

# ION SPECTROMETRIC DETECTION TECHNOLOGIES FOR ULTRA-TRACES OF EXPLOSIVES: A REVIEW

Marko Mäkinen,<sup>1\*</sup> Marjaana Nousiainen,<sup>1</sup> and Mika Sillanpää<sup>2</sup>

<sup>1</sup>Laboratory of Applied Environmental Chemistry, Department of Environmental Science, University of Eastern Finland, Patteristonkatu 1, 50100 Mikkeli, Finland

<sup>2</sup>Lappeenranta University of Technology Patteristonkatu 1, 50100 Mikkeli, Finland

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*In recent years, explosive materials have been widely employed for various military applications and civilian conflicts; their use for hostile purposes has increased considerably. The detection of different kind of explosive agents has become crucially important for protection of human lives, infrastructures, and properties. Moreover, both the environmental aspects such as the risk of soil and water contamination and health risks related to the release of explosive particles need to be taken into account. For these reasons, there is a growing need to develop analyzing methods which are faster and more sensitive for detecting explosives. The detection techniques of the explosive materials should ideally serve fast real-time analysis in high accuracy and resolution from a minimal quantity of explosive without involving complicated sample preparation. The performance of the in-field analysis of extremely hazardous material has to be user-friendly and safe for operators. The two closely related ion spectrometric methods used in explosive analyses include mass spectrometry (MS) and ion mobility spectrometry (IMS). The four requirements—speed, selectivity, sensitivity, and sampling—are fulfilled with both of these methods. © 2011 Wiley Periodicals, Inc., Mass Spec Rev 30:940–973, 2011*

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## I. INTRODUCTION TO EXPLOSIVE TRACE DETECTION

### A. Present Threats

The non-peaceful use of explosives and their extensive applications in vicious attacks have substantially increased in recent years causing the worldwide threats of terror activity. Information on the synthesis of toxic and explosive materials can nowadays be easily found from public domains, while raw materials for the synthesis of explosives are commercially available. This results in a growing risk of explosive-based attacks as well as increasing psychological impacts on population.

In addition to short-term attacks causing extensive damage, harmful substances originating from explosives can accumulate in the environment in the long term during their usage, handling, storage, and dumping. As solid materials, they can exist as fine particles in low concentrations, for example, in soil or in the groundwater. In spite of causing no explosive danger, they can remain hazardous in the long term when concentrated. Explosives can be considered as one of the most potential contaminants that possess serious health risks not only to public health, but also to the environment. Juhasz and Naidu published review discussing the environmental fate, dynamics, potential hazard and ecological impacts of explosives in terrestrial and marine environments. It was concluded, that urgent need to direct research towards explosive originated ecological risk assessments (Juhasz & Naidu, 2007). This concern has set a growing need to develop effective detection and analytical methods to improve environmental protection and public health. However, the normal background levels of explosive traces are low within the general public environment (Cullum et al., 2004).

### B. Objectives of This Review

The objectives of this review are to provide exhaustive but concise survey to the current status of the ion spectrometric detection techniques and various analytical applications of explosive detection. The coverage was divided into three discrete areas: sampling and preconcentration techniques, ion mobility spectrometric detection and mass spectrometric detection of explosives. In the first area several explosive sampling techniques are introduced and discussed. The second area is devoted to ion mobility spectrometry. Although this technique is extremely important and common for the detection of explosives it is presumably unfamiliar to majority of mass spectrometrists. Thus a large effort to explain the basics and variations of this technology has been included. The mass spectrometric section contains a survey to large number of different ionization, separation and detection techniques thus revealing the diverse field of explosive detection and analysis. In addition, the properties of some most common explosives are presented.

In short, this review is focused to expound the versatile field of ion spectrometric detection techniques and various analytical applications for different types of explosives. New methods and applications in recent years are emphasized. The discussions concerning timely and the most important articles are elaborated while the other discussions are succinct and condensed. Despite the secretiveness in the field of explosive detection, this review is

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\*Correspondence to: Marko Mäkinen, Laboratory of Applied Environmental Chemistry, Department of Environmental Science, University of Eastern Finland, Patteristonkatu 1, 50100 Mikkeli, Finland.

E-mail: marko.makinen@uef.fi

based on summary of the literature and public material printed in peer reviewed scientific journals.

### C. Ion Spectrometric Trace Detection

Trace detection is defined as the detection and the analysis of microscopic amounts of explosive residues, which can be vapors or particles. Vapors are emitted from the surface of the explosives, while particles are originated from direct contact to explosive materials. The rate of molecular evaporation is so low that the amounts of ionizable (and detectable) molecules are extremely low. For this reason, the two spectrometric techniques could be classified as explosive trace detection (ETD) methods. In the last decades, the development of sensor technologies has increased resulting in detectors with a smaller size and faster operation. Detection technologies in use have, however, their limits in sensitivity, selectivity, speed, versatility, and dynamic range. Most of them are applicable only for laboratory scale; very few analyzers are developed for field use. In real-time measurements one of the most common problems is caused by a background matrix that suppresses the signal of analyte of interest or produces false alarms. These challenges of the explosive detection (Steinfeld & Wormhoudt, 1998) and the instrumentation for trace detection (Moore, 2004) as well as field detecting and monitoring (Yinon, 2002) of explosives have been reviewed. A compact review assessing chemical techniques for detecting traces of explosives in walk-through portals have been written (Nambayah & Quickenden, 2004). A recent and versatile review of different sensor technologies for detection of explosives has been written, but the spectrometric techniques were not discussed (Singh, 2007). Some technical weaknesses can be overcome by multidimensional analysis by integrating two or three techniques that have different detection characteristics. However, these constructions may lack some other important properties. Miniaturization of technologies is also an up to date trend that enables in-field measurements using smaller size instruments.

### D. Traditional Classification of Explosives

Explosives are normally classified based on their properties and usage. In this regard, low explosives include propellants and pyrotechnics, while the compounds used in destructive purposes are classified as high explosives. High explosives are further divided into three subcategories based on sensitivity; these subcategories include primary, secondary, and tertiary explosives. Detailed information on particular explosives can be found from a comprehensive handbook covering the field of explosives (Meyer, Köhler, & Homburg, 2007).

#### 1. Primary Explosives

Primary explosives are materials with high sensitivity to ignition by electrostatic discharge, friction, spark, flame, heat, or impact. In spite of causing lower order detonation, due to their high sensitivity these materials can be used as initiators to detonate secondary explosives. *Triacetone triperoxide* (TATP) is an organic peroxide that displays properties of primary explosives: it has high heat and friction in addition to extreme shock sensitivity. TATP differs from other primary explosives as it explodes entropically without releasing heat. As it is easy

to manufacture, the compound is often used by terrorists (Dubnikova et al., 2002). Because of the absence of nitro group, it is more difficult to detect using conventional analytical methods.

#### 2. Secondary Explosives

The characteristic of secondary explosives is to intensify detonation; they are usually initiated by primary explosives. The secondary explosives are usually nitroaromatics and nitramines that can be either casted or plasticized. The ion spectrometric detection techniques of explosives are mainly based on the chemical properties (i.e., the presence of the nitro group) of the secondary explosives.

*2,4,6-Trinitrotoluene* (TNT) is very stable, insensitive to friction, moisture resistant, and commonly used as one of constituents in the mixtures of explosives. *Dinitrotoluene* (DNT) has six constitutional isomers; from those 2,4- and 2,6-dinitrotoluenes are normally abbreviated as DNT while the rest of these isomers are not used in large scale. *Pentaerythritol tetranitrate* (PETN) is one of the most powerful explosives. It is mainly used only in mixtures of military explosives. *Cyclotrimethylenetrinitramine*, Cyclonite, known commonly as RDX is stable and is used in various military explosive mixtures and in blasting caps. *Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine* (Octogen or HMX) is widely employed in military applications. *Nitroglycerin* (NG) is one of the most known explosives. It is used in manufacturing dynamite and gunpowder and serves as vasodilator in the field of medicine. *Composition explosives* contain different high explosive compounds that do not react with each other. They are usually plasticized and mixed with other additional agents such as waxes, oils, and stabilizers. The composition explosives include, for example, dynamite, Semtex, and C4.

#### 3. Tertiary Explosives

Compounds like ammonium nitrate and ammonium perchlorate are classified as tertiary explosives. They are insensitive to detonation impact and commonly need secondary explosive to initiate. The term “blasting agent” denotes explosive compounds usually based on ammonium nitrate.

#### 4. Propellants and Pyrotechnics

Explosive propellants are widely used to produce gases for propelling rockets and projectiles. Composition of explosive propellants varies depending on the amount of energy required for accelerating the used device. The common use of pyrotechnics is the special effects in entertainment industry; for example, in firework shows. There are also life-saving pyrotechnical applications, such as safety matches, flares, and the initiators of the airbags in automobiles.

### E. Physical and Chemical Properties

Explosives predominantly contain electronegative nitrogen and oxygen that serve as an oxidizing agent for maintaining combustion. Majority of the high explosives use nitrate (originating from nitro group) as the oxidant. Nitrogen and

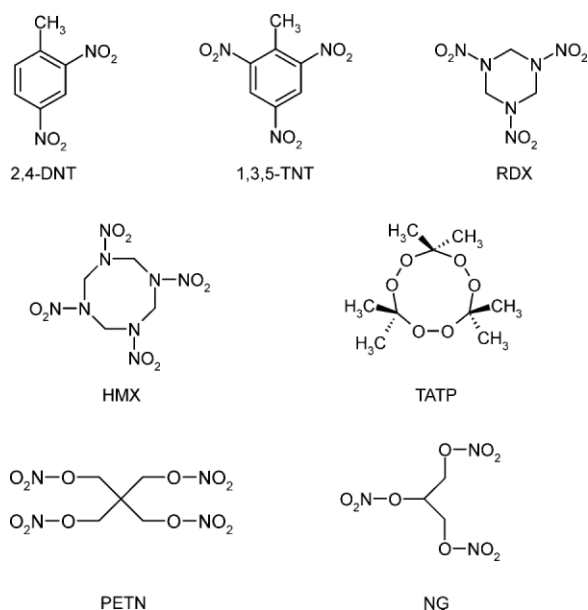


FIGURE 1. The structures of some common explosives.

oxygen content of explosive material correspond to each other, suggesting that the dual analysis of nitrogen and oxygen content can provide reliable indication of the presence of explosives. Oxidizing agents may include chlorates, perchlorates, chromates, and peroxides, too.

### 1. Classification Based on Chemical Groups

From analytical point of view, explosives are classified based on their chemical groups such as (i) nitramines (e.g., RDX, HMX, tetryl); (ii) nitrate esters (e.g., PETN, PGN, HAN); (iii) aliphatic nitro compounds (nitromethane); (iv) aromatic nitro compounds (e.g., HNS, TATB, DNT, TNT, ammonium picrate); (v) peroxides (e.g., TATP); and (vi) acid salts (e.g.,  $\text{NH}_4\text{NO}_3$ ) (Furton & Myers, 2001). Commonly used explosive agents both in military purpose and in scientific research include RDX, HMX, PETN, DNT, and TNT. The explosives containing functional nitro-group as oxidizing agent will produce characteristic signal in most of the detection systems used. Figure 1 represents some of the common explosives.

### 2. Vapor Pressures

The explosive compounds typically have very low volatility and vapor pressure ( $10^{-4}$  Pa or less). The explosives are divided into three classes based on their vapor pressures; (i) high, (ii) medium, and (iii) low. The vapor pressures at 25°C, molecular weights, and different compositions of common explosives are exhaustively presented in an article describing odor chemicals originating from explosives (Harper, Almirall, & Furton, 2005) (Table 1).

Compounds with high vapor pressure, such as TATP, DNT, and NG, have equilibrium vapor concentrations of approximately 1 ppm or higher. With medium class explosives, like TNT and  $\text{NH}_4\text{NO}_3$  the concentration level is approximately 1 ppb; and further decreases with low class explosives, such as HMX, RDX, PETN, to ppt level. This low concentration makes explosives

TABLE 1. Some common explosives and properties

Explosive Class	Explosive		Molecular weight (u)	Formula	Vapour pressure at 25 °C (torr)
Acid salt		Ammonium nitrate	80.04	$\text{NH}_4\text{NO}_3$	$5.0 \times 10^{-6}$
Aliphatic nitro		Nitromethane	61.04	$\text{CH}_3\text{NO}_2$	$2.8 \times 10^1$
	DMNB	2,3-Dimethyl-dinitrobutane	137.14	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_4$	$2.1 \times 10^{-3}$
Aromatic nitro	<i>o</i> -MNT	2- Nitrotoluene	137.14	$\text{C}_7\text{H}_7\text{NO}_2$	$1.5 \times 10^{-1}$
	<i>p</i> -MNT	4-Nitrotoluene	137.14	$\text{C}_7\text{H}_7\text{NO}_2$	$4.1 \times 10^{-2}$
	DNT	2,4-Dinitrotoluene	182.14	$\text{C}_7\text{H}_6\text{N}_2\text{O}_4$	$2.1 \times 10^{-4*}$
	TNT	2,4,6-Trinitrotoluene	227.13	$\text{C}_7\text{H}_5\text{N}_3\text{O}_6$	$3.0 \times 10^{-6}$
	Picric Acid	2,4,6-Trinitrophenol	229.11	$\text{C}_6\text{H}_3\text{N}_3\text{O}_7$	$5.8 \times 10^{-9}$
Nitrate ester	EGDN	Ethylene glycol dinitrate	152.06	$\text{C}_2\text{H}_4\text{N}_2\text{O}_4$	$2.8 \times 10^{-2}$
	NG	Trinitroglycerin	227.09	$\text{C}_3\text{H}_5\text{N}_3\text{O}_9$	$2.4 \times 10^{-5}$
	PETN	Pentaerythritol tetranitrate	314.14	$\text{C}_5\text{H}_8\text{N}_4\text{O}_{12}$	$3.8 \times 10^{-10}$
	NC	Nitrocellulose	327.21	$[\text{C}_8\text{H}_{13}\text{N}_3\text{O}_{11}]_n$	N/A
Nitramin	Tetryl	Tetranitro- <i>N</i> -methylamine	287.15	$\text{C}_7\text{H}_5\text{N}_5\text{O}_8$	$5.7 \times 10^{-9}$
	RDX	Trinitro-triazacyclohexane	222.12	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$	$1.4 \times 10^{-9}$
	HMX	Tetranitro-tetracyclooctane	296.16	$\text{C}_4\text{H}_8\text{N}_8\text{O}_8$	$1.6 \times 10^{-13a}$
	CL20	Hexanitro-hexaazaisowurtzitan	438.19	$\text{C}_6\text{H}_6\text{N}_{12}\text{O}_{12}$	N/A
Peroxide	TATP	Triacetone Triperoxide	222.24	$\text{C}_9\text{H}_{18}\text{O}_6$	$3.7 \times 10^{-1a}$
	HMTD	Hexamethylene triperoxide diamine	208.17	$\text{C}_6\text{H}_{12}\text{N}_2\text{O}_6$	N/A

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N/A, not available.

<sup>a</sup>Extrapolated values.

difficult to be detected by sensors which operation is based on sniffing the trace vapors of chemical from air. However, some of the decomposition products of explosive materials or the necessary additive (or taggant) chemicals can be volatile, thus giving characteristic information originated from specific explosive.

### 3. Other Physical Properties

Most explosives have molecular weight of 150 U or higher. They usually are solid though also the use of ionic liquids as energetic explosive materials has been recently reported (Drake et al., 2003). The melting and boiling points of explosives are relatively high ranging from 50 to 300°C, but because of sensitivity and thermolability explosives typically either decompose or explode at temperatures below their boiling points. In addition, many explosives are suspected carcinogens and toxic. Exposure by inhalation, ingestion or skin contact can cause health disorders varying from headache and skin irritation to poisoning, respiratory problems, or even heart attack.

## II. SAMPLING AND PRECONCENTRATION

Especially in the case of IMS, sampling can be undertaken efficiently because airborne vapors can be introduced directly into the instrument. For particulate analysis sampling can be carried by swiping the surface. However, the situation is not as simple for MS: sampling and sample preconcentration techniques which improve the quality of analysis are commonly needed. MS can be coupled with a pre-fractionation method when the sample is a complex mixture of different compounds. In this regard, the most widely used pre-fractionation methods are gas chromatography (GC) and liquid chromatography (LC). In addition, different extraction methods are used.

### A. Solid Phase Microextraction (SPME)

Solid phase microextraction (SPME) is a prominent solvent-free extraction technique for analyzing organic compounds from various matrices (Arthur & Pawliszyn, 1990; Lord & Pawliszyn, 2000). This technique has competitive advantages over conventional extraction methods particularly when low quantities of gaseous substances are analyzed. Sample preparation is significantly facilitated since no additional solvents are required. The extraction can be applied either in the sample or in the headspace above the sample using a small fused silica fiber coated with sorptive material. Interferences of impurities from sample matrices can be minimized by using headspace sampling. Extracted compounds are thermally desorbed from a fiber directly to the interface of chromatographic system for detection and analysis. SPME can be easily coupled with thermodesorber of the analytical system; gas chromatography (GC) or liquid chromatography (LC) has been typically used with SPME.

Solid phase microextraction (SPME) has been successfully used to recover explosives (Furton et al., 2008; Brown et al., 2004). Analysis of various explosives with SPME coupled to HPLC has been written (Furton, Wu, & Almirall, 2008; Gaurav et al., 2007). In addition, SPME has been employed with GC as a sampling method to explosives (Jenkins et al., 2001; Lorenzo et al., 2003; Harper, Almirall, & Furton, 2005) and to explosive

taggants (Li, Zeng, & Zeng, 2007). When SPME is coupled with MS, the extraction temperature for non-volatile explosives should be about 100°C, acceptable limits of detection are observed with relatively short extraction times (30 min); however the increase of extraction times enhances detection (Kirkbride, Klass, & Pigou, 1998). SPME sampling method has been used to analyze nitroaromatic compounds in complex water based samples (Jönsson, Gustavsson, & van Bavel, 2007); to detect explosive residues in a storage bunker with GC-MS (Harvey, 2008); to analyze TNT and HMX and their metabolites in seawater using GC-ion trap MS with detection limit level of low ppt range (Barshick & Griest, 1998); and to detect post-explosion exhibits of TATP with limit of detection 6.4 ng with GC-MS (Muller et al., 2004). Different solid phase extraction sorbents for explosives have been tested by SPE-LC-MS: the efficiency of polar sorbents to retain the more polar explosives like HMX and RDX (Tachon et al., 2008). An extensive review concerning the SPME technique and its applications in combination with MS has been written (Vas & Vékey, 2004).

Solid phase microextraction (SPME)-GC-MS method having fast analysis time and simple sample preparation to analyze TATP with detection limits being 5 ng has been reported (Kende et al., 2008). Same method has been used to analyze chemical degradation products of TATP after treatment with different acids and storage: the results indicated that both rate of degradation and the products formed are dependent from the acid. Exposure to AcOH caused no effect to the integrity of samples, while exposure to mineral acids degraded the peroxide significantly. Also, the conjugate base of mineral acid had a profound effect both to the rate of decomposition and on the types of products formed (Armitt, Zimmermann, & Ellis-Steinborner, 2008).

So far, only a few studies have been reported for the combination of SPME with IMS to detect explosives. A SPME-IMS interface, which consists of tube with resistor for thermal desorption and transfer of explosives from commercial SPME fiber to the IMS has been developed (Perr, Furton, & Almirall, 2005a). Same method has been used to detect smokeless powder stating that the SPME-IMS technique can potentially change the way pre-blast samples of smokeless powders and other low explosives are detected (Joshi et al., 2009). The detection of TNT and some chemical markers of explosives have been made by using a planar construction of SPME which increases the surface area by a factor of 50–100 times. This improves the extraction efficiency and decreases equilibrium time resulting in faster analyses (Guerra, Lai, & Almirall, 2008). Due to novel geometry of SPME, it is possible to eliminate difficulties of introducing SPME fiber to IMS detector and to improve the extraction efficiency of SPME for TNT. It has been stated that SPME-IMS significantly improves the probability of detection of explosives as compared to common IMS (Lai et al., 2008). Also, the construction of miniature-sized sample vapor preconcentrator prototype interface of IMS for trace explosive detection has been recently published. With TNT used as sample the magnitude sensitivity enhanced by an order (Martin et al., 2007a).

### B. Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) has been reported as an environmental friendly and efficient extraction technique for various types of materials including explosives (Sunarso &

Ismajdi, 2009). Extraction can be employed for either air, solid or liquid matrices as a sample preparation (purification or preconcentration) method prior to chemical analysis. Extraction in SFE is based on diffusion where a solvent diffuses into the matrix and the substances to be extracted dissolve and diffuse into the solvent under high pressure. SFE requires significantly lower quantities of organic solvent as compared to its alternative method of liquid phase extraction. The most commonly used supercritical fluid is carbon dioxide which can be easily removed after extraction. Selectivity in extraction can be improved either by changing the temperature or pressure conditions or by adding chemical modifiers. A disadvantage of SFE (in contrast to liquid phase extraction) is higher cost due to the pressure required.

Supercritical fluid extraction (SFE) has been coupled with HPLC, GC, CE or supercritical fluid chromatography (SFC); this feature enables fast on-line measurements. SFE is a potential extraction method for various explosives: air samples containing TNT, DNT and dinitrobenzene (DNB) in ng concentrations have been successfully detected by HPLC (Batlle et al., 2002) and GC (Batlle et al., 2003) using SFE as an on-line extraction method. SFE/GC with organic modifiers has been used to analyze explosives from solid matrices (Francis et al., 1995) Improved selectivity and sensitivity were obtained using a hyphenated technique including SFE and SFC: this method facilitates the analysis of explosive materials at pg levels. The separation of explosives prior to MS analysis with SFC has been demonstrated (McAvoy et al., 1999).

### C. Stir-Bar Sorptive Extraction (SBSE)

The principle of stir-bar sorptive extraction (SBSE) is based on the magnetic bar of 1–2 cm in glass capsule coated with sorptive material, such as polydimethylsiloxane (PDMS) (David & Sandra, 2007). Compared to SPME fiber, SBSE bar has a relatively large layer of sorptive material; hence the recovery of analyte can be enhanced. This is important considering that the concentration of sample is extremely low. SBSE can be used with chromatographic techniques such as GC, HPLC, and IMS. Out of the three, GC is the most prominent technique because of its efficient thermal desorption characteristics. Instead of thermal desorption, liquid desorption with suitable solvent can be used with HPLC (Vas & Vékey, 2004).

Despite the successful use in trace analyses for environmental and life sciences, SBSE has rarely been applied for explosive analysis. A challenge in integrating the SBSE and the IMS is the interface between the two techniques. This problem has been solved by using a platform consisting of Teflon ring and filter: the platform has a small heater and possibility to pass carrier gas through a desorption unit. Real-time thermal desorption processes of explosives have been examined successfully after extracting and pre-concentrating TNT and RDX from aqueous samples using this method with limits of detection 0.1 and 1.5 ng/mL, respectively. It was stated that SBSE has inherent advantages as sensitive, straightforward, solventless, and inexpensive method. The addition of SBSE as an extraction step reduced the matrix interferences thus improving sensitivity. The coupling of SBSE with IMS creates a suitable system for detecting explosives in water samples (Lokhnauth & Snow, 2006).

### D. Gas Chromatography (GC)

Basically, GC can be classified into two types depending on the stationary sorbent being liquid or solid. Separation in GC takes place in a column between a moving gas phase and a stationary phase (Bartle & Myers, 2002). The composition of the gas flow, containing the separated target substances, is monitored. Each eluting substance results in a signal in characteristic retention time, which can be further used for data analysis. A review that discusses GC combined with spectroscopic detection methods including mass spectrometry has been written (Ragunathan et al., 1999).

To detect explosives GC can utilize different detectors depending on the chemical characteristics: flame ionization detectors (FID), nitrogen-phosphorus detectors (NPD), electron capture detectors (ECD), thermal energy analyzers (TEA), and mass spectrometers (MS). These detectors are sensitive to nitro group present in most explosives. In general, it is possible to detect explosive compounds from ng to pg levels. Interferences are possible if other compounds present have similar characteristics of the explosives. These interfering compounds include negatively charged halogenated, organosulfur, or organophosphorus compounds; both co-elution and thermal degradation may cause problems in determination. In some cases sample clean-up or derivatization is required prior to analysis. Confirmation using second column or GC/MS/MS can improve the selectivity and specificity of the analyte identification (Perr, Furton, & Almirall, 2005b).

In this regard, thermally labile explosives have been earlier determined by liquid chromatography (LC) more often than by gas chromatography. GC has been applied for separation and detection of thermostabile (up to 300°C) compounds and mixtures. However, use of wide-bore capillary columns and injecting the sample into a deactivated liner enables the analysis of explosives with low boiling points (Hable et al., 1991). Since the sensitivity of GC is higher than that of LC, GC is widely used compared to LC especially when lower determination limits are required.

The pioneering work in analyzing nitro-compounds with GC-MS has been done by Burns and Lewis (1995): they have identified both different isomers of DNT and nitroglycerine-based explosives. Stambouli have demonstrated the technical feasibility of GC-MS to detect TATP lesser than nanogram level from real post-explosion debris (Stambouli et al., 2004). Also traces of explosives in water (Yinon, 1996) and TNT residues in soil (Weiss et al., 2004) have been defined. The analysis of five high explosives has been demonstrated (Fialkov, Gordin, & Amirav, 2003). A standard GC-MS method to analyze organic explosives has been created (Calderara et al., 2004).

Gas chromatography (GC) with TEA detector is often used to screen explosives because of the nitro-specific selectivity of TEA. For example, the separation and selective identification of NG, 2,6-DNT, 2,4-DNT, 2,4,6-TNT and PETN by solvating gas chromatography and detection have been described (Bowerbank et al., 2000). The combination of thermal desorption and gas chromatography with ECD is also commonly used because ECD is highly sensitive for nitroaromatic explosives. For example, method development of a mixture of multiple nitroaromatic and nitramine explosives (2,6-DNT, 1,3-DNB, 2,4-DNT, TNT, 1,3,5-TNB, 4-A-2,6-DNT, RDX, 2-A-4,6-DNT, tetryl, HMX) from dry wipe material (Waddell et al., 2005), from soils (Walsh, 2001),

and from animal tissue (Pan, Zhang, & Cobb, 2005) has been demonstrated. Also non-radioactive pulsed-discharge (PD)-ECD-GC has been used in analysis of explosive mixtures. This method might allow improved selectivity and sensitivity of nitro-containing compounds by eliminating the interferences (Collin et al., 2006).

### E. High Performance Liquid Chromatography (HPLC)

High performance liquid chromatography (HPLC) is often selected for the analysis of compounds that have high sensitivity to heat, low volatility, and high molecular weight. Before analysis, sample often needs to be sonicated, extracted, and preconcentrated. In HPLC, liquid sample is injected into a stream of liquid mobile phase to pass through a column that contains a solid stationary phase. Target compounds separate from each other on partitioning between mobile and stationary phases. HPLC is widely applied especially in pharmaceutical, biotechnology and polymer industries.

Independent explosive analysis using HPLC is feasible: UV absorption or photodiode array detection in isocratic conditions can be used to separate and to detect nitro-organic explosive residues in water, soil, and sediment matrices. For example, a combination of SPME and HPLC-UV has been used to quantify nine explosives from ocean and groundwater; detection limits range in the ppb level (Monteil-Rivera et al., 2004). HPLC is also employed as EPA method to determine explosives, such as nitroaromatic, nitramines, and nitroglycerine (Marple & LaCourse, 2005). HPLC is a useful technology to separate explosive samples that contain other explosives or explosive degradation products as contaminants (Lang & Burns, 1999; Borch & Gerlach, 2004; Paull et al., 2004).

Solid-phase extraction (SPE) and HPLC have been combined with photo-assisted electrochemical detection (PAED) to determine 14 explosives from groundwater with high sensitivity (Marple & LaCourse, 2005). To analyze TATP and HMTD, a HPLC-based method using post-column irradiation, derivatization to fluorescent species and their fluorescence detection has been developed (Schulte-Ladbeck, Kolla, & Karst, 2003). This method enables the quantification of peroxide containing explosives that otherwise do not absorb UV light.

High performance liquid chromatography (HPLC) can be combined with MS to improve sensitivity and selectivity. LC-MS (or LC-MS/MS) are suitable technologies for complicated environmental samples that require both high sensitivity and accuracy. An early study described the application of LC-MS for the separation and identification of common explosives (Berberich, Yost, & Fetterolf, 1988). Garofolo have used LC-MS and LC-MS/MS to characterize various explosives (Casetta & Garofolo, 1994) including thermostable explosives (Garofolo et al., 1996a). LC-tandem MS with solid-phase extraction was successfully employed for identifying and quantifying TNT, HMX, RDX, NG, and PETN in lake waters (Ochsenbein, Zeh, & Berset, 2008). A method for the sampling of explosives from air through SPE membrane and analysis by LC-MS/MS with APCI interface has been developed (Sanchez et al., 2003). This method was applied for fg/L concentrations and facilitated the determination of isomers of TNT and DNT. A method of reduction and detection of urea nitrate from traces has also been demonstrated (Almog et al., 2007). The emulsifiers present in explosives have been characterized using LC-MS (Tata, Collins, & Campbell, 2006).

A large number of explosives have been investigated using HPLC-MS and chemical ionization (Parker et al., 1982; Voyksner & Yinon, 1986). In addition, negative mode electron capture (EC) ionization of four explosives and their chromatographic separation has been studied using LC-MS (Cappiello et al., 1996). More recently, separation and identification of 21 explosive related compounds (Holmgren et al., 2005), and 16 explosives and their isomers (Tachon et al., 2007) was performed by LC having porous graphitic carbon (PGC) column followed by APCI-MS detection. This method showed good performance improving both selectivity and sensitivity of explosive analyses.

Also the analysis of stabilizers and explosive residues (RDX, PETN, TNT, and NG) in hand-swabs using LC-MS/MS has been demonstrated. The sampling was carried out with cotton swabs wetted with iso-propanol followed by methanol elution and direct injection to the instrument. The analysis can be made from ng levels of explosives, and it was stated that the possibility of false positives has been potentially eliminated (Perret et al., 2008). In addition, the effect of LC column packing to the speed, resolution and selectivity has been studied: this so-called ultra performance liquid chromatography (UPLC) improves resolution and increases speed of analysis. MS detection of low picograms was reported for the majority of explosives but unfortunately this data was not included in the article (Oehrle, 2008).

Yinon group attested using LC-MS that in ESI RDX readily formed adducts with various impurities (formates, acetates, hydroxyacetates, and chlorides) present in mobile phase in ppm levels. Instead in APCI some decomposition and abundant formation of  $[M+NO_2]^-$  cluster was observed (Gapeev, Sigman, & Yinon, 2003). They have also identified nitrate ester explosives (PETN, NG, EGDN) through adduct ion formation (Zhao & Yinon, 2002a) and defined the origin of explosive through its by-product isomers and impurities (Zhao & Yinon, 2002b). In addition, the competitive formation of various anion adducts in explosive mixtures, as well as the separation of these species with negative mode HPLC-ESI-MS have been studied. Additional specificity and sensitivity was illustrated using multiplexed detection scheme (Mathis & McCord, 2005). LC-MS has been concluded to be suitable technique for the identification and quantification of TATP (Widmer et al., 2002). A LC-ESI-MS method for quantitative analysis of HMX has been optimized exploiting the fact that it can form adducts with organic acids. Acetic acid was used as an additive. HMX concentrations were analyzed from water samples and from lizard eggs with the detection limit 0.78 pg (Pan et al., 2006a). Also a LC-MS method for trace analysis of hexamethylenetriperoxidodiamine (HMTD, cyclic peroxide explosive) has been developed (Corson & Beardah, 2001). A review concerning forensic applications of LC-MS including brief section of explosive detection was recently written (Wood et al., 2006).

### F. Capillary Electrophoresis (CE)

Capillary electrophoresis uses narrow-bore capillary filled with a buffer between two electrodes. When a voltage is applied to the buffer, ionic compounds start moving towards the electrode of their opposite charge. This separation is based on the difference between the electrophoretic mobilities of ions in an electric field. The mobilities of ions depend on their charge and

molecular size. A photoreceptor is used to detect the absorbance of ions passing through the buffer and the output is graphically represented.

Capillary electrophoresis (CE) is useful to separate explosives because sample requirements are low and CE can be applied to both anions and cations (Issaq, 2000). Other advantages include the separation of widely different compounds, relatively fast analysis time, and flexibility for on-site field testing. In addition, the separation is based on the differences in the charge-to-size ratio of the solvated ions under the influence of an applied electric field. This eliminates the need for gradients because CE separation relies on ionic migration. A disadvantage of CE is the lack of detection sensitivity that derives from small injection volumes (in nL level). This can be overcome by improving detectors and sample handling. Different preconcentration methods, including solid phase microextraction (Halasz et al., 2002) and the use of preconcentration columns coupled to CE have been demonstrated. Recently, the use of non-aqueous capillary electrophoresis (NACE) has been employed to enhance performance of CE in the quantitative analysis of assumed biodegradation products of explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (Guo et al., 2005).

The applications of conventional and miniaturized CE setups for analyzing different explosives have been reviewed (Pumera, 2005; Cruces-Blanco, Gámiz-Grazia, & García-Campaña, 2007). Particularly capillary electrochromatography (CEC) and micellar electrokinetic chromatography (MEKC) are used in explosive analysis to improve the resolution of compounds that cannot be resolved by LC. In MEKC, surfactant molecules are added to buffer solution to enhance the separation of hydrophobic compounds. Different components with properties to assist micellation have been tested: suitable components include charged cyclodextrins for CE analysis of aromatic and cyclic nitramine explosives (Groom et al., 2003). Cyclodextrin assisted CE-ESI-quadrupole ion trap system has been successfully applied to analyze various nitroaromatic and nitramine explosives (Groom et al., 2005).

Miniaturized CE systems, also referred to lab-on-chip devices, have recently attracted considerable attention because of their small size, minimal reagent and power consumption and high efficiency (Woodfin, 2007). Lab-on-chip devices are reliant upon electro-osmotic fluid pumping followed by the separation of ions in an electric field (electrophoresis). Analysis including sample preconcentration, extraction and derivatization can be performed with the systems. These devices can also be combined with an electrochemical or optical detector.

### G. Thermal Desorption (TD)

Thermal desorption (TD) is a low-cost and efficient sample introduction method for rapid explosive analyses. This method neither involves solvents nor follows complicated sample preparation steps. The sampling can be made by wiping from surfaces or by introducing sample material to filters by pipetting or by flow-throughs. After sample trapping step, the filters are placed to specific desorption units or inlet probes. Heating to high temperatures (up to 250°C) causes the particulate matter to desorb and to be flushed into the analyzer unit. Possible disadvantages include non-specificity and decomposition of thermally instable molecules. However, these decomposition products may have analytical values: the decomposition products

of TNT in soils have been used in *in situ* amperometric gas sensor detection (Buttner et al., 1997).

Thermal desorption sampling combined with GC (Sigman & Ma, 1999; Waddell et al., 2005) and with MS (Mayhew et al., 2010) has been used to analyze various explosives. TD-IMS has been used for screening harmful organic pollutants (Pozlomek & Eiceman, 1992) and chemical warfare agent simulants (Kanu, Haigh, & Hill, 2005). The latter also includes detailed schematic presentation of TD-IMS detector as well as discussion of the instrumental reliability and validity of the measurements. Design, fabrication and testing of a microfabricated preconcentrator having a TD unit by interfacing with handheld IMS have been reported (Voiculescu et al., 2006). A comparison between TD unit and injection port as inlet systems to single photon ionization (SPI)-MS has been recently made. As a result, injector port yielded less fragmentation and higher absolute signal thus having lower detection limits; however this injector port system is not suitable for field-use (Schramm et al., 2009a). In addition, IMS-MS-TOF analysis of black powder (BP) using TD-inlet has recently been published (Crawford et al., 2010).

## III. ION MOBILITY SPECTROMETRY (IMS)

### A. Principles of IMS

Having a real-time monitoring capability and possibility to automatic usage, the other attributes of IMS technology include sensitivity higher than GC or GC/MS, operation in atmospheric pressure, low cost, and analytical flexibility. In addition, they are practical and user-friendly. Due to its small size, IMS is most frequently used for field detection; some models are rugged enough for military purposes. Reviews concerning the basics, technology and different applications of IMS (Eiceman, 2002) as well as its use in process analysis (Baumbach, 2006), in defense applications (Eiceman & Stone, 2004) and in forensic sciences (Karpas, 1989) have been written.

The weaknesses of IMS include limited linear dynamic range and poor resolution. Also interferences from complex matrices typically cause problems if competitive charge exchange masks the analyte (Sielemann et al., 1999). This interferes also in quantitative determinations when the chemicals in the matrix are preferentially ionized over the analyte. Inaccurate results may occur when ions and neutrals collide in the sample. In this regard, some relatively common air contaminants may interfere the sensitivity of detection of the explosives (Matz, Tornatore, & Hill, 2001) or cause overlapping problems (Daum et al., 2001). However, these problems can be solved by changing the gas-phase ion chemistry, pre-fractionating the sample by chromatography or changing the ion source. For this reason, IMS can also be connected either with GC to improve separation capacity or with MS detector to enhance its specificity.

Various ionization systems using radioactive source, corona discharge, photo-ionization, metastable helium, electrospray ionization (ESI), matrix assisted laser desorption ionization (MALDI), and laser desorption have been demonstrated. The performance of other ion sources is reported to be better than the radioactive sources because the analyte ions can be created from a wider range of selected compounds. Laser desorption and ESI have been found to be one of the most suitable ionization methods for producing gas phase ions from explosives that otherwise

easily decompose when thermally volatilized (Huang, Kolaitis, & Lubman, 1987). A method producing particle-based standard test materials for portal IMS devices have been developed. HMX, TNT, and an explosive simulant were incorporated into polymer microspheres by inkjet printing. These PLGA spheres can be detected by IMS, and also quantitative results were close to predictions (Fletcher et al., 2008). A trace sampling method using adhesive coated stubs for gunshot residues (Zeichner & Eldar, 2004) and TNT, RDX, and PETN has been investigated: it was found that IMS was more sensitive technique when compared to GC/TEA (TNT as an exception); detection limits were 25–50 ng for TNT and RDX and 0.5–1 µg for PETN (Zeichner et al., 2009). Also divergent adsorbent packed column pre-separation method has been tested: false positive results may be reduced by adding the adsorbent tube (Kanu, Wu, & Hill, 2008). For the compounds that have high boiling points and good stability, sample volatilization can be undertaken using a thermal desorption chamber that is attached to the front end of the IMS instrument (Kanu, Haigh, & Hill, 2005).

## B. Ion Formation Processes in Radioactive Ion Sources

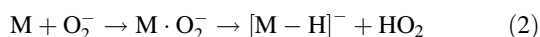
The formation and distribution of ions in IMS correspond to a type of the equipment and operating conditions. These effecting factors include ionization method, sample concentration and/or dilution, ion separation method, operating temperature of the instrument; drift voltage, type of drift gas, possible dopants or other additives, the distractions originating from matrices or impurities and the effect of moisture. The ion formation process in IMS with radioactive ion source (usually  $^{63}\text{Ni}$ ) is namely atmospheric pressure chemical ionization (APCI). With explosives the detection of ions typically occurs in negative polarity, that is, in the negative mode of IMS instrument. The main different ways in forming detectable ions from explosives include: electron capture, adduct formation, or dissociation of the parent molecule M. The formed fragments or deliberately added dopant chemicals may react further to produce new adduct ions suitable for detection. The formation of positive ions (measurements in positive mode) from nitrotoluenes is possible but the APCI process and the instability of these ions usually cause remarkable fragmentation. As a result, the fragment ions are neither sufficiently specific nor suitable for analytical purposes. By using radioactive ionization source the most common ion formation reactions for nitrogen containing explosives are as follows (Eiceman & Schmidt, 2009):

If the lifetime of free gas-phase electrons are long enough  $\text{M}^-$  ions could be formed when electron attaches to the sample molecule:



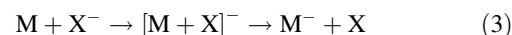
For TNT, this reaction occurs *via* intermediate in oxygen-free atmosphere.

In the presence of oxygen, the formation of  $[\text{M}-\text{H}]^-$  usually occurs with  $\text{O}_2^-$  as the reaction ion. In IMS, the effect of oxygen to the ionization processes of TNT has been thoroughly studied (Daum, Atkinson, & Ewing, 2002).



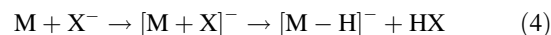
Similar reaction may occur with halogens.

The sensitivity in the detection of explosives can also be improved by adding halogen-contained compounds to the sampling system. For example, the presence of chlorine yields formed may also be an intermediate in charge transfer reaction



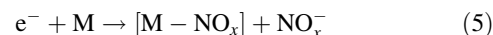
This occurs in air, where X is  $\text{O}_2$  or Cl and M does not have acidic proton.

The transition of adduct ion to hydrogen abstracted ion:



If M has acidic proton, X is normally  $\text{O}_2$  or Cl.

The covalent bond of nitro-group is so weak that cleavage of  $\text{NO}_2$  can easily take place. Cleavage of the nitro-group  $\text{NO}_2$  or nitrate  $\text{NO}_3$  can be presented as:



The cleaved groups ( $\text{NO}_2^-$  and  $\text{NO}_3^-$ ) are eager to form adducts with sample molecules:



$\text{NO}_3^-$  ions may arise from reactions between  $\text{NO}_2$  with  $\text{O}_2^-$  or  $\text{NO}_2^-$  with  $\text{O}_2$

The operation of IMS instruments occur at ambient temperature and pressure, thus clustering and dimerization may pose a problem to efficient detection. The ionic species originating from explosives detected with IMS have been extensively reviewed and also the effects of both different flow-gases and sample introduction methods were reported (Ewing et al., 2001). Also the effects of dopants to the ion-molecule chemistry and to IMS response have been recently reviewed (Puton, Nousiainen, & Sillanpää, 2008).

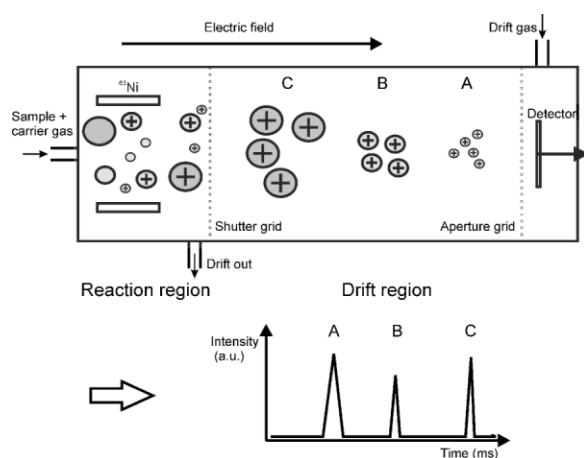
## C. IMS Detection Techniques

In IMS, the ions are separated based on their velocities in an electric field at ambient pressure. The mobilities of the ions depend on molecular mass, charge and shape of ion as well as operating conditions such as temperature, pressure, and the molecular properties of drift gas (Baumbach & Eiceman, 1999; Creaser et al., 2004; Eiceman & Karpas, 2005).

### 1. Conventional IMS

Scheme of conventional IMS analyzer is depicted in Figure 2. IMS consists of an ion reaction chamber, ion-gate, drift tube, and detector. IMS and mass spectrometric TOF have similar working principles except its operation at atmospheric pressure. Ionization processes have been described earlier. From the reaction chamber the ions are pulsed to a drift tube where they move to detector or a collector plate. Ions are separated in the drift tube through a counter-flowing drift gas in an electric field of about  $200 \text{ V/cm}^3$  in an atmospheric pressure. The flight times of detected ions are measured and converted into signal peaks, which positions are used in the determination of the sample chemical. The velocities of the ions are dependent on their size-to-charge ratios (Li et al., 2002; Borsdorf & Eiceman, 2006). Some IMS instruments are depicted in Figure 4.





**FIGURE 2.** The operation principle of conventional IMS instrument.

## 2. Aspiration IMS

Initially aspiration IMS (AIMS) was designed to detect chemical warfare agents, but recently it is also used to detect explosives. Unlike conventional IMS, aspiration IMS uses multi-channel detection (Tuovinen, Paakkanen, & Hänninen, 2000; Utriainen, Kärpänoja, & Paakkanen, 2002). The ions, formed by radiation, pass through orthogonal electric field which leads to continuous detection in the absence of ion-gate or shutter. The polarity of the electric field is altered sequentially, facilitating simultaneous detection of both positively and negatively charged ions. Instead of drift time, spatial distribution of the ion clusters is measured. The signal from multiple electrodes creates so called fingerprint vector that is a characteristic pattern in detecting the analyte. The resolution of ion mobilities can be modified by adjusting the strength of the electric field for electrode strip pairs. Dynamic sampling and screening for TATP by AIMS have been demonstrated: in quantitative analysis the determined concentrations were proportional to IMS intensities (Räsänen et al., 2008). The detection principle and a hand-held aspiration type IMS detector are presented in Figures 3 and 4, respectively.

## 3. Field Asymmetric Waveform Ion Mobility Spectrometry (FAIMS)

The field asymmetric waveform ion mobility spectrometry (FAIMS), also known as differential mobility spectrometry (DMS) or ion mobility increment spectrometry (IMIS) is an up to date IMS technology as a potential means to detect explosives (Buryakov et al., 1993; Shvartsburg, 2008). In FAIMS, ions are

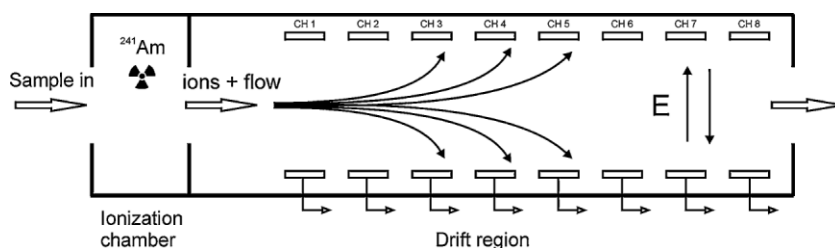
continuously pushed through a narrow gap between two parallel electrodes with a continuous drift gas flow. An asymmetric square waveform applied to one electrode generates an asymmetric electric field where the ions oscillate and separate from each other. DC voltage is usually used to maintain the selected ions in the center of the gap and selecting the ions for detection. Ions that have different polarities can be detected simultaneously because only gas flow is used for moving the ions (Guevremont, 2004a,b).

Field asymmetric waveform ion mobility spectrometry (FAIMS) combined with GC has been used to detect DNT, TNT, and PETN: detection limits of the explosives were of the order of magnitude 0.01 pg/mL (Buryakov, 2004). Other similar studies included nitrobenzenes and different mononitrotoluenes (Buryakov, 2003), the effect of ambient temperature and humidity to the ionization efficiency of explosives: it was stated that the concentration of water vapor affects the ionization of DNT and TNT while PETN remains independent. These observed differences are due to different ionization mechanisms (Buryakov, Kolomiets, & Lupp, 2001). Later study concerns the effect of humidity to the mobility increment coefficient in explosive detection. This dependency can be used for exploitation of similar sensor devices (Buryakov, 2007). In addition, the modification of drift gas to the detection of explosives has been studied with DMS/MS and DMS/GC experiments. It was stated that the separation of the ions can be controlled by the addition of small amounts of dopant (in this case methylene chloride). This makes the detection of explosive possible with microfabricated device. Also, the LODs for explosives in microfabricated DMS device were reported to be lower than 10 ppb or even at sub ppb levels (Eiceman et al., 2004).

## D. IMS Applications in Explosive Analyses

Since 1970s, IMS technology has been used to detect explosives in laboratory scale. The first analyses of TNT were undertaken by Karasek (1974) and Karasek and Denney (1974). Nowadays, IMS is routinely used for detecting explosives in military use and checking them from handbags and luggages at airports (Ewing et al., 2001; Fricano et al., 2001).

The applications for the purpose of IMS in explosive trace detection are very extensive (Fetterolf & Clark, 1993). IMS can be used in post-explosion detection of traces; for example, detection of PETN has been made from a detonating fuse and from a tissue sample taken from the thorax region during autopsy (Keller et al., 2006). IMS has also been used to detect explosive residues on the surfaces of metal scrap (Jung et al., 2004), and to detect taggants in explosives (Ewing & Miller, 2001). The field analysis of RDX vapors form pre- and post-detonation has been



**FIGURE 3.** The operation principle of AIMS-instrument.



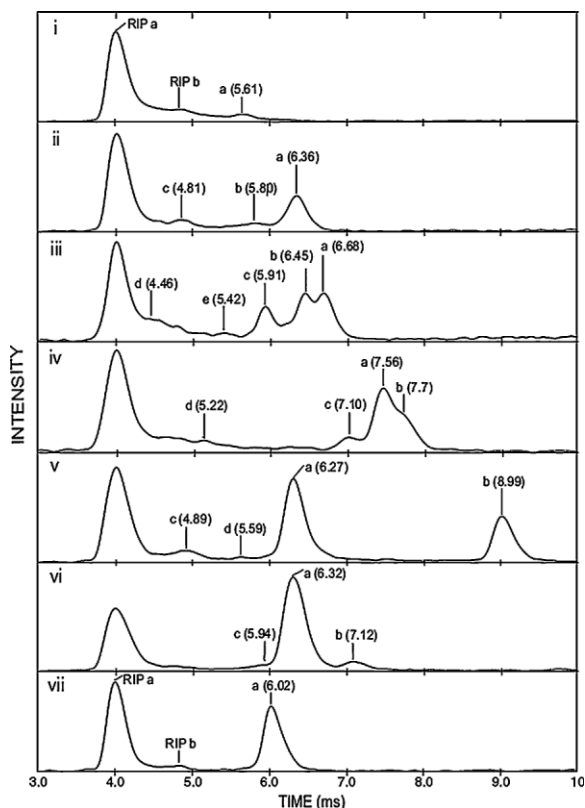
**FIGURE 4.** Some examples of IMS instruments. **Top left:** AIMS instrument model ChemPro100. Photo courtesy of Environics Oy. Used with permission. **Top right:** IMS instrument model LCD 3.3. Photo courtesy of Smiths Detection. Used with permission. **Below:** IMS instrument model Sabre EXV. Photo courtesy of Smiths Detection. Used with permission.

reported (Yelverton, 1988). Standard mixture solutions of TNT, RDX, PETN, and tetryl have been determined with additional task including identification of explosive traces from handswab samples (Koyuncu, Seven, & Calimli, 2005). The successful detection of explosives in hair has been recently reported: common military explosives (TNT, NG, and PETN) and TATP were detected with three different sampling modes: from direct insertion, swabs from hair or acetonitrile extracts from hair. All the military explosives were quite easily detected, when sensitivity of detection was compared to TATP required tenfold amount of explosives than PETN. In explosive detection mode of the instrument TATP was not detected after 2-day exposure with any of the three sampling techniques. Instead with 3 days exposure in narcotics mode of the instrument, the characteristic TATP peaks were detected. In conclusion, hair seems to be a suitable surface for explosive detection (Oxley et al., 2008). Studies on the optimization of IMS detection include collection efficiency for different particle sizes of TNT and a comparison of fingerprint and dry Teflon sampling systems of C4 containing RDX (Phares et al., 2000), the sizes of explosive residues prior to IMS analysis (Verkouteren, 2007), and the detection of smokeless powder from various surfaces like CD's and book covers (Colón et al., 2002) have been carried out.

The detection of TNT in marine environment at a concentration of 0.01 ppt (Rodacy et al., 2002) as well as various other explosives in aqueous samples has been reported (Buxton & Harrington, 2003). The detection of TNT from 10 ng of sample has been demonstrated (Pfeifer & Sanchez, 2002). The detection of ethylene glycol dinitrate (EGDN) with chloride reagent ions has been reported (Lawrence & Neudorfl, 1988). Spangler, Carrico, and Campbell (1985) have used background subtraction technique and additional chloride ions to facilitate explosive analysis. Also the effects of formation of halide reactant ions and the concentration of reagent chemical on the ionization of TNT has been studied (Daum, Atkinson, & Ewing, 2001) IMS has been applied for the quantitative determination of TNT within 0.2–1.0% errors (Garofolo et al., 1996b) and to analyze traces of several explosives (Garofolo et al., 1994). The formation of chloride adducts with dinitro-alkanes has been studied. Special focus was the association of chloride with DMNB (2,3-dimethyl-2,3-dinitrobutane) a prospective taggant for plastic explosives (Lawrence, Neudorfl, & Stone, 2001). Selective explosive capture by using filters impregnated with Lewis acidic  $\beta$ -diketonate polymers has been demonstrated. Based on the uptake kinetics of TNT passive sampling was applied to estimate the TNT concentration. Also the gas-phase uptake of RDX was

demonstrated (Harvey, Ewing, & Waltman, 2009). In a recent study an IMS device having miniature drift tube, low-radioactive ion source and custom detector was evaluated by measuring seven explosive compounds. The lower ion throughput caused by smaller drift tube and lower source activity was compensated by amplifier leading to higher sensitivity and equal resolution compared to current bench-top devices. The detection limits of the explosives were reported to be at levels below their room temperature vapor pressures (Babis et al., 2009). Figure 5 depicts measured chromatograms of various explosives. The interpretation of spectrum is mainly based on peak position (i.e., drift times of ionic species), supplementary information can be obtained from number, shapes, and intensities of the peaks. For example, the spectra of isomers 2,4-DNT and 2,6-DNT are clearly distinct.

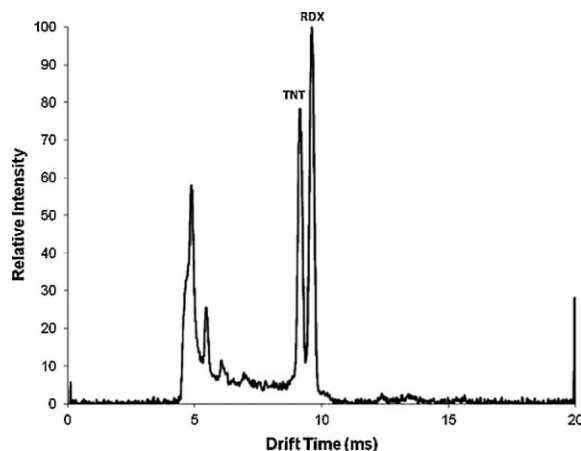
Nitrotoluenes have been studied in negative mode (Spangler & Lawless, 1978). McGann, Heigh, and Neves (2002) have shown that IMS is capable of detecting powder-based explosives, although the actual components were unidentified. Their identification, together with analyses of TNT, RDX, and NG, was made later with IMS-MS (Neves et al., 2003). RDX, HMX, and PETN have been analyzed using solid phase desorber with GC/IMS (Su & Babcock, 2002). MacCrehan has provided IMS response curves from TNT and RDX as standard reference material to NIST. All the response curves exhibited the non-linear behavior expected due to available concentrations of dopant ions limiting the maximum signal of explosives (MacCrehan, 2006, 2009).



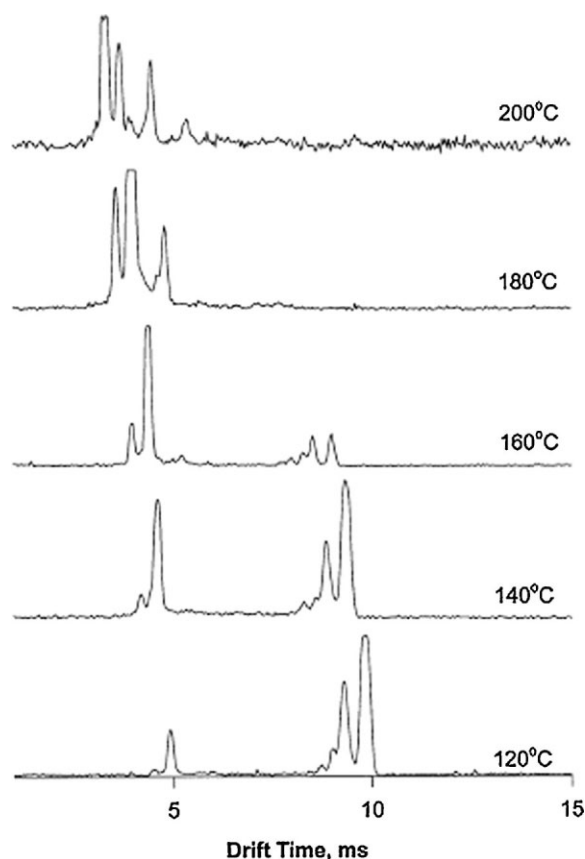
**FIGURE 5.** IMS spectra of various explosives. (i) 2,4-DNT; (ii) 2,6-DNT; (iii) NG; (iv) PETN; (v) RDX; (vi) Tetryl; (vii) TNT. Peak drift times are presented in parenthesis. Reprinted with permission from Babis et al. (2009), Copyright 2009 Springer.

Gas chromatography (GC) with cold IMS interface has been used to analyze RDX, NG, and PETN: in this construction sample vapors enter the reaction region without encountering cold surfaces (Thekkadath et al., 2006). ESI-IMS has been used to find out the response characteristics of nine explosives and explosive related compounds: the observed results were in good agreement with results obtained from previous experiments. In addition, the separation potential of IMS was tested from a mixture of three explosives TNT, RDX, and HMX: as a result a baseline separation was achieved (Asbury, Klasmeier, & Hill, 2000). RDX, NG, and PETN have also been investigated using secondary electrospray ionization (SESI)-IMS. With this ionization method, it was possible to detect both vapor and liquid explosive samples. Also the thermal stability of the explosives and the effect of added non-volatile dopant (sodium nitrite or nitrate) was investigated: It was hypothesized that the dopant will also be ionized (when dissolved in methanol/water solution) which is not the case in traditional radioactive ion sources. The experiments revealed that non-volatile dopants lowered limit of detection; the LOD to RDX was reported to be over 20-fold lower when compared to volatile dopant. Also, better sensitivity and higher limit of linearity were reported (Tam & Hill, 2004). High resolution ESI-IMS detection of explosives has an additional advantage. Impurities or components having similar mobilities may complicate detection, but HR-IMS is capable to resolve the components into individual peaks thus producing fewer false alarms (Krueger et al., 2009). Figure 6 presents HR-IMS spectra of mixture of TNT and RDX with resolving power roughly 60.

The possibility of using negative corona discharge ionization as the ionization source has been evaluated; TNT and PETN were used as examples (Tabrizchi & Abedi, 2002). Later this method was applied to analyze explosives TNT, PETN, and RDX. The total current obtained was reported to be 100 times higher than of  $^{63}\text{Ni}$  ion source resulting in lower detection limit and wider linear dynamic range. The increase of current also leads to shorter sample ion pulsing times thus improving the resolving power of the instrument. Also, the effect of temperature to the IMS spectrum was presented. It can be seen from the Figure 7 that in elevated temperatures the two peaks at



**FIGURE 6.** High resolution electrospray IMS spectrum presenting TNT and RDX in negative mode. Reprinted with permission from Krueger et al. (2009), Copyright 2009 Springer.



**FIGURE 7.** The effect of drift tube temperature to the outlook of RDX spectrum. Reprinted with permission from Khayamian, Tabrizchi, and Jafari (2003), Copyright 2003 Elsevier.

the right side are moving leftwards and at highest temperatures the intensities of these peaks decreases probably due to dissociation (Khayamian, Tabrizchi, & Jafari, 2003). Non-radioactive distributed plasma ionization source (DPIS) has been employed for the ionization of RDX, NG and PETN to IMS and to MS; with the help of dopant. RDX was easily ionized and typical  $[M+NO_3]^-$  adducts were observed. They concluded that DPIS performs well as the ionization source (Waltman et al., 2008). Both sensitivity and selectivity of explosive detection increased when temperature ramped thermal desorption with additional signal processing has been used (Buxton & Harrington, 2001). The quantitative performance of explosive analyses was enhanced by combining IMS with multivariate data chemometrics. A total number of eight Composition B samples were analyzed, most of them having diverse TNT/RDX ratio. The multivariate calibration methods used improved quantitative accuracy and precision approximately up to fivefold thus improving the possibility to identify these samples (Fraga, Kerr, & Atkinson, 2009).

A FT-IMS instrument affording sevenfold increase in sensitivity has been introduced. Other advantages over conventional IMS include improved signal-to-noise ratio, eliminations of peak tailing and elimination of the averaging of measurement cycles (Tarver, 2004). Coupled with a vapor generator, three explosives (TNT, RDX, and PETN) have been employed for calibration purposes in IMS (Davies et al., 1993). In this regard,

IMS can be used to quantitatively calibrate a prototype vapor generator thus creating a stream of explosive (TNT, HMX, and PETN) vapors (Eiceman et al., 1997). The construction of high flow and high resolution (HF-HR-IMS) enables TNT and RDX to be detected in positive ion analysis mode (Wu et al., 2001). For peroxide explosives, TATP can be detected in positive mode, but it does not generate suitable ions in negative mode. Instead, HMTD is detected in both modes (Marr & Groves, 2003). The thermal breakdown of HMTD and TATP has been examined: simultaneous monitoring of both positive and negative polarities was reported to provide additional advantages like using peaks in two modes as secondary identifiers, discriminate interferences or to add confidence into results (McGann et al., 2001). Also, effects of different drift gases to identity confirmation of explosives were studied: it was found that the relative mobilities vary significantly and reproducibly and the choice of drift gas may have a modest effect to separation selectivity. However, the use of secondary drift gas would add identity confirmation and reduce the number of false positives due to better discrimination between the target compounds and interfering ions (Kanu & Hill, 2007).

#### IV. MASS SPECTROMETRY (MS)

Compared to other techniques MS has better discrimination capabilities thus enabling it to detect wider range of chemicals. In addition, MS can be applied with different ionization methods and coupled with various detector and pre-fractionation systems. The detection limit in MS analysis for explosives ranges from pg to ng level. The complexity of the system, inconvenient size, cost and strict requirements for vacuum have been the limiting factors in practical applications of MS for on-site explosive detection. Therefore MS is widely used in stationary applications, such as research laboratories and as personnel screening portals in airports. Ongoing development of miniature mass spectrometers coupled with ambient sampling techniques may be able to overcome many limitations of the MS (Patterson et al., 2002; Blain et al., 2004).

##### A. Explosive Detection and Investigation

In analysis of explosive agents, MS technology could be used to detect and screen potential explosives, to classify and identify the types of explosives already used in destructive attacks and to measure the amounts of explosives or their metabolites in environmental or biological samples. The latter two features are different from IMS, that is, mainly used for pre-blast detection. MS technique is more accurate, reliable, and versatile than any other technique in the field of explosive analyses.

##### 1. Chemical Ionization Studies

The electron ionization (EI) mass spectra to HMX and RDX together with fragmentation pathways were reported in early 1970s (Bulusu, Axenrod, & Milne, 1970; Stals, 1971). EI induced fragmentation pathways of trinitrobenzene has been determined (Meyerson, Vander Haar, & Fields, 1972). The problem with EI is related to major fragmentation of the sample molecules yielding spectra difficult to interpret. To overcome these problems, softer chemical ionization (CI) was used. Generally, various

experiments both in negative and positive mode chemical ionization of explosives have been carried out from the middle of 1970s. These studies include, for example, dimethyl ether chemical ionization for nitroaromatics (Burrows, 1994) deuterated reagent gases for RDX, (Zittrin, 1982) hydrogen and deuterium (Gillis, Lacey, & Shannon, 1974), water (Yinon, 1974), isobutene (Yinon, 1980), and ammonia (Vouros et al., 1977) for various explosives have been investigated. Pyrolysis APCI has been used to analyze HMX and RDX (Snyder et al., 1989, 1990, 1991). Negative mode APCI has been used to investigate DNT isomers (Asselin & Paré, 1981). Field desorption mass spectrometry together with comparative EI and CI studies to various standard explosives and explosive mixtures have been reported (Schulten & Lehmann, 1977).

Yinon, Boettger, and Weber (1972) were first to report the use of negative ion mass spectrometry to detection of TNT. In addition, they have studied the ionization and fragmentation of glycoluril-type explosives (Yinon et al., 1994), deuterated TNT derivatives (Yinon, Fraisse, & Dagley, 1991) and synthetic metabolites (Yinon & Hwang, 1984). In another studies, Crellin, Dalleska, and Beauchamp (1997) and Crellin, Widmer, and Beauchamp (1997) tested chemical ionization of nitrate ester explosives TNT and RDX with  $\text{Si}(\text{CH}_3)_3^+$  cation using FTICR-MS. As a result, the explosives formed adducts with  $\text{Si}(\text{CH}_3)_3^+$ , and some specific fragmentation of TNT were observed. The fragmentation of HMX and RDX induced by electron impact (Yinon, Harvan, & Hass, 1982) and adduct formation of RDX have been studied (Burrows, 1991). The combined theoretical calculations and MS experiments suggested that HMX is present in the gas phase without decomposition prior to chemical ionization. In addition, chemical ionization spectra with ammonia as the reagent gas and field desorption ionization spectra of HMX were presented (Häußler et al., 2001). Sigman et al. have detected TATP at sub-nanogram levels using electron ionization and chemical ionization both in positive and in negative modes with both methane and ammonia as reagent gases. Positive mode ionization with ammonia reagent gas gives low limits of detection and easily recognizable adduct ion  $[\text{TATP}+\text{NH}_4]^+$  (Sigman et al., 2006).

The early studies of nitrogen containing explosives have been reviewed (Yinon, 1982). The early MS investigations of thermal decomposition of HMX and RDX have been reviewed (Farber, 1992). In addition, the early EI and CI ionizations and tandem MS analysis of various explosives have been reviewed (McLucky, Glish, & Carter, 1985).

## 2. ESI and APCI Ionization Studies

Current commonly used ionization methods in the analysis of explosives include ESI and atmospheric pressure chemical ionization (APCI). The applications of explosive analysis presented in this section are summarized in Table 2.

Electrospray ionization (ESI) and APCI are based on the protonation/deprotonation or the addition of a cation to a molecule in an electrical field. A fine mist of droplets is formed from the liquid by charging with high voltage. A carrier gas is commonly used for nebulization and evaporation of solvent in the droplets, subsequently followed by desolvation of charged analyte molecules (Gaskell, 1997; Cooks et al., 2006). ESI-MS has been used to clarify the negative ion formation from four explosives, while the positive mode was not successful (Straub &

Voyksner, 1993). Marshall et al. have tested explosive analyses using ESI-FTICR in negative mode; they demonstrated the potential of this technique for identification and discrimination of military explosives (Wu et al., 2002). The identification of explosive surfactant laurylamine acetate was undertaken (Burns, Lewis, & Doolan, 1997) and the intermediates and the final products in the synthesis of TATP were analyzed using ESI-MS: added sodium acetate leads to formation of sodiated TATP and the precipitated formed in the TATP synthesis contains oligoperoxides (Sigman et al., 2008). Also RDX-halide complexes have been studied. Both monomeric and dimeric complexes are formed, but the relative amount of dimeric 2:1 RDX-halide complexes decreases through the series  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ . The equilibrium partitioning model describes well the experimentally observed formation of dimeric complexes (Sigman et al., 2005). The explosives TNT, RDX, and propellant CL-20 have been examined using negative mode ESI-MS, the major ions detected were  $[\text{M}-\text{H}]^-$  and  $[\text{M}-\text{H}+\text{Cl}]^-$  to the explosives, respectively; and  $[\text{M}+\text{Cl}]^-$  and  $[\text{M}+\text{ONO}_2]^-$  to CL-20 (Campbell et al., 2007). Also  $\text{Fe}^0$  induced decomposition of CL-20 has been monitored using negative mode ESI-LC/MS indicating that elevated concentrations of CL-20 can be efficiently decomposed in the presence of  $\text{Fe}^0$  in water (Balakrishnan et al., 2004). ESI-quadrupole ion trap has been used to investigate the effects of fragile ions originating from of nitro explosives on mass resolution (McLellan et al., 2002). A novel ion chromatography IC-ESI-MS study made to black powder substituent containing ascorbic acid as the fuel revealed that this technique is capable to identify organic oxidizers and inorganic fuels both intact or post-blast residues of BP substituents containing ascorbic acid. Ascorbic acid is identified through its dissociation products like oxalates and threonates; however it was stated that the identifying process should be based on complete anion profile (Lang & Boyle, 2009).

Recently, a construction of a neutral desorption device with extractive electrospray ionization (ND-EESI) has been employed to characterize explosives such as TNT, RDX, NG, HMX, and TATP from human skin at pg levels (Chen et al., 2009) and to detect TNT and RDX from polluted river water and mouse urine, respectively (Chen, Venter, & Cooks, 2006). Figure 8 depicts the mass spectrum from a mixture of TNT (10 pg) and RDX (20 pg);  $[\text{TNT}]^-$  and  $[\text{RDX}+\text{CH}_3\text{COO}]^-$  ions are detected at  $m/z$  227 and  $m/z$  281, respectively. The CID inset of TNT radical anion (left) shows fragment ions by the loss of  $\text{CH}_3$ ,  $\text{OH}$ ,  $\text{NO}$ , and assumably  $\text{NOCH}_2$  at  $m/z$  212, 210, 197, and 183, respectively. The CID inset of RDX-acetate anion (right) shows fragments by loss of  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_3\text{COOH}$  at  $m/z$  263, 237, and 221, respectively. The ND-EESI method is capable of sampling explosives at pg levels directly from surfaces. Recently developed nanoextractive electrospray ionization (nano-EESI) has been characterized *in situ* ambient analysis of various compounds including trace amounts of explosives without sample pretreatments: TNT and RDX were analyzed from groundwater in negative and positive mode, respectively. Also some dissociation results were reported. Nano-EESI allows the experiments without sheat or discharge gases thus making the operation simple (Li et al., 2009).

APCI-MS has been used for analysis of nitroaromatics, nitramines and nitrate esters explosives including the most common encountered explosives in forensic science (Xu, van de Craats, & de Bruyn, 2004a). It has been stated that APCI exhibits

better limits of detection for TNT, NG, PETN, and RDX than electrospray; with the supplementary feed of dichloromethane, the chloride adduct formation improves the sensitivity of detection by almost one order of magnitude (Evans et al., 2002). SFC-APCI-MS provides a rapid and definitive method for explosive analysis providing sufficient sensitivity for application to casework samples. On interfacing with chromatographic system, the sensitivity was further increased (McAvoy et al., 1999). The HPLC-APCI-MS method to analyze peroxide explosives like HMTD and TATP has been applied successfully for analyzing peroxides in the bulk state or from post-blast extracts (Xu et al., 2004b). APCI with counter flow introduction (CFI) sampling has been successfully used to analyze TNT and RDX thus showing that system is suitable technique for explosive detection (Kojima et al., 2000; Takada et al., 2002). The negative mode APCI behavior of HMX and RDX together with their stable isotope labeled analogues has been studied: the base peak

$[M+NO_2]^-$  resulting from dissociation of  $NO_2^-$  group forming adduct with intact parent molecule. With the excess of ammonium acetate added  $[M+OAc]^-$  became the base peak; thus the acetate ions are suppressing the formation of nitrite adducts (MacCrehan, 2009).

Cooks et al. have demonstrated the ionization of nitroaromatic explosives like TNT and DNT using APCI and desorption APCI (DAPCI)-technique with acetonitrile or air as reagents. They stated that DAPCI is suitable method for selective detection of explosives adsorbed on surfaces (Song & Cooks, 2006). In addition, they have used thermal desorption APCI to analyze TNT, RDX, and PETN adsorbed on cotton swabs or as fine dust particulates (Popov et al., 2005); and to analyze RDX and TNT of cloths (Chen et al., 2007). ESI and APCI techniques were used to characterize an improvised explosive urea nitrate, and in both cases characteristic adduct ions:  $[M+NO_3]^-$  and  $[M+HNO_3+NO_3]^-$  were present (Fig. 9) (Tamiri, 2005). Recent

**TABLE 2.** Summary of MS explosive studies reported in Sections IV.A.2–IV.A.4.

Separation/analysis method	Explosives studied	Detection limits/sample conc.	Reference
<b>ESI &amp; APCI</b>			
ESI, quadrupole	HMX;RDX;PETN;Tetryl	170 fmol/ $\mu$ L	Straub & Voyksner, 1993
ESI-FTICR	TNT;RDX;HMX	Conc: ~ 1 mg/ml	Wu et al., 2002
SPE; ESI	Laurylamine acetate	DL: 8 pg	Burns, Lewis, & Doolan, 1997
ESI, positive mode	TATP	62.5 ng	Sigman et al., 2008
LC-ESI	RDX	Conc: 4*10 <sup>-8</sup> M or higher	Sigman et al., 2005
ESI; MS/MS	CL-20; TNT;RDX	-	Campbell et al., 2007
HPLC; ESI	CL-20	Conc: 100 mg/l	Balakrishnan et al., 2004
ESI;quadrupole	RDX;TNT;HMX; PETN	~20 ppm	McLellan et al., 2002
IC, ESI, quadrupole	BD substitute ascorbic acid	-	Lang & Boyle, 2009
ND–EESI	TNT;RDX;HMX;TATP;NG	DL: ~0.5-10 pg	Chen et al., 2009
EESI	TNT;RDX	1×10 <sup>-12</sup> M	Chen, Venter, & Cooks 2006
nanoEESI	TNT, RDX	1 ppt; 1 ppt	Li et al., 2009
HPLC;APCI–MS, ESI–MS, API–MS	21 nitrogen containing	DL: 0.012 ng or higher	Xu, van de Craats, de Bruyn, 2004
APCI; MS/MS	TNT;NG;PETN;RDX	5 fg; 200 pg; 250 pg; 5 ng, resp.	Evans et al., 2002
SFC;APCI–MS	DNT;TNT;PETN;RDX;HMX	DL (theretical): 119 ng or higher	McAvoy et al., 1999
HPLC; APCI–MS(/MS)	HMTD;TATP	DL: 0.26 ng; 3.3 ng, resp.	Xu et al. 2004
APCI–CFI; quadrupole	TNT, RDX	-	Kojima et al., 2000
APCI–CFI; quadrupole	TNT, RDX	10-20 ppt; 0.3 ppt in MS/MS (TNT)	Takada et al., 2002
APCI; DAPCI	TNT;nitroaromatics	-	Song & Cooks, 2006
Thermal desorption/APCI	TNT;RDX;PETN	<10 ng; <30 ng; <10 ng, resp.	Popov et al, 2005
DAPCI	RDX;TNT	<10 pg	Chen et al., 2007
APCI ;ESI	Urea nitrate	DL: 3 $\mu$ g; 6 $\mu$ g, resp.	Tamiri, 2005
APCI	Urea Nitrate	-	Tamiri et al., 2009
<b>DESI &amp; DART</b>			
DESI	RDX	DL: $\geq$ 0.5 ng	Cotte-Rodriguez & Cooks 2006
LTP, DESI	RDX; TNT	100 ng; 500 pg	Harper et al., 2008
DESI	TNT;RDX;HMX;PETN	10 pg or higher	Takáts et al., 2005; Cotte-Rodriguez et al., 2005

**TABLE 2.** (Continued)

DESI	TNT;RDX;HMX;PETN	5; 500;-;50 pg, resp	Justes et al., 2007
DESI	TNT;RDX;HMX;PETN	2,5 ng	Talaty et al., 2006
DESI	TATP	10 ng	Cotte-Rodriguez, Chen & Cooks, 2006
DESI, DAPCI	HMTD;TATP;TrATrP	10-15 ng	Cotte-Rodriguez et al., 2008
DESI	RDX; TNT; HMX; TNB	LOD: 10 ppb (RDX); 1 ppb (TNT)	Mulligan et al., 2007
DESI	TNT	10 µg/ml	Miao & Chen, 2009
DESI	RDX	various	Szagal & Brewer, 2009
DART	NG; various	~ 3 ppm	Cody, Laramée & Durst, 2005
DART	nitroaromatics	2 µg/ml	Song et al., 2009
DESI	RDX; PETN	1 ng; 250 pg	Wells et al., 2008
SESI	PETN;TNT	0.2 ppt; 0.4 ppt	Martínez-Lozano et al., 2009
SIMS	RDX;PETN;TNT;C-4; Semtex-H	-	Gillen et al., 2006
TOF– SIMS	gunpowders	-	Coumbaros et al., 2001
TOF– SIMS	gunpowders	-	Collins et al., 2003
TOF– SIMS	gunpowders	-	Mahoney, Gillen, & Fahey 2006
DBDI	RDX; TNT; PETN	LOD: 0.1 ng; 10 pg; 1 ng, resp	Na et al., 2007
PTD; DBDI	RDX, TNT, PETN	LOD: 1 pg; 500 fg; 500 fg, resp	Zhang et al., 2009
<b>OTHER</b>			
MALDI	16 different	-	Zhang et al., 2006
IS	RDX;HMX;TNAZ	-	Bakhtiar & Bulusu, 1995
READ	RDX;PETN;TNT	-	Boumsellek, Alajajian, & Chutjian, 1992
Laser thermal desorption	RDX		Morgan et al., 1999
APPI	DNT;TNT;RDX;HMX	3.3 pg or higher	Song et al, 2007; Song et al. 2009
LC;NI-APPI	DNT;TNT;RDX;HMX	0.029 ng and higher	Song & Bartmess, 2009
Laser ionization; TOF	DNT;TNT;RDX;PETN;Semtex	-	Marshall et al., 1994
Femtosecond laser TOF	nitroaromatics	-	Kosmidis et al., 1997
Femtosecond laser	TNT	-	Ledingham et al., 1995

(Continued)

**TABLE 2.** (Continued)

TOF			
Femtosecond laser MPI;TOF	DNT, TNT		Hankin et al., 2002
Femtosecond laser MPI;TOF	nitroaromatics	-	Mullen, Coggiola & Oser, 2006
Femtosecond laser MPI;TOF	TATP	670 pg	Yamaguchi et al., 2009
Laser MPI; TOF	nitrotoluenes	-	Tönnies et al 2001
Laser MPI; TOF	nitrotoluenes		Weickhardt & Tönnies, 2006
Laser PI; TOF	TATP	-	Mullen et al., 2006a
Laser PI;MPI; REMPI; TOF	nitrobenzenes	-	Pond et al., 2007
SPI; ion trap	TNT	-	Schramm et al., 2009a
SPI;ion trap	various	-	Schramm et al., 2009b
SPI	NTO	-	McMillen et al., 1997
SPI; TOF	nitroaromatics	-	Schramm et al., 2008
SPI;TOF	TATP; nitroaromatics	-	Mullen et al., 2006b
SIFT	TATP	10 ppb	Wilson ,Prince, & McEwan, 2006
PTR	TATP	15 ppb	Shen et al., 2009
PTR-TOF	RDX, TNT, HMX, PETN, Semtex A	-	Mayhew et al., 2010
ASGDI	TNT	1.4 pptr	McLuckey et al., 1998
ASGDI; Ion trap	DNT;TNT	-	Asano, Goeringer, & McLuckey 1995
ASGDI; MS/MS	various	-	McLuckey et al., 1996
UV laser; ion trap	NC	-	Yang, Ramsey, & Kim, 1996
DEA	TNT	-	Sulzer et al., 2008
DEA	TNT	-	Mauracher et al., 2008
Laser; quadrupole	TNT	-	Dale et al., 1994
SPAMS	TNT;RDX;PETN	LOD: ~1 pg	Martin et al., 2007b
PD	HMX;RDX;PETN;TNT; NC;CL-20	-	Håkansson at al., 2000
PD	HMX;RDX;NC	-	Zubarev et al., 1997
PD	HMX	-	Håkansson et al, 1999.
CI	RDX	-	Florián et al., 2007
EI/CI; quadrupole	TNT	-	Mathurin et al., 2000
EI/CI GC-MS	various	-	Sigman & Ma, 2001
CI	TNT;HMX;RDX	-	Chen et al., 2004
CI	TNT	-	Riter, Fraley, & Cooks 2000
CI	TNT	-	Yinon et al., 1995; Chen, Chen, & Cooks, 2004
APCI; quadrupole	TNT; nitrobenzenes, nitrotoluenes	0.1 µg/ml	Song, Chen, & Cooks, 2005; Song & Cooks, 2006
EI; TOF	NC; RDX	-	Zhou et al., 2009
IRMS	RDX	-	Lock & Meier-Augenstein, 2008
IRMS	TATP;PETN	-	Benson et al., 2009a
IRMS	Ammonium nitrate	-	Benson et al., 2009b
IRMS	TNT	-	Berg, Bolotin, & Hofstetter 2009
IRMS	Black powder	-	Gentile, Siegwolf, & Delémont, 2009
IRMS	Mimic compounds	-	Meier-Augenstein, Kemp, & Lock, 2009

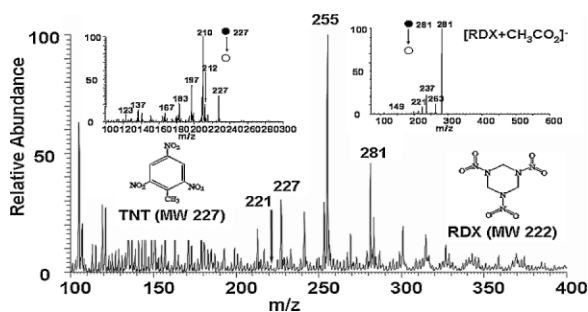
LC-APCI studies revealed that UN can be extracted into non-polar solvents containing crown ethers. However, UN has low survivability of detonation: only 1 out of 28 samples showed typical adduct ions with the main decomposition products being urea and ammonium and nitrate ions (Tamiri et al., 2009).

### 3. DESI and DART Ionization Studies

Desorption electrospray (DESI) mass spectrometry has been introduced recently as a new, promising method for explosive

analysis (Takáts et al., 2004; Takáts, Wiseman, & Cooks, 2005). The mechanism for the formation of gas phase reagent ions in DESI takes place in the same way than that in electrospray ionization, followed either by the ionization of analyte molecules and electron or proton transfer, or by the attachment of reagent ions. Compared to other mass spectrometric methods, DESI can operate at ambient conditions directly from a wide variety of surfaces without prior sample preparation. DESI has been applied for qualitative and quantitative analysis (having precision of 2.3% in quantitative measurements). Analysis of different



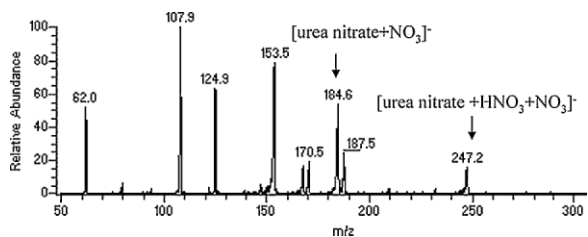


**FIGURE 8.** Simultaneous detection of TNT and RDX mixtures on human skin by ND-EESI-MS<sup>n</sup>. The insets show the CID spectra of ions of interests. Reprinted with permission from Chen et al. (2009), Copyright 2009 Elsevier.

components in the explosive mixtures is possible because the characteristic ions, for example, chloride adducts, can be recorded in the same mass spectrum. The detection of explosives from ambient surfaces is possible at distances from 1 up to 3 m from the mass spectrometer, even though with the latter the limits of detection are multiplied (Cotte-Rodriguez & Cooks, 2006). Also, a specific and gentle sampling system to DESI has been introduced: the low-temperature plasma (LTP)-probe interacts directly with the sample without damaging it. This probe is suitable for solid, solution, and gas-phases for fast MS analysis. Because air can be used as discharge gas in ionization process LTP probe could be used in portable IMS devices (Harper et al., 2008).

Desorption electrospray ionization (DESI)-MS is relatively fast (analysis time 5 sec), highly sensitive and specific when analyzing complex mixtures and trace amounts of various explosives such as RDX, HMX, TNT, PETN, and their plastic compositions from a wide variety of surfaces (Cotte-Rodríguez et al., 2005; Takáts et al., 2005) and from human skin (Justes et al., 2007). DESI-MS has been applied to *in situ* analysis of explosives from different fabrics including, for example, cotton silk, leather and spandex. Even if the physical properties of the fabric may affect detection limits, all the fabrics were suitable surfaces for investigation thus proving that DESI may be implemented for safety and forensic applications (Talaty et al., 2008).

In addition, peroxide explosives like TATP (Cotte-Rodríguez, Chen, & Cooks, 2006) and TATP, PETN, and TrATrP (Cotte-Rodríguez et al., 2008) have been analyzed. The articles state that DESI is suitable for detection of TATP and other peroxide based explosives located at different surfaces. The addition of alkali metals to the spray as dopants improves selectivity and sensitivity. The unique CID behavior to alkali

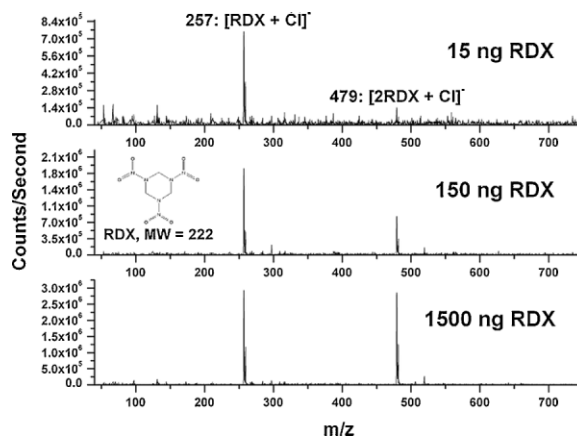


**FIGURE 9.** Negative ion ESI mass spectrum of urea nitrate. Reprinted with permission from Tamiri (2005), Copyright 2005 Wiley.

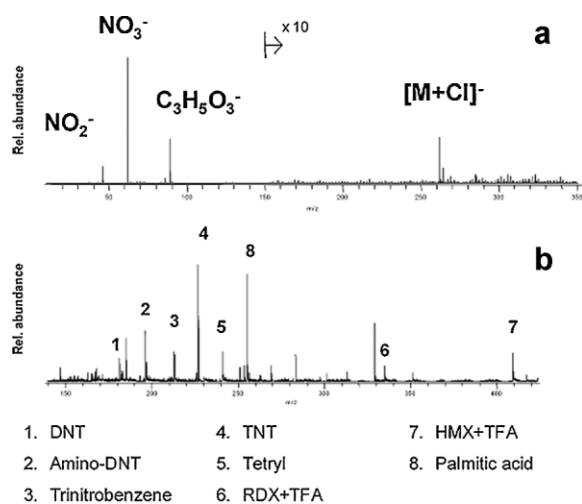
metal complexes of TATP and PETN may serve as mass spectrometric fingerprints to these peroxide explosives. DESI-MS can also be used in latent fingerprint chemical imaging (Ifa et al., 2008b).

Desorption electrospray ionization (DESI)-MS has been used for fast analysis of explosives and agricultural chemicals in water: the results indicated that DESI is efficient method to analyze low levels of chemicals present in aqueous samples (Mulligan et al., 2007). When TNT was analyzed from the liquid sample it was noticed that ESI-MS produces radical anion M<sup>-</sup> due to reduction (electron capture) in the ESI source in which electrolysis is inherent, while DESI yielded deprotonated species [M-H]<sup>-</sup>; probably due to lack of voltage apply to the sample solution (Miao & Chen, 2009). This deprotonation in liquid sample is also contrast to solid sample results where radical anions of TNT have been observed (Takáts et al., 2005). The general ion chemistry of RDX including the analysis and mechanisms of ion formation has been recently studied. It was shown that the dimer to monomer peak ratio increases when the amount of deposited material increases (Fig. 10). Additionally, a method for quantitative analyses based on peak intensities to determine the amount of explosive present on surface was created (Szakal & Brewer, 2009). The principles of and applications of ambient pressure MS-techniques focusing on the DESI method have been reviewed (Cooks et al., 2006) as well as the forensic applications of ambient mass spectrometry (Ifa et al., 2008a).

Other techniques similar to DESI have been recently introduced. Direct Analysis in Real Time (DART) source has been used to detect hundreds of chemicals including nitroglycerin and various explosives from different surfaces. The detection sensitivity to NG was demonstrated from particles adsorbed to clothes. Exposure occurred near to construction site where dynamite was used: 8 hr later NG was clearly detected from test person's tie. In addition, wide range of explosives including peroxides produced detectable peaks as seen in Figure 11 (Cody, Laramée, & Durst, 2005). A Negative Ion Direct Analysis in Real Time (NI-DART) has been used to investigate the ionization mechanisms of over 42 compounds including some nitroaromatic explosives. NI-DART showed high sensitivity to ionize nitroaromatic explosives even though it was 50 times less sensitive than APPI; and it was found to be efficient



**FIGURE 10.** Background-subtracted DESI-MS spectra for deposited RDX amounts. Reprinted with permission from Szakal and Brewer (2009), Copyright 2009 American Chemical Society.



**FIGURE 11.** a: Nitroglycerin detected on tie after exposure to the plume from blasting. b: Explosives detected at a concentration of 3 ppm in water. Reprinted with permission from Cody, Laramée, and Durst (2005). Copyright 2005 American Chemical Society.

ionization method for nitramine explosives through anion attachment reaction when halogenated solvents were used. The operation of DART was found to be easier than of atmospheric pressure photoionization (APPI) (Song et al., 2009).

A prototype API-MS having implementation of DESI and DART ionization on fieldable mass spectrometer has been described. In the field of explosives, this instrument was used to detect chloride adducts of RDX and PETN anions (Wells et al., 2008). SESI has been used to determine the sensitivity of detection towards PETN and TNT vapors. Although the limits of detection were low ppt levels, 0.2 and 0.4 ppt, respectively, the number of analyte molecules required to identification was implied to be too numerous. The inefficient use of sample was concluded to result from low charging probability, finite ion transmission, low counting probability of mass spectrometers and from interfering background (Martinez-Lozano et al., 2009).

Cluster SIMS has been used to characterize high explosives dispersed as particles on silicon substrates: they were bombarded with carbon cluster primary ion beams. These cluster projectiles increase the signal intensity and eliminate the degradation when compared to monoatomic ion beams. Thus this method provides greater speed and sensitivity in analysis of explosives than conventional static SIMS (Gillen et al., 2006). TOF-SIMS has been utilized to characterize gunpowder samples. Preliminary studies indicated the TOF-SIMS potential for powder residue analyses (Coumbaros et al., 2001; Collins, Coumbaros, & Horsley, 2003). More recent results indicate that mass spectral characteristics of each individual sample were successfully obtained and being consistent with known compositions thus proving TOF-SIMS to be useful for forensic analysis of gunpowder samples (Mahoney, Gillen, & Fahey, 2006).

Dielectric Barrier Discharge Ionization (DBDI)-MS has been used to investigate RDX, TNT, and PETN; this method allows trace detection from various surfaces and matrices without any sample preparation. This method is reported to be sensitive from picogram to nanogram range. The additional advantages include low cost, small size, and handiness thus making it

suitable to combine with portable mass spectrometers (Na et al., 2007). Very recently, a combined construction of low temperature plasma desorption (LPT) using DBDI was undertaken to detect explosives from solid surfaces. This construction has greatly improved sensitivity; limits of detection were reported to be as low as 500 fg. Other advantages include direct ionization of explosives under ambient conditions without restriction of substrates, simple structure and no requirement of spray solution, comparable sensitivity to DESI, small size, and low power consumption (Zhang et al., 2009).

#### 4. Other Ionization Techniques

Various other ionization techniques suitable for explosive analysis have been studied. The inclusion complexes of 16 explosives with  $\beta$ -cyclodextrin have been determined using MALDI-MS with satisfactory results (Zhang et al., 2006). Complex formation of HMX and RDX with  $\alpha$ -,  $\beta$ -, and  $\gamma$ -cyclodextrins has been studied using Ion Spray-MS (Bakhtiar & Bulusu, 1995). Reversal electron attachment detection (READ)-MS technique has been used to detect RDX, PETN, and TNT in negative mode (Boumsellek, Alajajian, & Chutjian, 1992). RDX has been analyzed by laser thermal desorption MS (Morgan et al., 1999).

Recently, a negative mode atmospheric pressure photoionization (APPI)-MS has been introduced. It has been used to study various compounds including nitroaromatic explosives, HMX and RDX. In case of nitroaromatics, three different ionization mechanisms were shown to be involved: electron capture (EC), dissociative electron capture and proton transfer. Also, fourth novel mechanism, anion attachment, was found for negative ion APPI. It was stated that with the available four mechanisms this method can ionize wider range of compounds than other negative ionization methods (Song et al., 2007, 2009). The construction of LC/Ni-APPI decreases the limit of quantification to explosives even two orders of magnitude when compared to corresponding GC/NiCI-MS and LC/Ni-APPI-MS methods (Song & Bartmess, 2009).

Laser ionization-TOF-techniques have been introduced to ionize explosive species (Marshall et al., 1994); femtosecond laser TOF has been used to analyze TNT and other nitro-aromatic molecules (Ledingham et al., 1995; Kosmidis et al., 1997). Recent studies have demonstrated the ability of ultrafast laser ionization to generate analyte molecular and structure-specific ions from nitro-aromatic compounds. It was also noticed that the presence of  $\text{NO}_2$  functional group influenced strongly to the ionization/fragmentation behavior of these molecules (Hankin et al., 2002). Also, photoionization and photodissociation processes of nitroaromatic explosives and explosive related compounds have been investigated at three laser wavelengths and power densities. The results indicated that ultraviolet and visible wavelengths are better at generating the molecular ion than 795 nm irradiation. In addition, the effect of Coulomb explosion in the photoionization of nitroaromatic compounds has been revealed (Mullen, Coggiola, & Oser, 2009). In study of TATP, femtosecond laser was utilized for both detection of the molecular ion and enhancement of sensitivity leading to detection limit of 670 pg to the molecular ion. A shorter laser pulse width would be more useful for measurement of molecular ion, and shorter wavelength would increase the sensitivity for TATP (Yamaguchi et al., 2009).

Laser multiphoton ionization-MS with sub-picosecond pulses has been employed to detect and identify nitrotoluenes: the mass spectra are characterized by intense fragmentation. To DNT and TNT the OH loss fragment becomes dominant peak at higher mass range (Tönnies et al., 2001). Latter study showed that the relative intensity of the molecular ion peak of nitrotoluene decreases with increased degree of substitution whereas in the case of TNT this peak vanishes. The abundant presence of  $\text{NO}^+$  was found not to be related to laser intensity but probably a different formation pathway (Weickhardt & Tönnies, 2002). Investigations of peroxide based TATP with two separate photoionization instruments revealed differences in spectra depending on pulse time. Femtosecond pulse provides appreciable parent ion signal, while it is not seen in nanosecond pulsed spectra. In addition, nanosecond pulses yielded greater fragmentation. These results are in agreement with corresponding results reported for explosives and explosive related compounds (Mullen et al., 2006a). A comparative study between three ionization methods, SPI, MPI, and Resonance Enhanced Multi Photon Ionization (REMPI) has been made to explosive-related compounds. SPI was concluded to be the most promising method for ionization of these compounds (Pond et al., 2007). In addition, TD-SPI-ion trap-MS has been used to detect TNT and DNT; it was shown that trace detection of security relevant substances within complex matrices was possible with this novel combination (Schramm et al., 2009a,b).

Single photon ionization (SPI) has been used to analyze the decomposition of NTO (5-nitro-1,2,4-triazol-3-one) (McMillen et al., 1997). SPI-TOF has been used for determination of ionization potentials (IP) of various explosives: the results indicate that IP's of the explosives much below 10.5 eV with the exception of EGDN having IP 10.7 eV; thus the IP's of explosives are slightly lower than the photon energy used in SPI lasers (10.5 eV at 118 nm). This means that SPI is capable of ionizing explosives and only a minor amount of additional energy is transferred to the explosive resulting in little fragmentation. Thus SPI can be called a "soft ionization" method in case of explosives (Schramm et al., 2008). It was shown earlier that using this ionization method the nitro-containing explosives yielded mass spectrum dominated by molecular ion and minor amount of dissociation products; whereas, with TATP fragmentation occurs readily (Mullen et al., 2006b).

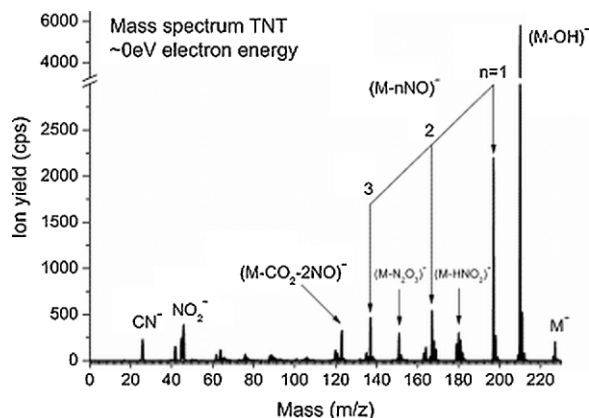
Wilson, Prince, and McEwan (2006) have tested the potential of selected-ion flow tube (SIFT) MS with  $\text{H}_3\text{O}^+$ ,  $\text{O}_2^+$  or  $\text{NO}^+$  as the reagent ions to real-time detection of TATP. They concluded that only  $\text{NO}^+$  yields significant reaction product ion thus showing unequivocal evidence for the presence of TATP. Proton transfer reaction (PTR)-MS with  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  as the reagent ions has been used to detect TATP. It was shown that in reduced electric field typical protonated  $[\text{TATP}+\text{H}]^+$  and adduct  $[\text{TATP}+\text{NH}_4]^+$  ions are formed, respectively (Shen et al., 2009). In recent article five different high explosives were analyzed comparatively with two different PTR-TOFMS instruments. They concluded that this method can be used to unambiguously detect explosives from VOCs emitted from solid samples or from traces present on surfaces. Thus this novel method seems to be suitable for the rapid detection of a broad range of solid explosives (Mayhew et al., 2010).

Another ionization method, atmospheric sampling glow discharge ionization (ASGDI) has been employed to ionize and detect various explosives. McLuckey group used ASGDI to

determine TNT in ambient air (McLuckey et al., 1988), to perform targeted compound detection for DNT and TNT (Asano, Goeringer, & McLuckey, 1995), and to detect and perform dissociation reactions to various explosives (McLuckey et al., 1996).

The selective dissociation of nitrocellulose has been demonstrated by irradiation of UV-laser and ion trap MS (Yang, Ramsey, & Kim, 1996). Electron attachment to TNT in the gas phase causes remarkable fragmentation: the most dominant dissociative electron attachment (DEA) reaction is the loss of neutral OH radical yielding  $[\text{M}-\text{OH}]^-$  anion (Fig. 12) (Sulzer et al., 2008). This DEA-technique is a powerful technique to identify small traces, therefore it has been stated to be a fingerprint in future sensing and field detection of explosives (Mauracher et al., 2008). The detection of TNT using single-particle quadrupole ion trap has been demonstrated (Dale et al., 1994). To identify high explosives single-particle aerosol mass spectrometry (SPAMS) has been employed. With this method detection limit of  $\sim 1$  pg of explosive compound is reported and analysis of composite explosives revealed the potential of this method to identify the individual components. It was stated that SPAMS is sensitive, specific, reliable, and reagent-free and may provide a viable option for airport passenger and baggage screening (Martin et al., 2007b). Since high explosives are also used as matrices in plasma desorption mass spectrometry (PDMS) various low-mass ions originated from their decomposition are present both in negative and positive modes. With the explosives HMX, RDX and CL-20 abundant presence of  $\text{NO}_2^-$  and  $\text{NO}^+$  ions were detected indicating decomposition. Presence of  $\text{C}_2\text{H}_4\text{N}^+$  and  $\text{CH}_2\text{N}^+$  ions may explain the observed high charge state observed with these matrices. TNT did not produce any of the aforementioned ions neither works as matrix (Håkansson et al., 2000). The presence of explosives such as RDX or HMX in matrices also enhances the protonation of peptides, proteins (Zubarev et al., 1997), and insulin (Håkansson et al., 1999).

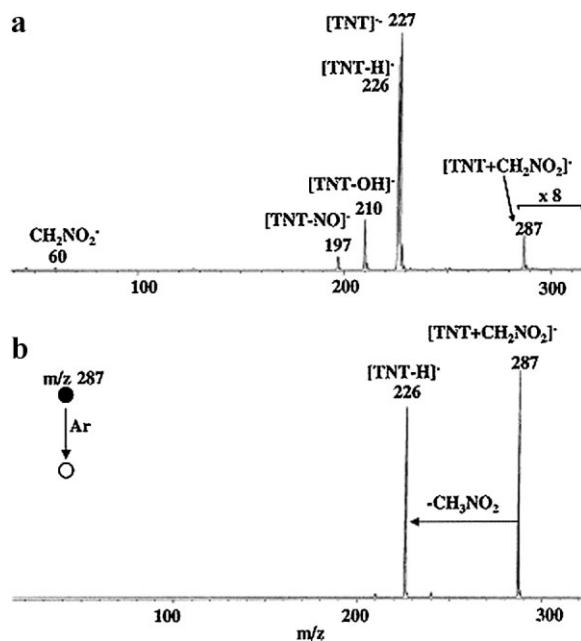
Recently, the dissociation of RDX and its three metabolites was studied by monitoring the fragment ions to elucidate the fragmentation mechanisms using negative chemical ionization (NCI) and methane as the reagent gas. With the help of isotope-labeled standards and additional free energy calculations the fragmentation pathways and intermediates were determined.



**FIGURE 12.** Negative ion mass spectrum of TNT recorded at electron energy close to 0 eV. Reprinted with permission from Sulzer et al. (2008), Copyright 2008 Elsevier.

The most abundant anions detected were  $[\text{C}_2\text{H}_4\text{N}_3\text{O}]^-$  at  $m/z$  86 and  $[\text{C}_2\text{H}_4\text{N}_3\text{O}_2]^-$  at  $m/z$  102 originating from the dissociation of  $[\text{M}-\text{NO}_x]^-$  species (Florián et al., 2007). The combination of dual EI/CI instrument has been used to study TNT: in positive mode the fragment ion  $[\text{TNT}-\text{OH}]^+$  dominates, in negative mode after  $\text{O}_2^-$  addition the molecular  $[\text{TNT}]^-$  ion dominates without remarkable fragmentation (Mathurin et al., 2000). The detection limits of various organic explosives using GC-MS with electron ionization and both positive and negative mode chemical ionization methods (PICI and NICI, respectively) have been determined. The detection limits were lower with NICI with the exception of RDX where PICI achieved the lowest detection limit (Sigman & Ma, 2001). Cooks' group has demonstrated gas-phase synthesis of arylnitrenium ions from TNT and related nitroaromatics: this was made by nitro-reduction and ionization with 1,2-dichloromethane as the reagent gas. Additional ionization of explosives HMX and RDX produced typical  $[\text{M}+\text{CH}_2\text{ClCH}_2-\text{CH}_2\text{NNO}_2]^-$  ions: this selective ionization increases selectivity and sensitivity of the detection thus providing enhanced method to detect these explosives from mixtures (Chen et al., 2004). Other studies include the highly selective gas-phase reactions with ethyl vinyl ether of fragment ions of TNT and RDX (Meurer et al., 2004). The applicability of denitration of nitroaromatic compounds by aryl nitrile radicals have been tested with TNT (Riter, Fraley, & Cooks, 2000).

The formation and dissociation of Meisenheimer hydride complex of TNT  $[\text{TNT}+\text{H}]^-$  has been studied (Yinon et al., 1995). More recently, the formation of Meisenheimer complexes with TNT in the gas phase have been studied using NCI. Two different types of complexes: carbon-bonded complex  $[\text{TNT}+\text{CH}_2\text{NO}_2]^-$  and oxygen bonded  $[\text{TNT}+\text{CH}_3\text{OCH}_2\text{O}]^-$  were observed with nitromethane and methanol/formaldehyde (i.e., hemiacetal) as the reagent gases, respectively (Fig. 13).



**FIGURE 13.** a: Negative ion CI mass spectrum of TNT using  $\text{CH}_3\text{NO}_2$  as the reagent gas. b: CID product ion MS/MS spectrum of the Meisenheimer complex  $[\text{TNT}+\text{CH}_2\text{NO}_2]^-$  ( $m/z$  287). Reprinted with permission from Chen, Chen, and Cooks (2006), Copyright 2006 Elsevier.

Dissociation of  $[\text{TNT}+\text{CH}_2\text{NO}_2]^-$  complex yielded  $[\text{TNT}-\text{H}]^-$  ions indicating higher gas-base acidity of TNT than nitromethane (Chen, Chen, & Cooks, 2004). Corresponding complexes,  $[\text{TNT}+\text{CH}_3\text{OCH}_2]^-$ , are also formed with acetone as the reactant gas producing a highly specific method to detect TNT from mixtures (Song, Chen, & Cooks, 2005). With acetonitrile or oxygen from air as the reactant gas complexes the formation molecular radical anion  $[\text{TNT}]^-$  together with corresponding anionic complexes  $[\text{TNT}+\text{CH}_2\text{CN}]^-$ ,  $[\text{TNT}+\text{CN}]^-$  and  $[\text{TNT}+\text{O}]^-$ ,  $[\text{TNT}+\text{OOH}]^-$  are detected (Song & Cooks, 2006).

Recently a time-of-flight mass spectrometer combined with temperature jump technique was described. This new construction allows fast heating of the sample thus enabling the time-resolved characterization of the decomposition, ignition and combustion of energetic materials. Time-resolved spectra for the ignition of nitrocellulose and RDX were used as samples. The simultaneous measurement of temperature reveals the ignition temperature and the characteristic reaction time providing a new tool for the analyses of energetic materials (Zhou et al., 2009).

In addition, a specialized application of mass spectrometry, isotope ratio mass spectrometry (IRMS) has been recently used to analyze the isotopic compositions of the starting materials, intermediates and the final products in the synthesis of RDX (Lock & Meier-Augenstein, 2008) and explosives like TATP and PETN (Benson et al., 2009a) and ammonium nitrate (Benson et al., 2009b). A combination of SPME-GC-IRMS has been used to determine  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  signatures of TNT (Berg, Bolotin, & Hofstetter, 2007) and the isotopic variations of black powder (Gentile, Siegwolf, & Delémont, 2009). It has been reported that the presence of nitrogen may interfere the  $^2\text{H}$  isotopic analysis of nitrogen-rich explosives because of partially overlapping signals (Meier-Augenstein, Kemp, & Lock, 2009).

## B. Tandem MS

Some advanced detection techniques, such as ion trap and FTICR, offer one remarkable advantage in analyses of unknown compounds. Unlike other chemical identification methods, these methods above allow more information on target substances *via* Tandem Mass Spectrometry (MS/MS) experiments by generating structural information on individual fragments produced from the first fragmentation (Sleno & Volmer, 2004). These fragment ions are generally specific, thus increasing the reliability of the analysis. MS/MS enables the analysis of samples from mixtures or without prior separation and purification.

One of the pioneering studies of  $\text{MS}^n$  and CID of explosives demonstrated the capability of quadrupole-TOF to analyze DNT, RDX, and PETN (McLuckey, Glish, & Grant, 1990). Selected reaction monitoring (SRM)—technique has been applied to qualitative analysis of explosives in post-blast debris (Werweij et al., 1993). Tandem MS has stated to be crucial in detection and identification of peroxide explosives from debris. In addition, the presence of molecular ion  $[\text{TATP}+\text{H}]^+$  was demonstrated (Xu et al., 2004b). ESI-CID-experiments to various nitro-explosives has been made to show the typical fragmentation pathways (Yinon, McLellan, & Yost, 1997). Nitro-group containing explosives can be also detected through denitration reaction using aryl nitrite radical cations; MS/MS has been used to

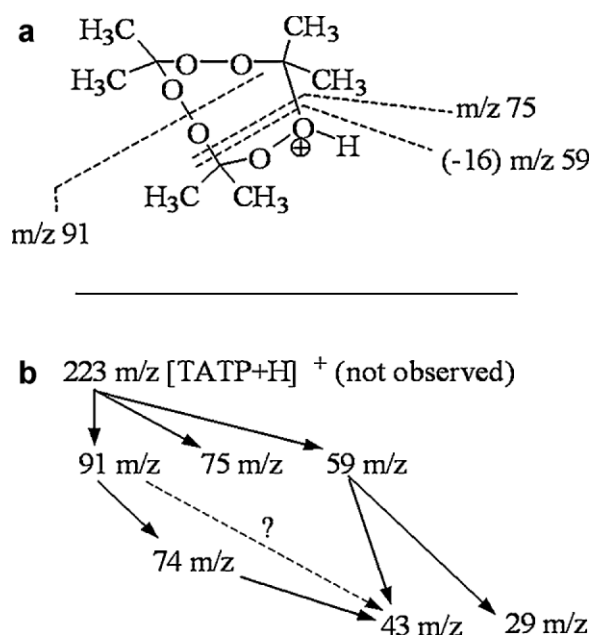
investigate the pathways of the occurring ion–molecule reactions (Riter, Fraley, & Cooks, 2000). The fragmentation patterns of hexanitrostilbene (HNS) have great similarity to that of TNT (Yinon et al., 1991). This was later confirmed when the fragmentation pathways of three explosives with similar structures (HNS, RDX, and TNT) have been studied using ion trap MS with ESI and APCI sources (Fu et al., 2006).

The complex formation and dissociation of ammonium nitrate both in positive and negative modes have been investigated using ESI-MS/MS (Zhao & Yinon, 2001). Latter studies included several inorganic explosive oxidizers (nitrates, sulfates, chlorates, and perchlorates). The identities of formed clusters were confirmed with isotopic label compounds and with CID reactions. Additional three explosive samples were used to test validity and feasibility of this method. It was stated that ESI-MS is well suited for the analysis of explosive oxidizers (Zhao & Yinon, 2002c).

Positive CI-GC-tandem MS has been found suitable, sensitive, and selective method to analyze explosives like TNT, DNT, and RDX from complex matrices (Perr, Furton, & Almirall, 2005b). Very recently, GC-tandem MS with negative chemical ionization has been used to analyze nine explosives using selective reaction monitoring for eliminating any interferences. The combination of fast GC method with dynamic collision-induced dissociation (DCID) offered a method for analysis of explosives with detection limits between 0.5 and 5 pg. This evokes statement NCI-DCID-tandem MS being at least comparable if not superior to other MS techniques (Collin, Zimmermann, & Jackson, 2009).

The characterization of smokeless powders and detection of its stabilizers using nanoelectrospray ESI (nESI) and tandem MS has also been reported. The MS study was focused for the simultaneous detection of the organic stabilizers present in powders: all but two out of seven samples were distinguished. However, these two were different brands from the same manufacturer (Scherperel, Reid, & Waddell Smith, 2009). Another recent study revealed the fragmentation pathways of DMNB. It was found that the protonated molecule  $[\text{DMNB}+\text{H}]^+$  is susceptible to dissociation induced by heat or collision. It was also stated that the propensity of DMNB to form stable sodium adducts can be exploited *via* DESI-MS detection (Paine et al., 2009). Very recently, the presence of oligoperoxides in TATP was analyzed using CI-MS and ESI-MS with CID reactions. The results suggested that these oligomers may be useful in forensic investigations to track the origin of the explosive due to changes in relative amounts and distributions of oligomers even though they seem to decompose under gentle heating (Sigman et al., 2009).

Cooks' group has dissociated Meisenheimer complexes of various nitroaromatic compounds including TNT (Song, Chen, & Cooks, 2005; Song & Cooks, 2006). The selective detection of TNT by monitoring the characteristic fragmentation patterns makes this method suitable for confirmatory detection of explosives. A LC-ESI-MS/MS method for quantitative analysis of HMX has been developed in negative ionization mode: the acetate adduct  $[\text{HMX}+\text{CH}_3\text{COO}]^-$  at  $m/z$  355 is the precursor ion used in CID experiments. The major product ions were  $[\text{HMX}-2 \times \text{CH}_2\text{NNO}_2]^-$ ,  $[\text{HMX}-\text{H}-\text{CH}_2\text{NNO}_2-\text{HNO}_2]^-$ , and  $[\text{HMX}-\text{CH}_2\text{NNO}_2-\text{NO}]^-$  at  $m/z$  147,  $m/z$  174, and  $m/z$  192, respectively. This method is useful for detection HMX in soil samples (Pan et al., 2006c).



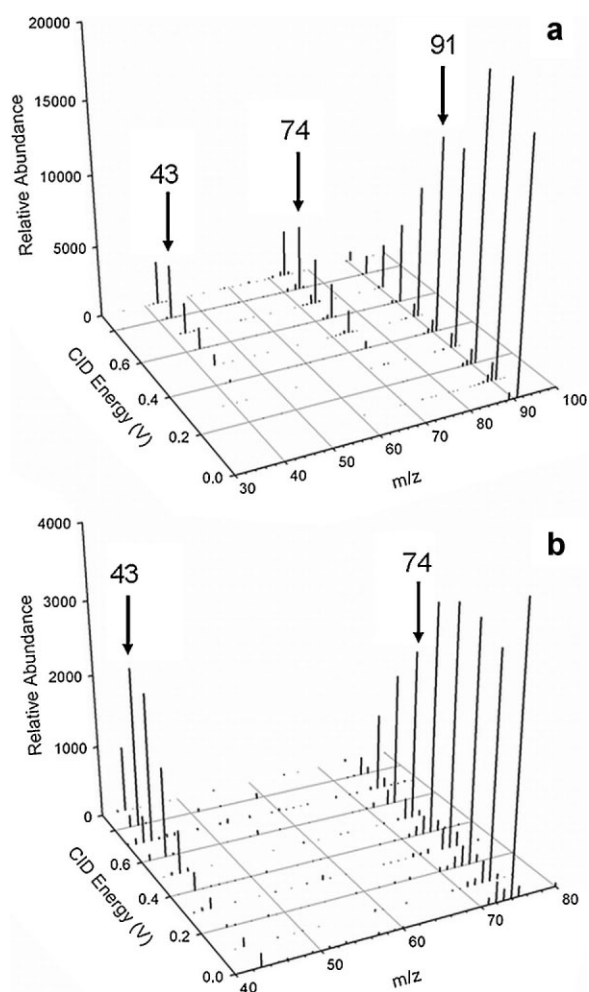
**FIGURE 14.** Proposed  $[\text{TATP}+\text{H}]^+$  fragmentation pathways. a: Primary and b: secondary fragmentation pathways. Reprinted with permission from Sigman et al. (2006), Copyright 2006 Wiley.

The dissociation of ammonium adduct of TATP  $[\text{TATP}+\text{NH}_4]^+$  produces low abundance of product ions (Sigman et al., 2006). The dissociation pathway and spectrum of TATP are depicted in Figures 14 and 15.

### C. MS in Environmental and Biological Explosive Studies

In addition to explosive detection and identification, MS is a powerful tool for analyzing various explosives and their degradation products in soil, water, and biological samples. In its applications in the aquatic environment, nitroaromatic explosives and their degradation products in water samples can be detected by using LC-MS (Gates et al., 1996). The nitroaromatic and nitramines and their metabolites present in former military sites have been investigated using GC-MS (Levsen et al., 1993). EI-MS has been used to analyze the metabolites of PETN (Binks et al., 1996). Using HPLC-MS, explosive residues in drainage water collected from ammunition plant have been analyzed: several explosives, by-products and metabolites were found (Schreiber, Efer, & Engewald, 2000).

The presence of RDX, its metabolites and other explosives in the groundwater has been studied by using LC-APCI-MS (Cassada et al., 1999). Latter studies concerning presence and biodegradation of RDX and HMX in soils revealed two degradation pathways: one included the sequential reduction of  $\text{NO}_2$  while the second route involved the enzymatic cleavage of C–N bonds producing nitramine ring cleavage products that autocompose further (Groom et al., 2001, 2002). They also reported that analysis of explosives using HPLC-MS method (in negative mode) offers detection limits 50-fold lower as compared to electrokinetic chromatography methods (Groom et al., 2003). LC-ESI-MS has been demonstrated for determination of RDX and its derivatives in soils (Pan et al., 2006b). The study of degradation products of RDX in groundwater revealed three



**FIGURE 15.** a: Methane PICI MS/MS product ion spectra for TATP shown as a function of CID energy following isolation of  $m/z$  91. b: MS<sup>3</sup> product ion spectra showing the isolated  $m/z$  74 decomposing to produce  $m/z$  43 as the CID energy is increased. Reprinted with permission from Sigman et al. (2006), Copyright 2006 Wiley.

different product ions. These ions are good indicators of RDX because they do not have natural neither industrial sources and have also unique chemical properties (Beller & Tiemeier, 2002). Another study discussed the anaerobic biotransformation of RDX by aquifer bacteria (Beller, 2002).

Eight different explosive traces from military area soil were measured with pressurized fluid extraction LC-MS or GC-MS: with the exception of NB this method provides satisfactory results (Campbell et al., 2003). Further study using similar methods investigated the presence of organonitrogen explosives and their degradation products present in the groundwater at a former military site: it was concluded that the explosive residues were widely distributed in the underlying groundwater (Spiegel et al., 2005). A total number of 12 explosive related compounds were analyzed from water samples originating from the area of former ammunition plant by using LC-ESI-MS/MS: the identification and quantification of polar degradation metabolites and technical by-products of explosives was conducted by using specific precursor/product ion transitions, so called multiple reaction monitoring (MRM) detection (Schmidt et al., 2006b).

Later, it was reported that LC-MS is able to analyze HMX and RDX present in water samples. The formation corresponding of explosive anion adducts was achieved by adding chloroform into the nebulizing gas. The concentrations as low as  $0.2 \mu\text{g L}^{-1}$  were detected (Vigneau & Machuron-Mandard, 2009). The fragmentation pathways of RDX have been studied with zerovalent iron nanoparticles. It was concluded that the dissociation of RDX occurs *via* two different routes (Naja et al., 2008). The reduction of HMX with zerovalent iron has been studied: the LC-ESI-MS of intermediate products: the results suggested the occurrence of initial denitration by cleavage of the N-NO<sub>2</sub> bond (Monteil-Rivera et al., 2005).

The presence of traces of TNT and DNT in seafloor sediments originated from 50 years old unexploded ordinances have been studied using SPME-GC/MS (Darrah, Chutjian, & Plett, 1998). The products and isomers of anaerobic bacterial biodegradation of DNT isolated from earthworm intestine (Shin et al., 2005) and aerobic bacterial biodegradation products of TNT (Tope, Jamil, & Baggi, 2000) have been analyzed with LC-MS and GC-MS, respectively. ESI-TOF-MS has been used to identify and characterize TNT mediated stress shock proteins (Ho et al., 2004). The reduction products of TNT by yeasts leading to mono- and dihydride complexes of TNT have been analyzed using GC-MS (Ziganshin et al., 2007). A pilot study concerning the biomonitoring of nitroaromatics and monoaminodinitrotoluenes (metabolites of TNT) in urine by GC-MS has been reported: the lowest detection limits were of the order of magnitude of  $0.5 \mu\text{g L}^{-1}$  (Bader et al., 1998). GC-MS has been used to detect not only nitroglycerin and its metabolites in urine (Akrill & Cocker, 2002), but also adducts of dinitrobenzenes with hemoglobin (Myers et al., 1999). ESI-MS has been used to study *in vitro* adducts of prosthetic heme and TNT (Bakhtiar et al., 1997). Polar metabolites of nitroaromatic explosives have been characterized using ESI-LC-MS/MS: the ortho effect plays significant role in elucidation of these compounds (Schmidt et al., 2006a). Recent similar study presenting *in vitro* method for simulation of human metabolic transformations of four explosives was undertaken. Only TNT was successfully metabolized while no biotransformations were observed for RDX, HMX, and tetryl. To these explosives the best biomarkers of human exposure are not the metabolites but the parent compounds (Bell, Gayton-Ely, & Nida, 2009).

#### D. IMS Coupled with MS

When being integrated, IMS and MS form a powerful tool to analyze and identify any chemical compound considering the fact that capabilities and advantages of MS are combined with the specific feature of IMS. IMS provides value added information prior to mass analysis by providing second dimension of separation. In IMS the separation is mainly based on ionic properties, thus IM-MS is capable to separate isomers, isobars, conformers or chiral compounds that have the same molecular mass. In this combination IMS instrument usually serves both as rapid analyte ion separator and as filter for the undesirable background ions before MS measurements. This improves the signal/noise-ratio and detection limits (Guevremont, 2004a). One such construction is API-IMS/MS, where IMS module provides fast separation before mass spectrometric detection (Sysoev et al., 2004). In explosive analysis, the IM-MS combination provides detailed information of the ionic species

present in IMS-spectra confirming the accuracy of the analyses. In early IMS-MS analyses of explosives the mass selective mode has been used as the mass filter to eliminate the unwanted background ions (Asbury, Klasmeier, & Hill, 2000). A recent study investigated the behavior of sterically hindered phenols and TNT on negative corona discharge APCI-IMS. A mass-selected mobility spectrum for TNT was measured; as a result the TNT's suitability as mobility standard was confirmed (Laakia et al., 2009).

The two dimension separation increases the selectivity and furthermore reduces the possibility of false positive responses. Other advantages include higher resolving power when compared to chromatographic techniques, operation in air and in-field conditions, protection of MS from contamination and the compatibility to large numbers of ionization sources. An example of reduction of false positives is the analysis of TNT and hand cream. Both produce same IMS and MS signals, but when combined into 2D spectrum the peaks are distinguished. This demonstrated that the interfering ion in MS regime could be separated in IMS regime and *vice versa* (Hill, Dwivedi, & Kanu, 2007).

A seminal article concerning successful analysis of explosives by combined IM-MS has been recently published (Crawford et al., 2010). In this feature three different black powder (BP) samples were investigated with three IMS instruments; a custom-built stand-alone IMS, a commercial IMS used in field analyses and the combined IM-TOFMS. The reduced mobility values of the BPs were separately determined with each instrument, but the most important results were obtained with negative mode IM-MS. The mass spectral data of each BP (not shown here) produced same response ions, but the variation in IMS drift times suggested formulation differences between the powders. When these data are combined a two-dimensional form, 2D ion mobility-mass spectrum is created.

Figure 16 shows the 2D mobility-mass correlation spectrum of Chinese black powder. In Figure 16a one-dimensional mobility spectrum is shown on the right margin and one-dimensional mass spectrum on the top. All the peaks present in MS spectrum are originating from different sulfur-containing species like allotropes and oxygen adducts. The IMS response at 8,200 and 11,000  $\mu\text{sec}$  are representing the drift times of the major components: the horizontal lines also indicate possible fragmentation of  $m/z$  128 and  $m/z$  193 species. In addition, linear mobility-mass correlation curve from  $m/z$  128 via  $m/z$  160 to  $m/z$  193 is indicating the relationship between species  $\text{S}_4^-$ ,  $\text{S}_5^-$ , and  $\text{HSO}_4^- \cdot \text{S}_3^-$ , respectively.

The plots present in 2D-spectrum are magnified in Figure 16b to elucidate the mass and mobility peaks thus underlining the peak separations. For example peaks at  $m/z$  96–99 (2nd row right side) have different masses but also fairly distinct mobilities. This means that the IMS separation prior to MS analysis is able to produce valuable additional information for explosive identification and analyses.

In addition, FAIMS and MS form an effective combination for isomer analysis (Purves et al., 1998; Eiceman, Nazarov, & Miller, 2001). The separation of isomers with IMS and detection with MS has been reported with three isomers of phthalic acid (Barnett et al., 2000) and amino acids such as leucine and isoleucine. In the latter study, negative mode ESI-FAIMS-MS enabled the selective determination of isomers present in mixtures even with 625-fold excess of the other (Barnett et al.,

1999). For TATP dissolved in toluene, various species present in the IMS spectrum were confirmed by MS (Buttigieg et al., 2003). The combination of AIMS and quadrupole MS has been reported. This combined instrument is useful to gather fundamental information concerning the functionality of AIMS instrument (Adamov et al., 2007). The principle of FAIMS and its application to MS has been extensively reviewed (Guevremont, 2004a). An early review of IMS coupled to MS has been written (Collins & Lee, 2002); and more recent review in which various types of IMS-MS instruments are described has been published (Kanu et al., 2008).

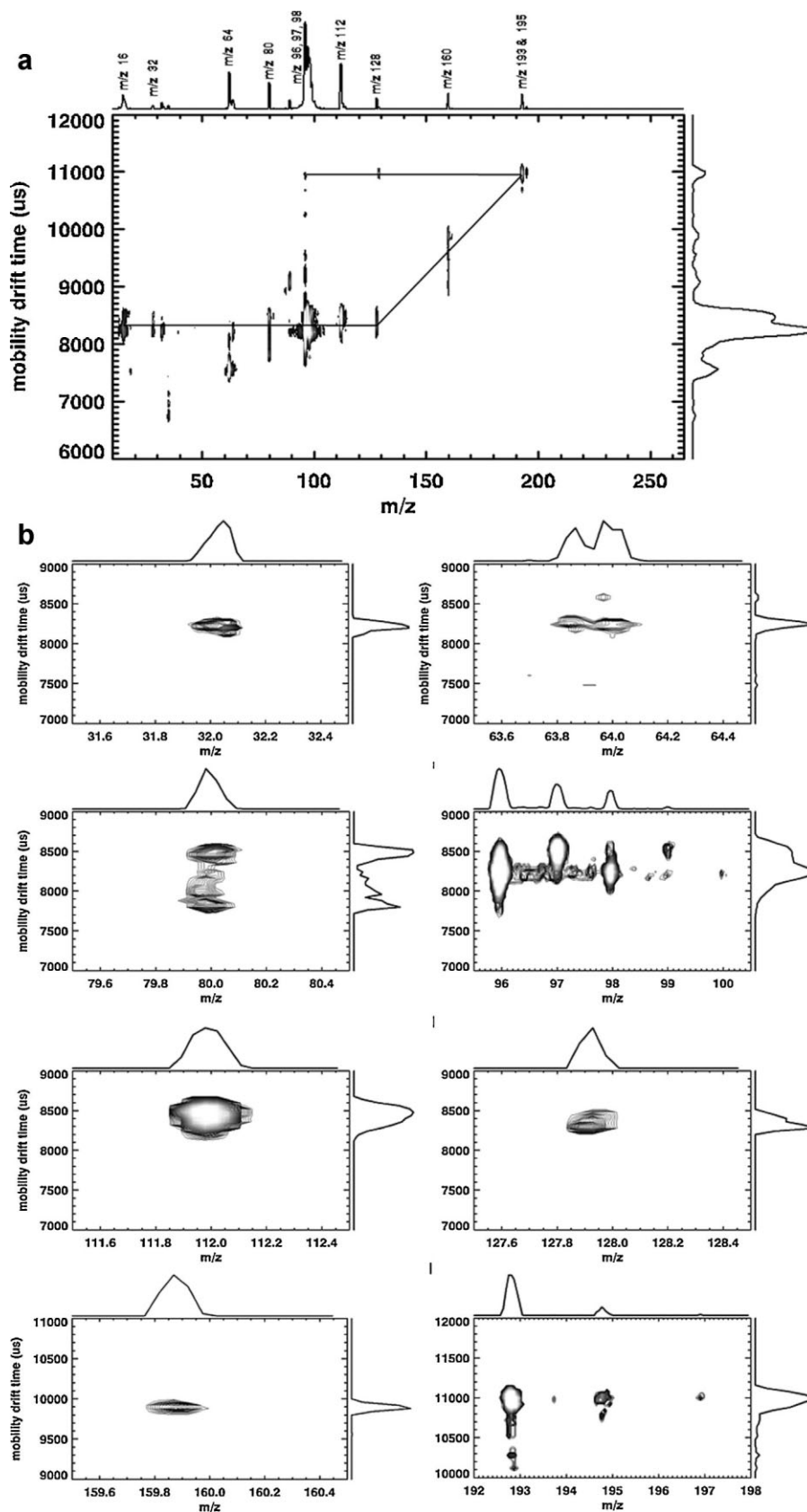
## V. CONCLUDING REMARKS

It is evident from this review, that mass spectrometry and ion mobility spectrometry are effective tools to detect explosives. The recent and divergent spectrometric applications presented in this paper are used mainly in qualitative but also in quantitative analyses.

Ion mobility spectrometry is a widespread method used mainly as an explosive trace detector before detonation. Its popularity in this monitoring is attributed to ease of use and several advantages including ruggedness, portability and in-field use. Instead, mass spectrometry has versatility and accuracy to identify the explosives after detonation being the most powerful laboratory tool for explosive investigations. In addition MS is effective to undertake environmental analyses of explosives and their derivatives and metabolites. In both of these techniques the theories of ion formations and fragmentations are quite well established. Also, the laboratory practices are workable. Several related sampling and preconcentration methods together with variety of ionization, ion separation and ion detection methods allow the analysis of explosives at ultra-trace levels from a wide range of matrices. However, the research work done in analytical laboratories is often highly both explosive-specific and method-specific; therefore they are not necessarily directly suitable for comprehensive *in situ* screening of all kinds of explosives.

From the current and diverse field of ion spectrometric explosive detection techniques several future trends can be found. In the field of ion mobility spectrometry these trends include miniaturization, alternative non-radioactive ionization sources and enhanced performance of the instrument. In the field of mass spectrometry the first main trend is focused on easy sampling. This means that sampling will be made directly from different surfaces or materials without any complicated or time-consuming sample preparation steps. Together with the second trend, the instrumental design directed towards miniaturization and ambient pressure ionization, the MS instruments are becoming truly portable and suitable for in-field detection of explosives thus entering the area dominated by IMS instruments. The third trend includes the increase in sensitivity and selectivity by more efficient ionization methods and control of gas-phase ion chemistry, respectively. The fourth trend includes integration of MS with other preparation techniques like IMS to improve the analytical performance even further. All these above mentioned improvements should be achieved without any loss of feasibility, reliability nor validity and with shorter analysis times.

The ongoing development of these detection techniques will yield novel and even more accurate applications while the need for rapid and reliable detection of explosives is on the increase. At the present moment the ion spectrometric detection technologies



**FIGURE 16.** (a) 2-dimensional mobility-mass spectrum of black powder. The IMS spectrum is on the right margin, the mass spectrum on the top margin. (b) 2D mobility-mass spectrum correlation plots magnified to enhance the clarity of analysis. Reprinted with permission from Crawford et al. (2010), Copyright 2010 American Chemical Society.



are state-of-the-art in the field of explosive analyses. Therefore it can be anticipated that they will also play important role in the future.

## VI. ABBREVIATIONS

AIMS	aspiration ion mobility spectrometry
APCI	atmospheric pressure chemical ionization
APPI	atmospheric pressure photoionization
ASGDI	atmospheric sampling glow discharge ionization
BP	black powder
CE	capillary electrophoresis
CEC	capillary electrochromatography
CFI	counter flow introduction
CID	collision induced dissociation
DAPCI	desorption atmospheric pressure chemical ionization
DART	direct analysis in real time
DBDI	dielectric barrier desorption ionization
DCID	dynamic collision-induced dissociation
DESI	desorption electrospray ionization
DMNB	2,3-dimethyl-2,3-dinitrobutane
DMS	differential mobility spectrometry
DNT	2,4-dinitrotoluene/2,6-dinitrotoluene
DPIS	distributed plasma ionization source
EC	electron capture
ECD	electron capture detector
EESI	extractive electrospray ionization
EGDN	ethylene glycol dinitrate
EPA	environmental protection agency
ESI	electrospray ionization
ETD	explosive trace detection
FAIMS	field asymmetric waveform ion mobility spectrometry
FT	Fourier transform
GC	gas chromatography
HAN	hydroxylamine nitrate
HMTD	hexamethylene triperoxide diamine
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocane
HNS	hexanitrostilbene
HPLC	high performance liquid chromatography
IC	ion chromatography
ICR	ion cyclotron resonance
IMIS	ion mobility increment spectrometry
IMS	ion mobility spectrometry
IRMS	isotope ratio mass spectrometry
IS	ion spray
LC	liquid chromatography
LOD	limit of detection
LTP	low-temperature plasma
MALDI	matrix assisted laser desorption ionization
MEKC	micellar electrokinetic chromatography
MPI	multi photon ionization
MRM	multiple reaction monitoring
MS	mass spectrometry
NACE	non-aqueous capillary electrophoresis
NCI	negative chemical ionization
ND	neutral desorption
NG	nitroglycerin
NI	negative ionization
NTO	5-nitro-1,2,4-triazol-3-one
PAED	photo-assisted electrochemical detection
PD	pulsed discharge

PDMS	plasma desorption mass spectrometry
PETN	pentaerythritol tetranitrate
PGC	porous graphitic carbon
PGN	polyglycidyl nitrate
PTR	proton transfer reaction
RDX	cyclotrimethylenetrinitramine
READ	reversal electron attachment detection
REMPI	resonance enhanced multi photon ionization
SBSE	stir-bar sorptive extraction
SESI	secondary electrospray ionization
SFC	supercritical fluid chromatography
SIFT	selected-ion flow tube
SIMS	secondary ion mass spectrometry
SPAMS	single-particle aerosol mass spectrometry
SPI	single photon ionization
SPME	solid phase microextraction
SRM	selected reaction monitoring
TATB	triaminotrinitrobenzene
TATP	triacetone triperoxide
TD	thermal desorption
TEA	thermal energy analyzer
TNAZ	1,3,3-trinitroazetidine
TNT	2,4,6-trinitrotoluene
TOF	time-of-flight
TrATrP	tetraacetone tetraperoxide
UPLC	ultra performance liquid chromatography
UV	ultraviolet

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