawful authority" [51]. The inquiry standard "is whether a reasonable person would feel free to decline the officer's requests or otherwise terminate the encounter."

The scope of a search is limited by the scope of the consent, based upon what a reasonable person under the circumstances would believe it extends. If a reasonable expectation of privacy does not exist, then the Fourth Amendment is not implicated. Merely asserting an unreasonable expectation of privacy without more does not validate it. Either the government must obtain a search warrant or demonstrate that society does not recognize the particular expectation of privacy as reasonable [52]. Law enforcement officers employ a variety of tactics and technologies to protect the public. Permissible utilized methods have included aircraft, flashlights, microphones, pen registers, drug-sniffing dogs, and an officer's hands. Impermissible intrusions have included thermal imaging devices [53]. Thermal imagers were initially developed by the US Army to detect warm objects in cooler environments. They passively collect infrared radiation from a scanned object and "translate" the radiant signal into a visual image. Thermal imagers can distinguish objects with temperature differentials of 0.05°C from a distance of a quarter mile directed at a private residence from the street without a warrant [54]. The device measures infrared radiation (heat) emitted from a residence, compared with other heat emissions from neighboring houses, to detect presence of high-intensity lamps used to grow marijuana plants. This interior information could not have been otherwise available without physical intrusion into a constitutionally protected area. The technology was not in general public use. The Court held, permitting off-the-wall observations "would leave the homeowner at the mercy of advancing technology – including that could discern all human activity in the home" [55].

5.3. Search and seizure exceptions

Searches conduced outside the judicial process are per se unreasonable – subject to only a few specifically established imperative exceptions. Even if reasonable at inception, a search may violate the Fourth Amendment by how it is carried out. Recognized exceptions to this Amendment have been growing in breadth and number (i.e., motor vehicles, marine vessels, open fields, abandon property, plain view, evanescent evidence, electronic surveillance, national security electronic surveillance).

The following noninclusive searches are applicable to various situations, which may involve explosives and dangerous chemicals.

5.3.1. Motor vehicles

Motor vehicles are subject to the Fourth Amendment prohibition against unreasonable search and seizure. The Supreme Court, has, however, created the automobile exception to the Fourth Amendment's warrant requirement. A police officer generally needs a reasonable suspicion of evidence of a crime and exigent circumstances justifying the search. Under various Court rulings, vehicles have less privacy expectations than a home and, as they are mobile, an automobile occupant may conceal or destroy the evidence in the time law enforcement officers may take to acquire a warrant. A vehicle can be stopped for a variety of reasons, and circumstances of these stops can induce a search.

A vehicle moving erratically or in apparent violation of a traffic law can prompt a stop [56]. If, for example, the officer notices the smell of marijuana or alcohol in the vehicle, they can search for contraband as the circumstances warrant. Because of the reduced privacy expectations in automobiles, even closed containers may be subject to searches. These include when, for example, drug or explosive sniffing dogs identify the likelihood of contraband in the vehicle. The fact that the container belongs to the driver or passenger does not affect the ability to search. After a valid stop, all occupants may be ordered out of the vehicle in the interest of officer safety [57]. A passenger in a detained motor vehicle has the right to challenge the constitutionality of the search as it affects them [58].

If a car is impounded for a valid reason, police may conduct inventory searches. If these searches yield evidence of a crime, the evidence will likely sustain a challenge to the legality of the search.

Many of the Supreme Court's holdings on the validity of a search are not usually affected in applicability by the type of contraband, other than the type of suspicion that it may arouse. Thus, rules that apply to the seizure of drugs should equally apply to the seizure of explosives or weapons, or any other illegal item.

The jurisprudence of vehicle searches is fact dependent. Consequently, varying fact patterns may always lead to the same conclusion on the legality of a search. The exigencies of the situation and the strength of the officer's good-faith belief whether there is evidence of a crime, are integral to justification of the search at the time.

General Circumstances where the Supreme Court upheld warrantless motor searches:

- Incident to a lawful arrest. Police have the power to search a vehicle after the driver or occupants are arrested [59].
- Plain view. Where contraband is within plain view of the officer at the time of the stop. This could be obvious material on the seat, in view on the floor, or on the dashboard [60]. The officer does not have to enter the car to make the observation.
- Consent. Once a stop is made, the officer may request permission to search the vehicle. If permission is granted, the search is generally valid [61].
- Investigatory stop. When police have reasonably reliable information from an informant that a vehicle was transporting contraband, they may perform a stop and search. Information that is vague or indirect, however, may not be used as a pretext. A valid stop based on traffic law violations such as, a missing license plate or a lack of lights, can institute a search [42, 62].
- Inventory search. Once a vehicle is impounded, it can be searched in the ordinary course of police procedure to identify the contents as part of the

vehicle inventory [63]. However, a search may not be justified if it deviates from the standard inventory process. If there is no inventory process, the search would have to be justified under other grounds.
- Regulatory search. Commercial vehicles are subject to more pervasive regulation than are private passenger vehicles. A search of a commercial vehicle can occur incident to a stop, to verify compliance with these extended regulations [64].
- Immigration control. Authorities may stop vehicles and search them for illegal aliens in border control situations. However, the need for a warrant becomes greater the farther from the border where the search occurs [65].
- Stop and frisk. If the officer reasonably believes occupants of the vehicle are armed, a search can be initiated. A search can be justified on the basis of protecting the safety of the officer or the general public [66, 67].
- Vehicle checkpoints. Searches incident to stops at vehicle checkpoints are valid, provided the checkpoint is valid. Checkpoints must evidence a reasonable, rational relationship to highway safety to be valid [68].

Within each set of circumstances, facts determine the justification and validity of the stop, search, and seizure. Each case must be individually researched with care to ascertain Fourth Amendment protections and compliance.

5.3.2. Marine vessels

The United States has established a 3-mile territorial limit and a 12-mile customs limit beyond its shores. There is also a 200-mile fishery conservation zone as well. By statute, the Coast Guard, Customs agents, and authorized agents of the Treasury Department, are permitted to board vessels within the customs waters to examine and inspect a ship and its contents, including cargo and closed containers [69]. The Coast Guard is authorized under the same statutes to stop vessels on the high seas, "for the prevention, detection, and suppression of violations of the laws of the United States." The Guard may "examine the ship's documents and papers, and examine, inspect, and search the vessel and use all necessary force to compel compliance." A "substantial" government interest exists concerning enforcement of documentation laws.

These laws have granted consistent authority through an act from the very first Congress [70]. On this basis, the Supreme Court has generally allowed searches of marine vessels without warrants due to marine vessels being easily transportable, and the lack of ability to set up roadblocks at sea as on land [71, 72]. The analysis is not dissimilar to those of motor vehicles, as both ships and vehicles are instruments of transportation.

Even though broad statutory authority exists authorizing the Coast Guard to stop vessels outside territorial waters, courts still require probable cause. This may take the form of a ship in distress, or appearance of distress, or prior credible information a crime is being committed. The Coast Guard may also stop ships to conduct a safety inspection or to check for proper registration. While the Coast Guard can make these types of stops, it may not inspect the private areas of a ship unless evidence of a crime against the Laws of the United States becomes apparent. A pervasive odor of marijuana, for example, or when evidence of a crime is in plain view, can elicit a probable cause search that does not offend the Fourth Amendment.

There are some variations on the validity of a search when the Coast Guard is joined by agents of the Drug Enforcement Agency or the Customs Department. In a situation of this nature, the Coast Guard may not delegate its authority to other government agents, and those agents do not have authority to board a vessel and conduct a search [73]. Custom agents, however, do have some independent statutory authority and the legality of searches by these agents is measured against their authority and the Fourth Amendment [74].

Once the authority of an agent of the United States is established, the analysis turns on standard Fourth Amendment mechanisms for upholding or not upholding a warrantless search of a vessel.

5.3.3. International border searches

Warrantless, suspicionless searches and seizures are reasonable simply because they occur at the border. People may be stopped and searched at the international border or its functional equivalent (i.e., international airport). Agents can search their belongings without suspicion of wrong doing pursuant to the long-standing right of the sovereign to protect itself from the entry of persons, dangerous objects, or mail into the nation [75, 76]. A person lawfully stopped at the border may be further detained, beyond a routine customs search, if law enforcement officials have reasonable suspicion of criminal activity. However, "Terry" protections concerning length and intrusiveness of the search do not apply [77]. Common application is a person suspected of alimentary canal drug smuggling being stripped searched, receiving a body cavity search, and then either having an abdominal X-ray or monitored bowel movements.

Inland or roving border patrol search and seizures are subject to traditional Fourth Amendment standards. A person, however, appearing only to have foreign ancestry, is not reasonable suspicion for the intrusion. Other factors must exist [78].

5.3.4. Open fields

Open fields are not protected. They are not "effects." No legitimate expectation of privacy exists outside of the curtilage, or in an open field regardless of fences, regardless of posted no trespassing signs or its secluded location. (pastures, wooded areas, open water, vacant lots) The Fourth Amendment applies to curtilage [9]. It does not apply to aerial observations (flyovers) and aerial photographing of open fields within navigable airspace [79, 80].

5.3.5. Abandoned property

Protection does not extend to abandoned effects, including garbage left for collection outside of the curtilage [81].

5.3.6. Plain view

An item of an incriminating nature may be seized without a warrant if it is in "plain view" of an officer who is lawfully present at the scene. The item is in plain view if the officer (1) observes it from a lawful vantage point; (2) has a legitimate right to be on the premises or physical access to it; and (3) its nature as an instrumentality or fruit of a crime or contraband is immediately apparent when observed – probable cause to seize it. This doctrine allows a warrantless seizure. The use of a flashlight or field glasses is not prohibited [60]. Courts have expanded this doctrine to plain hearing, plain smell and plain feel principles [82]. Complications arise when the government uses sensory enhancements to see, hear, or smell [83]. A sniff test by dogs is not a search [41].

5.3.7. Electronic surveillance

Electronic surveillance generically refers to interception of a communication's content (conversation) or acquisition of call identifying information (number dialed). The application has been expanded to include all forms of analog and digital telephonic, electronic, and computer communications. It is generally defined as obtaining, or monitoring the contents of any wire, radio communication by use of any electronic, mechanical, or other surveillance device through which the person has a reasonable expectation of privacy, and a warrant is required for law enforcement purposes [84]. The three primary lawful techniques authorized for electronic surveillance to law enforcement are pen registers, trap and trace devices, and content interceptions.

Advances in technology have resulted in surveillance being conducted in greater secrecy and with greater expediency. Which is why Justice Scalia in *Kyllo v. United States* told society to be wary of "this power of technology to shrink the realm of guaranteed privacy" [85]. The *Kyllo* decision is limited to sense enhancing technology used on a person's home and importance from governmental intrusion in the home. Any detail about the home is protected. The Fourth Amendment controls technologically enhanced searches, including those of wiretapping, eavesdropping, computer conversations, and electronic communications. Basic warrant requirements for wire tapping and eavesdropping must be fulfilled, these being (1) probable cause to believe a specific crime has or is being committed; (2) specific persons must be identified; (3) conversations must be described with particularity; (4) limited to short specified duration; (5) termination provisions; and (6) return to court evidencing intercepted conversations. However, the conversation is not considered private, if the person makes no attempt to keep it private [24].

5.3.8. National security electronic surveillance

In cases of domestic subversive investigations, compliance with the Fourth Amendment's warrant provision is required. The President cannot authorize domestic surveillance without prior judicial approval. "These Fourth Amendment freedoms cannot properly be guaranteed if domestic security surveillance may be conducted solely within the discretion of the Executive Branch." Even Congress cannot exempt the President from warrant requirements in protection of domestic security [86].

The Executive Branch and government's duty to preserve national security does not supersede the warrant requirement. Adherence is more necessary than in cases of ordinary crime. Claims of national security are too often utilized to investigate opponents of governmental policies in violation of the First and Fourth

Amendments. All electronic communication surveillance must comply with federal statutes, including Title III of the Omnibus Control and Safe Streets Act [87], which regulates interception and contents of private wire, oral, or electronic communications.

Congress, however, enacted the Foreign Intelligence Surveillance Act of 1978, creating a special court to determine the validity of electronic surveillance requests in foreign intelligence situations. It authorized the President to conduct warrantless surveillance for foreign intelligence exclusively between or among foreign powers, providing there was no substantial likelihood of any US person being overheard in the monitored communications [88, 89]. National security issues and potential abuse of executive powers are germane to creation of the USA Patriot Act and confronting terrorism.

5.3.9. Good faith exception

The most severe curtailment of the Fourth Amendment is the "good faith exception" [90]. This judicially created exception is for evidence obtained as a result of the officer's objective, good faith reliance on a warrant, later found to be defective, issued by a detached and neutral magistrate (e.g., clerical errors, case law later changed by another judicial opinion, facially valid statute or ordinance as then exists even if later declared unconstitutional, law is changed by court decision, or acting on a defective search warrant). The standard has evolved to "permit the introduction of evidence obtained in the reasonable good-faith belief that a search or seizure was in accord with the Fourth Amendment"... " '[the rule]' cannot be expected, and should not be applied to deter objectively reasonable law enforcement activity" [91, 92]. "Good faith" is limited to "the objectively ascertainable question whether a reasonably well trained officer would have known the search was illegal despite the magistrate's authorization." It is an objective test [91]. The exception does not cover improperly obtained or executed warrants. This being, erroneous information provided to the magistrate, abandonment of judicial impartiality, lacking of probable cause based on a totality of the circumstances [93].

The same objectively reasonable "good faith" rule applies in determining whether officers obtaining warrants are entitled to qualified immunity from suit [94].

5.3.10. Future surveillance technology searches

Constitutional principles do not exist in a vacuum. They are framed by and for the affairs of a modern state [95]. Justice Scalia's opinion in *Kyllo* was written in anticipation of considerably more sophisticated and powerful imaging devices. Many of the newest technologies however, which are designed to "sniff out" drugs, explosives, identify terrorists or illegal aliens when they travel are probably going to be more constitutionally acceptable to the Supreme Court. How the judicial and other branches of government balance emerging invasive technologies with ancient right to privacy will be indicative of this nation. It will further impress upon the judiciary to be conversant in the latest technology and scientific research [96].

5.4. Remedies

The Fourth Amendment is a restriction against government action only. Evidence obtained in violation of the Fourth Amendment is excluded subject to recognized limitations and remedies. It is immaterial that the intrusion was in aid of law enforcement. The police have the burden of establishing their conduct is within the exception.

5.4.1. Exclusionary rule

The Fourth Amendment is enforced through use of the Exclusionary Rule. This is a judicially created doctrine which prohibits introduction of evidence obtained in violation of a defendant's Fourth, Fifth, and Sixth Amendment Rights. Evidence procured by illegal police conduct, although otherwise admissible, will be excluded at trial and not used against the defendant [7]. Evidence obtained in violation of the Fourth Amendment is excluded subject to certain recognized limitations. This exclusion is used as a deterrent to illegal police action. The Exclusionary Rule is one remedy for deprivation of a defendant's constitutional rights. Other remedies can include civil suits and injunctions.

5.4.2. Scope of rule: fruit of the poisonous tree

The Fourth Amendment exclusionary rule applies not only to direct products of illegal governmental conduct, but also to secondary evidence. Generally, illegally obtained evidence is excluded, and so is all other evidence obtained or derived from that evidence. Colloquially, this is known as "fruit of the poisonous tree doctrine" [97]. The courts have begun narrowing the rule's scope by balancing its purpose (deterrence) against its cost (exclusion of probative evidence). The stronger the link between police misconduct and the evidence, the greater likelihood it will be excluded. This sanction is subject to the prosecution establishing any of the following exceptions: (1) an independent source for the evidence [98]; (2) intervening act of free will by defendant to break the causal connection [99]; (3) inevitable discovery [100]; (4) live witness testimony concerning police conduct [101]; and (5) in-court identification of defendant [102].

5.4.3. Limitations to exclusionary rule

The Exclusionary rule is usually not applicable to grand jury proceedings, civil proceedings, internal agency rules, and parole revocation hearings.

5.4.4. Standing

The appropriate party to contest the illegal search or seizure of allegedly illegal evidence must have "standing" to do so. Standing is when a person has some legitimate interest in the premises searched. It must violate the person's own reasonable expectation of privacy [103]. It is based on the totality of the circumstances. Constitutionally, the same illegal search might affect the rights of one person and not another. Standing is not normally applicable to, for example, third party premises, co-conspirators, things held out to the public. The practical effect is to limit the number of people who can contest an unconstitutional search.

5.4.5. Tort

Given the number and importance of Supreme Court rulings on police procedure, the Fourth Amendment lacks the capacity to ensure compliance on a daily basis. Compliance with court decisions in the field is uneven at best. If an illegal search does not result in a prosecution and conviction, there are no grounds for an appeal [7]. Tort litigation to protect civil rights and civil liberties under state and federal law has little impact on police reform, even when confronted with rising costs of litigation. Despite achievements in minimum standards of lawful behavior, American policing falls short of genuine accountability [104].

6. SURVEILLANCE TECHNOLOGY

Electronic monitoring is surreptitious. It allows for monitoring when individuals believe they are conducting activities in confidence. The very intrusiveness of these techniques and technologies requires controls on their use and Fourth Amendment protections. Electronic surveillance is undiscriminating. Everything is collected upon activation. Probable cause is now measured against modern surveillance and sense enhancing technology.

6.1. New surveillance technology

New technologies test the judicial conscience [105]. Effective law enforcement and abatement of crime are envisioned through new technology. Unfortunately, it is often achieved by unanticipated intrusions into Fourth Amendment protections. When the government utilizes a device that is not in general public use, to explore details of a private home that would previously have been unknowable without physical intrusion, the surveillance is a Fourth Amendment "search," and is presumptively unreasonable without a warrant [106]. The courts have not applied the *Kyllo* decision to any devices other than thermal imagers [107]. The *Kyllo* standard, however, does not affect technologies used in contexts of border patrols and industrial complexes [108].

Sense-enhancing technologies are predominantly derived from the military and applied to domestic surveillance. These impressive devices permit detection of heat radiating from a building (thermal imaging), identify particles on a person's body, see through walls, and peer through clothing [109]. Operational technology for electronic strip searches through body scanners is available using low-intensity X-rays to see concealed weapons, reveal images of all items in pockets, purses, briefcases, and underneath clothing. "The images, although explicit, are not pornographic" [110].

Justice Scalia expressed concern over developing technology that "could discern all human activity in the home" [111]. The same concern was previously published in the American Bar Association (ABA)'s standards for technology-assisted physical surveillance [112]. The ABA's commentary predicts increased use of illumination, magnification, and detection devices by law enforcement.

Surveillance technology can be divided into general categories: video surveillance, tracking, illumination, and telescopic and detection devices. The technical developments in each method have been dramatic.

Video surveillance allows viewing of a building's interior, workplaces, and public thoroughfares at anytime. Conspicuously overt and covert observation can be obtained in virtually any circumstance through wide-angle and pinhole lenses, night vision equipment, and super magnification capacity. They are used to examine private areas and public places. Cameras can be placed in picture frames, briefcases, pens, suit lapels, cellular telephones, stuffed animals, etc. Permanent records of the observed intercepted activities can be transmitted simultaneously to the recipient. Digitalization of video provides sharper images, easier storage, indexing, and quicker retrieval of desired images.

Two devices of interest are the radar flashlight and "Millivision" concealed weapons detector. The radar flashlight is a through-the-wall handheld hair dryer size device that can penetrate 8 inch concrete to detect motion, which is translated in light signals for determining source of movement. The device is able to detect subtle breathing and was used for rescue work at Ground Zero after the September 11, 2001 attack. It can be used at a distance of 250 ft [113].

6.2. Tracking

Tracking surveillance technology is varied in design and form. It ranges from simple beepers to sophisticated "intelligent transportation systems." For example, there is: radar to monitor over the horizon; bi-static sensors for passive retrieval of emissions (cellular phones) or active sonar-like capacity; tagging systems that use projectiles to attach transmitters to moving objects; illumination; telescopic; and detection systems.

6.3. Telephonic wiretap

A pen register is a mechanical device that records the numbers dialed on a telephone by monitoring the electrical impulses caused when the dial on the telephone is released. It does not overhear oral communications and does not indicate whether calls are actually completed. They can be used to record the telephone number dialed by the subject of the surveillance. "Trap and trace" devices, are used to record the telephone numbers of incoming calls received by the subject [114]. They are also used to capture source and address information for computer conversations (electronic mail) [115].

The Patriot Act expands the definition of pen registers and trap and trace devices for use with electronic communications (such as e-mail). Police officers can now determine the routing and addressing information of outgoing e-mail (but not the actual contents of the communication), while a tap and trace device permits similar information to be gathered from the incoming messages that the subject receives [114, 116].

6.4. Internet software

At the request of law enforcement, Congress enacted the Communications Enforcement Assistance for Law Enforcement Act (CALEA) [117] to assist them in conducting electronic surveillance. CALEA requires the telecommunications industry, manufacturers of telecommunications equipment, and support service providers to comply with these objectives. Manufacturers and carries are required to design, develop, and deploy equipment, facilities, and services that are compatible with legally authorized electronic surveillance. These requirements include, for example, unobtrusive interception of information, protecting the privacy and security of nonauthorized communications, expeditious isolation and interception of the communication's content, and identifying characteristics. The FBI, Justice Department, and Drug Enforcement Agency, among other law enforcement agencies, are actively utilizing CALEA [118].

The FBI uses a variety of software packages to affect an electronic wiretap. The general practice is to take a device and attach it directly to an Internet provider's (ISP) system to conduct the surveillance. The FBI's capacity to intercept Internet traffic for a given suspect continues to evolve. Carnivore or DCS1000 was abandoned in by the FBI in January, 2005 for commercially available eavesdropping content interception software [119]. The FBI usually requested court orders to use Internet wiretaps during investigations of terrorism, child pornography and exploitation, espionage, information warfare, and fraud. Wiretaps in these circumstances are easily abused. These surveillance operations have to be conducted in a way that safeguards against privacy violations regardless of intent. A lack of public auditing may shield these abuses.

6.5. Data mining

The US Constitution, federal statutes and regulations, and state law combine to govern the collection, use, and disclosure of information. The Constitution provides certain privacy protections, but does not explicitly protect information privacy. Generally, federal law addresses privacy issues and personal information by topic (e.g., education, telecommunications, privacy, health information, motor vehicle, communications and communications records, financial and credit information, children's online (Internet) privacy) The individual's interests are usually balanced with the government's need, with authorization for personal information normally being sought through warrants, subpoenas, and court orders [120].

Data mining is the search for significant patterns and trends in expansive databases, using sophisticated statistical techniques and software, for analysis and prediction. It is used to reveal patterns and relationships. The government uses data mining technology for various purposes, including patterns of criminal behavior and terrorist activities (e.g., money transfers, communications, identify and track individual terrorists through immigration and travel record). It does not, however, provide the value or significance of these patterns, causal relationships, use of data for purposes other than which it was intended ("creep"), and privacy concerns [121]. The government relies on law enforcement, intelligence, and information collected in the public sector. The collective information is combined into a centralized repository. The Department of Homeland Security, Department of Justice, FBI, and numerous state and local law enforcement agencies have access to this information. But they do not necessarily collaborate with each other on its analysis or use. Access to information raises a plethora of legal and policy issues that will not be discussed in this chapter, other to acknowledge they exist. For further information see Ref. [122].

Expansive amounts of unique identifying characteristics of individuals are kept in a multiplicity of databases, thereby creating an enormous repository of information. This information can consist of transactions and biometric data. Transactional data may include financial (e.g., banks, credit cards, and money transmitters, casinos, and brokerage firms), educational, travel (e.g., airlines, rail, rental car), medical, veterinary, country entry, place and event entry, transportation, housing, critical resources, government, and communications data (e.g., cell, landline, Internet). Biometric data could include face, fingerprints, gait, DNA, and iris data. Some of the data is useful for anti-terrorism purposes – connections between passports, visas, work permits, driver's license, credit card, airline tickets, train tickets, rental cars, gun purchases, chemical purchases, criminal history, etc. Data mining techniques facilitate use of this information to analyze patterns of behavior. This information in combination with other information is used, for example, in airline passenger profiling systems [123]. The Patriot Act [124] has authorized the sharing of information between investigators. It permits sharing of information between FBI and federal agencies without judicial oversight. It includes disclosure of grand jury information without judicial supervision and is applicable to all criminal investigations without regard to citizenship.

7. TERRORISM

Relevant sections of the Homeland Security Act of 2002 (HSA) [125] and the Safe Explosives Act of that law, which is Title II of that Act, are presented with applicable definitions of explosives and terrorism.

The term "terrorism," according to HSA, Sect. 4(15), is defined as: any activity that – (A) involves an act that – (i) is dangerous to human life or potentially destructive of critical infrastructure or key resources; and (ii) is a violation of the criminal laws of the United States or of any State or other subdivision of the United States; and (B) appears to be intended – (i) to intimidate or coerce a civilian population; (ii) to influence the policy or a government by intimidation or coercion; or (iii) to affect the conduct of a government by mass destruction, assassination, or kidnapping.

7.1. Explosives

Explosives have enabled people and society to accomplish many remarkable engineering feats. They also are used maliciously to commit crimes such as murder, burglary, extortion, anarchy, sabotage, and terrorist activities [126]. As explosive devices become more sophisticated, their use and detection will affect society's notion of privacy. Affected perception will include access to civic administration buildings and transportation systems.

An "explosive" is defined as a substance, or combination of substances, designed to undergo a violent bursting with expansion, noise, and destructive effect, such as and including, dynamite, gunpowder, and nitroglycerin, blasting caps, detonating fuses, black powder, gunpowder, or other like explosive. To be distinguished from substances such as gasoline, oils, and gases, which are usually regarded as combustible rather than explosive [127]. Courts usually categorize gasoline, oils and other combustible substances as incendiary devices. The statutory definition was expanded to include any materials "that spontaneously emit ionizing radiation" [128]. Even if the item is incapable of detonation, it is still a destructive device.

The term "explosives and dangerous articles" comprises not only explosives but also other dangerous articles such as, inflammable liquids, inflammable solids, oxidizing materials, corrosive liquids, compressed gases, and poisons. Gasoline and certain other petroleum products are classed as inflammable liquids. Explosives and dangerous articles are synonymous for motor carriers and vessels [129].

An investigative search for explosives and dangerous articles by the government usually includes computer software, books, data, paraphernalia, information on creation, and other items. The dual use of goods and technologies (recombination of domestic household or agricultural products, flammable liquids, inflammable liquids, inflammable solids, oxidizing materials, corrosive liquids, compressed gases, and poisons) all of which may be a basis for normal use, entertainment, suspicious activities, civil disobedience, threats of terrorism or possible worse (e.g., ammonia bombs, flash powder, and "Drainobombs").

Homeland Security Act, Title XI, Subtitle C contains the Safe Explosives Act [130]. The Act is designed to heighten security for explosive materials by requiring all persons desiring to obtain explosives, for any use, to possess a federal permit or license [131]. The Safe Explosives Act [132] addresses procedures and requirements in the following areas: permits (Sect. 1122(a)–(e)); inspections (Sect. 1122(f)–(g)); background checks and clearances (Sect. 1122(h)); prohibitions on distribution and possession (Sect. 1123); required samples (Sect. 1124); relief from disabilities (Sect. 1126); theft report requirements (Sect. 1127); and authorization for appropriations (Sect. 1128).

It is a violation of federal criminal law to knowingly transfer any explosive materials, knowing or having reasonable cause to believe that such explosive materials will be used to commit a crime of violence, or drug trafficking crime [133, 134]. Generally, state statutory provisions have prohibited as criminal offenses the sale, offering or exposing for sale of fireworks [135, 136].

The law also prohibits use of the mails as a method of transporting and delivering explosive devices [137] and weapons [138].

The federal requirements [139] state no person shall "knowingly transport, carry or convey" liquid nitroglycerin, fulminate in bulk in dry condition, or other similarly dangerous explosives, radioactive materials, or etiologic agents "on or in any car or vehicle of any description operated in the transportation of passengers or property" by any carrier "engaged in interstate or foreign commerce, by land," except under regulations prescribed by the appropriate agency with respect to the safe transportation of such commodities. (Carrier means any person engaged in the transportation of passengers or property by land, as a common, contract, or private carrier, or freight forwarder, as used in the Interstate Commerce Act, and officers, agents, and employees of the carriers [140].) The section also requires the agency to "determine and prescribe what explosives are 'other similarly dangerous explosives,' " and permits it to prescribe the routes over which they shall be transported.

Validity of 18 U.S.C.A. Sect. 832. et seq. [141] and its predecessor statutes have not been questioned. Courts upheld criminal actions by stressing the statute's importance in the protection of passengers aboard public conveyances.

Additionally, it is unlawful for any person to barter, sell, dispose of, or pledge or accept as security for a loan, any stolen explosive materials which are moving as, which are part of, which constitute, or which have been shipped or transported in, interstate or foreign commerce, either before or after such materials were stolen, knowing or having reasonable cause to believe that the explosive materials were stolen [141]. The constitutionality of the statute making it unlawful to transfer stolen materials has been upheld, despite its failure to require an evidentiary nexus between the prescribed activity and interstate commerce [142].

The bombing of government buildings, public transportation systems, and using certain weapons of mass destruction is illegal [143].

It is illegal to dispose of explosive materials or compounds with the knowledge, intent, or reason to believe that such materials or compounds are to be used to injure persons or property [144]. It is also, illegal to transfer any item designed to explode or produce an uncontained combustion with the intent to cause bodily or physical harm [145].

Taggants are plastic, microscopic, color-coded chips, which can be embedded in explosives at the time of manufacture and are identifiable after detonation. The Bureau of Alcohol, Tobacco, Firearms and Explosives (ATF) maintains records regarding the color coding of the taggants, thereby permitting tracing of the explosive to its manufacturer and purchasers. Placing of taggants in explosive does not violate the Fourth Amendment right from unreasonable searches and seizures and penumbral right of privacy. Taggants do not reveal intimate information about the person [146].

The federal government is the only entity that can authorize the manufacture, sale, storage, and use of explosives. Therefore, it can issue administrative regulations requiring mandatory and random inspection of facilities as a licensing requirement.

The ATF, the Department of Labor (storage and industrial use), and the Nuclear Regulatory Commission (access to restricted areas storing nuclear material) do not focus on Fourth Amendment restrictions. These agencies do not address a waiver of any privileges relating to: Fourth Amendment rights or searches in their regulations; statutes; forms for licensing explosive storage; sale; commerce; and forms for reporting the theft of explosives. Individuals seeking reinstatement of lost rights to handle explosives are not requested to waive their Fourth Amendment rights as part of the application process [147].

In 2000, the US government began publishing a list of explosives covered by federal law in the Federal Register. It includes in excess of over 200 specific chemical and trade name items [148]. The Federal Register does not reference any Fourth Amendment waivers in federal laws or regulations specific to explosives.

When the theft of explosives is investigated, the threat is balanced against known facts to create a low threshold of probable cause for a search. If a genuine threat is represented, exigent circumstances would aptly permit a warrantless search in a criminal investigation.

Improvised explosive devices (IEDs) or homemade bombs are limited by the creativity and ability of their maker. They can be lethal, destructive, noxious, or of an incendiary nature. IEDs consist of, in simple form, a charge, detonator, and mechanical or electrical initiator. Step-by-step instructions and diagrams for bomb making are available from publications and the Internet. Do-it-yourself explosive devices can be made from household and agriculture products. It is not particularly difficult for someone to improvise from a large number of household chemicals, that when mixed together, can produce highly destructive explosive devices. Bombs can take the form of exploding light bulbs, computer diskette bombs, tennis ball bombs, fertilizer bombs, napalm, mailbox bombs, pipe bombs, car bombs, and paint bombs, among others.

Common materials found in homemade bombs are, for example, treated starch, flour, sugar and cellulose, powder from small arms ammunition, firecrackers, match heads, and ammonium nitrate from fertilizers. Detonators may consist of: blasting caps; percussion primers from gun ammunition; flashbulbs; flashbulbs to ignite heat-sensitive explosives; black powder; smokeless powder; incendiary mixtures; match heads; ammonium or urea nitrate fertilizer mixed with fuel oil; acetone peroxide; potassium or sodium chlorate. The list of possible chemicals for improvised explosive devices is endless. Locations with large quantities of chemicals such as nitrates, chlorates, perchlorates, nitric acid, aluminum powder, magnesium, sodium, sulfur, charcoal, sugar, and sulfuric acid, may provide circumstances giving rise to probable cause for a police officer to obtain a warrant to search the premises [126].

Registration requirements for purchasing, possessing, and using explosives have been revised with increased restrictive requirements in recent years [149]. Increased scrutiny and regulation of commercially available components of IEDs can be anticipated.

Domestic bombings are characteristically accomplished by utilizing improvised “low-yield” explosives. An example of a low-yield explosive is black powder.

Notable domestic terrorist bombings from do-it-yourself explosive devices within the United States, include the Unabomber – 25 May 1978 to 3 April 1996 (Theodore Kaczynski referred to by the FBI referred as the UNABOM from “university and airline bomber,” a.k.a. Unabomer, Unibomber, and Unabomber); Oklahoma City – Alfred P. Murrah Federal Building 19 April 1995 (Timothy James McVeigh); Olympic Park in Atlanta, GA, 27 July 1996, abortion clinics in both Atlanta, GA and Birmingham, AL, and homosexual nightclub (The Others Lounge), Atlanta, GA, 16 January 1997 to 29 January 1998 (Eric Robert Rudolph); Rural mail box pipe bomber – 3 May 2002 (John Luke Helder, a 21-year-old University of Wisconsin student who planted 18 pipe bombs in rural roadside mailboxes in Colorado, Illinois, Iowa, Nebraska, and Texas while in the process of arranging a geographic "smiley face" bomb pattern. They injured four postal carriers and killed two residents before he was apprehended. Helder later pled guilty by reason of insanity [150]); and World Trade Center, Manhattan, New York, 26 February 1993, Islamist terrorists. (A 1300 lb (600 kg) bomb was made of urea nitrate, nitroglycerin, and bottled hydrogen.)

Common types of bombs obtained or produced by international terrorists are car bombs, letter bombs, parcel bombs, nail bombs, suicide bombs, mortar bombs, drop bombs, buried bombs, and dirty bombs [151]. These bombs contain high yield explosives. Examples of high-yield explosives are dynamite, trinitrotoluene (TNT), nitroglycerin, detcord, C-3, C-4, RDX (cyclonite), PETN (pentaerythritol tetranitrate), and Semtex. Semtex was popular with terrorists because it was difficult to detect and easily obtained. As little as 250 grams could down an airliner. Only 9.5 ounces (271 grams) were used in the case of Pan Am Flight 103 [152]. Manufacturers now add ethylene glycol dinitrate to Semtex for a distinctive vapor signature and also an identifying metallic code as a detection taggant in industrial explosives and military bombs.

Selected noteworthy international terrorist bombings of civilian targets: Madrid, Spain train bombings of 11 March 2004; Shoe Bomber on 22 December 2001 (Richard Colvin Reid); Pan American Flight 103 Lockerbie, Scotland on 21 December 1988; and London Bombings (trains and bus) 7 July 2005 London, England, all of which were perpetrated using high-yield explosives.

8. TECHNICAL SECURITY ADMINISTRATION – ADMINISTRATIVE SEARCHES AND SEIZURES

Transportation is an essential component of the US economic structure. Events subsequent to September 11, 2001 in the United States and other countries, reveal the high vulnerability of transport systems. Given the safety and political consequences, more attention is placed on system security.

8.1. Transport security

The Federal Aviation Administration Reauthorization Act of 1996 – requires passenger profiling, explosive detection technology, procedures for passenger to bag matching, and certification for screening companies. On 21 November 2001 Congress created the multimodal Transportation Security Administration (TSA), within the US Department of Transportation, to regulate aviation security for all transportation modes. Its primary mandate is to prevent entry of terrorists and implements of terrorism into the United States. A predominant focus of the TSA security mandate is to search for weapons, explosives, and illicit chemicals. TSA is headed by the Under Secretary for Border Transportation and Security [153]. The undersecretary and employees have certain law enforcement powers including carrying of firearms, making searches of baggage and passengers, make arrests – with or without warrants when probable cause exists. TSA's duties predominately focus on airport and aircraft security, even though its mandate is much broader and encompasses all forms of transportation. Its duties include: regulating security in all modes of transportation; researching and developing security issues; administrative searches of baggage, passengers, vehicles and cargo; assessing security threats; criminal history checks, identification systems; developing and maintaining security facilities; and much more [154]. The use of diversified technologies and tools is permissible at an administrative level providing it results in a good faith effort to protect the transportation system, deterring passengers from carrying weapons and contraband, and enforcement of constitutional rights [155]. However, TSA cannot intrude unnecessarily into individual privacy or civil liberty. This includes random searches at airport security checkpoints of carry-on bags that are passed through an X-ray scan for explosives, even though they are not suspicious [156]. Therefore, trace analysis screening on passengers should be non-intrusive or minimally intrusive, while maintaining an unimpeded flow of passenger movement.

8.2. Explosives detection

The Department of Homeland Security (DHS) is required to place high priority on developing and deploying equipment to screen all checked baggage for explosives. It is also required to screen selected passengers for explosives [157]. In response to this mandate, TSA, through the Department of Homeland Security, deployed two types of screening equipment: (1) explosive detection systems (EDS) that use computer-aided tomography X-rays (CAT scan technology adopted from the medical field) to recognize explosives. It resembles a large dumpster with a conveyor belt; and (2) explosives trace detection (ETD) that uses chemical analysis to detect vapors and explosive residue. The ETD units are approximately the size of photocopy machines. It requires a worker to rub luggage with a swab that is analyzed for chemical compounds. The test can detect the presence of explosives with 10 seconds [158, 159]. TSA is pursuing research and development of new technologies for explosive screening of air cargo shipments.

The equipment for screening passengers and baggage is designed to identify trace amounts of specific known explosives. Analytic trace detection is conducted using mass spectrometry, gas chromatography, chemical luminescence, or ion mobility spectrometry. Ion mobility spectrometry is most commonly used. Novel explosive material will not be probably detected by these systems. Information on the equipment's technical performance is not publicly available because of security reasons, which inhibits an independent analysis of equipment's performance [160].

In 2005, TSA began using explosive trace portal machines in an attempt to confront the presence of explosives in the country's 40 busiest airports. The units resemble oversize walk through metal detectors. Passengers are randomly requested to walk into trace portal detectors, stand still for a few seconds while several "bursts" or "puffs" of air are released on the person dislodging microscopic size particles. These particles are then collected from the air and analyzed for traces of explosive material. A computerized voice and light indicates when the person may leave the portal. The average cost is $150,000 per unit.

A handheld vacuum wand is used for collecting vapors along a surface and surrounding air of objects and people. Collected samples from the handheld screening device utilize any of several technologies to analyze the sample for different explosives and related energy decomposition products (i.e., colorimetry, ion mobility spectrometry, pressure activation, quadrupole resonance). Dogs trained to sniff for explosives are additionally used to prevent explosives from entering aircraft.

TSA is considering two different types of portal X-ray machines for screening handheld baggage. These are a backscatter phototype image machine and a multi-view X-ray machine [161].

Regulations and screening of passengers for detection of explosives have been established [162]. Detection on passengers is more difficult because of possible privacy concerns, difficulty in sampling, and different analytic sensitivity requirements. It remains a constant concern of TSA and the airline industry.

8.3. Passenger profiling

Travel creates unique circumstances where usual search warrant application requirements would frustrate the ability of law enforcement to do their job. The exigencies of immediacy and mobility are invoked to reduce a person's constitutional rights. The Fourth Amendment does not prevent the government from developing and using a profiling system for the purpose of ensuring security of the mass transportation system (airlines, mass transit, railroads, marine vessels, etc.). The obvious question is whether passenger profiling will deter, if not stop, use of explosives on mass transit systems.

In 1996 the Federal Aviation Reauthorization Act authorized the development of computerized system known as Computer-Assisted Aviation Prescreening System (CAPS). It was designed to determine which passengers were unlikely to have an explosive device in their checked baggage, thereby focusing on a smaller number of passengers and baggage. Upon review by the FBI and Department of Justice's Civil Rights and Criminal Divisions, CAPS did not account for characteristics related to ethnicity, gender, or religious faith. CAPS was expanded and renamed CAPPS II in response to the September 11, 2001 terrorist bombings.

Data technology was developed by Lockheed Martin Management and Data Systems was developed into a controversial computerized system known as Computer-Assisted Passenger Pre-Screening II ("CAPPS II"). It is used for security risk assessment. CAPPS II collects nearly, if not everything, available on persons purchasing airline tickets. Creates a profile and stores it in a central database. The information would be available to local, state, federal, and international law enforcement agencies [163]. CAPPS II allegedly identifies potential terrorists by comparing flight reservation data with information contained in governmental and commercial databases. CAPPS II is required to provide a system to correct erroneous information and address due process rights. It is used in conjunction with the No-Fly and Secure Flight Program (Selectee List) to deter, detect, and prevent known or suspected terrorists from boarding commercial aircraft [164].

The No-Fly and Selectee lists are Security Directives. They were created by TSA pursuant to legislation [165], which authorizes the TSA Under Secretary to issue Security Directives without providing notice or an opportunity for comment to protect transportation security.

The notice requirement of an administrative search must be made with passengers being free to withhold their consent to be profiled before completing the reservation process. (e.g., producing a valid photo ID) However, should the passenger withhold their consent, their alternative would be to choose a different mode to travel. This exception to the Fourth Amendment permits governmental profiling of passengers [46]. Information on "no fly lists" and profiling programs does not have to be produced because of security concerns. Material categorized as "sensitivity security information" (SSI) does not have to be disclosed by the federal government under the Homeland Security Act. The Homeland Security Act covers 16 areas, including security programs and contingency plans, security directives, security measures, security screening information, and a general category of "other information" [166].

9. USA PATRIOT ACT

9.1. Creation

Recent events, including the World Trade Center and Pentagon terrorist attacks of September 11, 2001, have induced rapid fundamental changes from historical perspectives of constitutional rights and governmental interests. Necessary questions to ask are (1) does the technology, practice, and procedure make society safer or provide an illusion of safety; (2) is the privacy intrusion proportional to the security benefit; and (3) are there other demonstrable less privacy intrusive methods available that attain the same objective.

Americans generally agree the government should aggressively pursue and confront terrorism with all appropriate means available. The question is what means are appropriate to deter and protect Americans from terrorism while maintaining democracy and justice. Today's use of emergency powers are trade-offs between freedom and security. These may become permanent over time.

> "Experience should teach us to be most on our guard to protect liberty when the government's purposes are beneficent. Men born to freedom are naturally alert to repel invasion of their liberty by evil-minded rulers. The greatest dangers to liberty lurk in insidious encroachment by men of zeal, well-meaning but without understanding [167]."
>
> "The erosion of conditional releasees' liberty makes us all less free. Privacy erodes first at the margins, but once eliminated, its protections are lost for good, and the resultant damage is rarely, if ever, undone. . . . [168]."

Constitutional safeguards, including active utilization of governmental checks and balances, must be highly maintained. The system of "checks and balances," through a separation of powers between the Legislative, Executive, and Judicial Branches of government, was created by the Constitution to prevent consolidation or abuse of power by any single branch. “Checks” refers to responsibility of each branch to monitor activities of the other branches. “Balances” refers to the ability of each branch to limit the powers of the other branches in general and specific cases.

Congress passed the Uniting and Strengthening America by Providing Appropriate Tools Required to Intercept and Obstruct Terrorism (USA PATRIOT ACT) Act of 2001 [169]. On 26 October 2001 President George W. Bush signed the USA Patriot Act into law. The Patriot Act is a series of amendments to numerous sections of the US Code. The Act’s 156 sections amend several Acts of Congress ranging from the International Emergency Economic Powers Act, to Title III of the Omnibus Crime Control and Safe Street Acts of 1968 (Title III). The stated purpose of the Act is to provide law enforcement with the necessary enhanced investigatory tools to combat terrorism. The Act’s predominant use is to deter and punish terrorist acts in the United States and elsewhere. The Patriot Act as originally passed consists of 10 titles which intensify and promote domestic security against terrorism. The areas generally encompass: surveillance procedures; international money laundering and financing; border protection; investigative mechanisms for detecting terrorism; victim assistance; pubic safety officers; increased information sharing for critical infrastructure protection; fortifying criminal laws; and improving intelligence collection and integration. It also covers important noncontroversial areas important to law enforcement and America’s critical infrastructure. These provisions have nominal or no impact on civil liberties. The few, but controversial provisions relating to potential enhanced governmental powers pose significant problems for abuses of First Amendment freedoms, Fourth Amendment privacy rights, and other legal concerns. These statutory changes are not mere legal technicalities.

The Executive Branch sought to change warrantless searches and surveillance restrictions of the Fourth Amendment through congressional passage of the Patriot Act. The Act has engendered significant debate over the historic role of civil liberties and comparative abuse of power by previous administrations.

In 2002, President George W. Bush ignored Fourth Amendment protections by ordering a potentially illegal program of secret electronic surveillance (domestic spying) of American citizens. The classified Executive Order is perceived as an abuse of the National Security Act of 1978 (NSA) and Foreign Intelligence Surveillance Act of 1978 (FISA) based on historical principles of the Fourth Amendment. The Executive Branch premised their action upon claims of “hot pursuit” and a novel interpretation of the law, emanating from the war on terrorism (domestic and international) [170, 171].

The Justice Department euphemistically calls electronic surveillance “signal intelligence activities,” as part of its warrantless surveillance program of terrorists and domestic security [172]. The strategy of President Bush’s administration is to combat terrorism by restricting civil liberties. Secrecy and absence of accountability not only jeopardize liberty and privacy, but wastes resources and foster misuse of legitimately acquired information for illegitimate purposes [173].

Pursuant to the President’s (unpublished) Executive Order in 2002, it is estimated over 5000 Americans were subjected to covert electronic surveillance in the subsequent 4 years. Fewer than 10 citizens or residents aroused enough suspicion to consider obtaining a warrant to justify interception of domestic telephone calls. The Bush Administration refused to disclose the actual number of people who were subjected to domestic spying. The discrepancy illustrates pervasive conflicts between operational objectives, compared with the legal and political ramifications in the President's Order to justify the program [174].

Lawsuits were filed by various parties including the American Civil Liberties Union challenging the President's authority to conduct domestic surveillance. The Federal Court for Eastern District of Michigan found surveillance by the National Security Agency to be unconstitutional [175].

9.2. Conflicts between Patriot Act and civil rights

The Justice Department, which is largely responsible for the implementation of the Patriot Act, has provided only limited information to the public regarding how and when the new provisions have been used. The Department is not required to produce this information due to national security interests. In a private group's Freedom of Information Act (FOIA) request, directed to the Department of Justice, seeking disclosure of statistics regarding use of new information and authority for it conferred by the Patriot Act. The Court held the statistical information sought could be withheld on national security grounds [176].

In practice, the Patriot Act and its successors, has circumvented the check and balance system. The Executive Branch has, for example, lowered the threshold of probable cause to the level of suspicion; it has equated criminal activity with terrorist activity; it has removed or delayed notice requirements for warrants; it has required mandatory compliance on third parties for the production of information gathered secretly; it has imposed a gag order upon notice and production of information; it permits sharing of confidential personal information between investigative units; and minimized the role of the judiciary. The overall effect is the Executive Branch and Justice Department are assuming power to define application of the Fourth Amendment. An additional result is the collection of a wide variety of highly personal and sensitive information on law-abiding individuals.

9.3. Discussion

Based on the Patriot Act and its progeny, there no longer appears to be a clear distinction in the law between foreign intelligence and criminal investigations. Significant sections include:

- The "probable cause" requirement being amended for conducting secret searches or surveillance to obtain evidence of a crime (Sect. 218).
- Law enforcement authorities are permitted broad access to sensitive mental health, library, business, financial, and educational records despite previously adopted state and federal laws strengthening the protection of these types of records. (Sect. 215, 218, 358, and 508)
- The Secretary of State has broad powers to designate domestic groups as "terrorist organizations."

- The Attorney General has power to subject immigrants to indefinite detention or deportation even if no crime has been committed (Sect. 411 and 412).
- State and local public universities are mandated to collect information on students that may be of interest to the Attorney General (Sect. 507 and 508).
- All federal investigators from any branch, and prosecutors, may use and share the same data among different agencies.
- Federal investigators are able to use material derived through the grand jury process (Sect. 203).

It is the function of the grand jury to investigate criminal activity and bring indictments of wrongdoing if so warranted. It also has the power to compel testimony and protect the secrecy of its investigations to facilitate its mandate. The grand jury's ability to collect evidence and operate in secret no longer exists. The judicial oversight process between investigative agencies and federal grand juries has been removed. Instead, the grand jury process may now be widened and used as an intelligence investigatory tool without controls, except for possible internal guidelines [177].

The Patriot Act, to some Americans is a threat to democracy and civil liberties; to other Americans, it provides a promise of protection against endangerment of their society. Both opinions are justifiable. The Patriot Act and its progeny are well intended. However, based upon legal traditions, it is philosophically, constitutionally and practically contrary to America's foundational constitutional rights and civil liberties. The Patriot Act, especially concerning the Fourth Amendment, should be periodically revisited by Congress to coincide with basic civil liberties and tenets of constitutional law.

9.4. Application

In the aftermath of September 11, 2001 individuals appear more willing to sacrifice their privacy and constitutional rights to protect the nation. The search and seizure of explosives and dangerous chemicals is representative of areas of constitutional protections. "(H)istory reveals that the initial steps in the erosion of individual rights are usually excused on the basis of an 'emergency' or threat to the public. But the ultimate strength of our constitutional guarantees lies in their unhesitating application in times of crisis and tranquillity alike" [178, 179]. Americans must appreciate that their constitutional rights and safety are not mutually exclusive. "Those who would give up essential Liberty to purchase a little temporary Safety, deserve neither Liberty nor Safety" (Benjamin Franklin [180]). This quotation, slightly altered, is inscribed on a plaque in the stairwell of the Statute of Liberty: "They that can give up essential liberty to obtain a little safety deserve neither liberty nor safety" [181].

10. CONCLUSION

There are two paradigms of legal viewpoints for the detection of explosives and illicit chemicals based upon the Fourth Amendment. The traditional constitutional search and seizure aspects of the law, and second, the informal transitional perspectives predicated upon its manipulation for national security interests. Because of recent domestic and international terrorist acts upon America, the US Government under the Department of Justice, originally through Attorney General John Ashcroft, designed and instituted the abridgement of society's civil rights upon the pretext of homeland security.

The Patriot Act and subsequent legislation dramatically transformed domestic intelligence gathering and law enforcement. The delicate balance between liberty and social order has been affected. It will be many years before Americans can assess the full impact on civil liberties, and especially their long-term consequences for security of the United States. The ability to evaluate these changes in the short term is hampered by the government exercising a high degree of secrecy under the guise of threatened terrorism. As a consequence, the Fourth Amendment's future is in a state flux.

The US Constitution, its Bill of Rights, and corresponding laws are designed and intended to promote peace, prosperity, tranquility, equal justice and freedom. The government must not abrogate the population's personal rights. Therefore, it is incumbent upon all people relying on the legal safeguards to maintain, perpetuate and protect these freedoms. People should always remember – freedom is just a word until it is lost.

DISCLAIMER

This chapter is intended to provide general information; it does not provide legal advice applicable to any specific matter and should not be relied upon for that purpose. Interested parties should review the laws with their legal counsel to determine how the laws will affect them.

DEDICATION

Dedicated by Gil Sapir to his nieces Ella Gili Barzel and Aela Sapir, and nephews Zev Barzel, Elan and Hillel Sapir.

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[178] *United States v. Edwards*, 498 F.2d 496, 502 (2nd Cir. 1974) (Oakes, J. concurring).

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