

Ion Mobility Spectrometry: A Tool in the Forensic Science for the Post Detonation Residue Analysis

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Abstract

The emergent threat of terrorism activities has caused an urgent need of improved forensic explosive analysis. Complex matrices, limited samples, and confusing interpretations serve as challenges for a forensic chemist in order to link the evidence to the perpetrator of the crime. Forensic investigators use the analysis of explosive residues to spot materials and people concerned in an exceedingly crime. Over the past several decades, Ion mobility spectrometry (IMS) has evolved into an inexpensive and powerful analytical technique for the detection of gas phase samples at ambient pressures and temperatures. Each and every one of IMS instruments operate with an electric field that provides the space separation, but a number of IMS instruments also operate with a drift gas flow which provides also a temporal separation. Each type of IMS has four main regions: sample introduction system; ionization area; drift tube (where separation or selection occurs) and detection area. The availability of analyzers for general use from instrument vendors has initiated a new stage of development with IMS. IMS may be a sensitive analytical technique that's used for detection, identification and watching of chemicals, chiefly explosives, extremely nephrotoxic gases and drug interdiction. It offers a wide range of applications configurations and possibilities for use in field and process analytical applications. Post-detonation debris contains residues of unexploded materials which have to be sorted out from innocent debris. The excellent mass detection limits, rapid analysis time, superior resolution, and extremely small sample requirements of IMS method is attractive for the forensic analysis of the explosive materials. When fast detection of chemical warfare agents in the field is required, the IMS may be the only suitable option. This article provides a vital survey of the different IMS detection technologies. This critique review will provide the reader with a perceptive view of the main uniqueness and aspects of the IMS technique.

Keywords: APCI; Explosives; Forensic Science; Post-Detonation; IMS; Terrorist

Introduction

Forensic chemistry is exclusive among chemical sciences in its analysis, practice, and presentation should meet the wants of each the scientific and also the legal communities. As such, forensic chemistry research is applied and derivative by nature and design, and it emphasizes metrology (the science of measurement) and validation. Forensic chemistry has captive far from its analytical roots and is incorporating a broader spectrum of chemical sciences. A notable trend in forensic chemistry research is the increasing application of fundamental chemical science to diverse aspects of physical and pattern evidence [1]. In some instances, this means examining old methodology with new scrutiny; in others, it means developing novel applications of instrumentation.

Forensic examination of evidence from an explosive scene includes not only the chemical analysis of explosive residues, but also examination of debris and components from the scene which can be used to aid the investigators in determining how the device was initiated. Chemical analysis of explosive residues offers unique challenges to the analyst due to the fact that explosives often are nearly entirely consumed during the explosion. Forensic science can be applied to a variety of situations, and as new analytical techniques are being developed, the forensic scientist can provide more and more information to the investigator.

In recent years, rapid and sensitive detection of improvised explosive devices (IEDs) has become the most pressing issues with the increase of the globalization of terrorist acts during the last 2 decades, such as those in Oklahoma, U.S.A. (1995), Bali, Indonesia (2002, 2005), Pune, India (2010), Oslo, Norway (2011), Boston, U.S.A. (2013) and Abuja, Nigeria (2014) [2-4]. On-site screening is an effective way to reduce the risk of explosion, which demands the analytical methods with high requirements in terms of speed, sensitivity, and robustness [5-11].

Forensic Science Laboratories have historically used the most modern scientific methods available to assist investigators in determining what may have occurred during the commission of a crime. As advances in analytical capabilities have improved, rhetorical scientists are ready to offer a lot of careful and valuable data to enforcement investigators within the field. This article will focus on the applications of forensic science, specifically Ion mobility spectrometry (IMS), to the field of explosion investigations.

Portable instrumentation for onsite examination and analysis of post blast rubbish and structural elements of targets (such as buildings and vehicles) has to be developed. Such equipment will allow investigators to more accurately and quickly determine whether an explosion was due to an improvised device or was caused by other factors. The findings from these transportable devices might facilitate investigators and examiners perceive and faster focus investigations on the causes of explosions. In addition, they may provide more rapid preliminary identifications of source materials.

Hill and Martin have provided the analytical strategies that square measure presently used for the detection and identification of war agents that square measure reviewed and classified by the quantity of dimensions of data [12]. The recommendation for analytical field verification during inspections under the Chemical Weapons Convention (CWC) is to use simple two-dimensional analytical methods, such as gas chromatography (GC) or IMS, for on-site screening of chemical weapons (CW) agents or to fully equip a modern, mobile analytical laboratory located in an aircraft, which can be moved rapidly throughout the world to each inspection site and provide high-quality analytical data on-site. Although the CWC of 1993 calls for the on-site verification of chemical warfare agents by analytical methods, no such verifications are performed. Yet, verification is needed to insure that CW is not present or that agents being destroyed have been identified correctly. To date, the only approved equipment for field verification of chemical warfare agents is a GC coupled with a mass spectrometer (GC/MS). While GC/MS is one among the foremost powerful analytical instruments on the market, it's additionally one among the foremost advanced and troublesome to keep up and operate a routine basis. For example, field-portable GCs are readily available and relatively easy which is much easier than the approved GC/MS instrument to operate under field conditions [13]. IMSs are also relatively reliable these days, perhaps nowadays they are used for explosive detection in most airports. Thus, it should be possible to use a variety of simple analytical instruments to obtain on-site supporting data on the presence or absence of chemical weapons.

IMS is a well-known technique; offering small size and a sensitivity in the ppb range makes it a typical technique for the detection of explosives or chemical warfare agents. Ordinary IMS devices use in general a continuously working radioactive ionization source. IMS is an atmospheric pressure technique in which reactant ions, generated by exposure to a β -emitter, react with the sample to produce product ions which are separated in an electric field. IMS can be used to identify explosives on suspects or on their belongings. This evidence [14-18] can provide probable cause for a search warrant, help in identifying a potential terrorist, and locate concealed explosives.

As improved technology allows explosive detection at lower and lower levels, precautions must be put in place to prevent cross contamination and to monitor all aspects of the evidence collection and examination procedures. Hence, there is a need for the development of a rapid, portable and selective monitor for different explosive residues is of interest to environmental land and sea remediation efforts, forensic analysis following terrorist or other criminal activity, and land mine and under water unexploded ordnance identification for the military.

The continuing threat of worldwide terrorism has prompted the need for new and innovative explosives detection systems. IMS is a rugged, inexpensive, sensitive, field portable technique for the detection of organic compounds. It is widely employed in ports of entry and by the military as a particle detector for explosives and drugs of abuse. IMS is a very common sensing method deployed today for early detection of explosive compounds. A hallmark of IMS is that the fundamental operating principles are quite simple; the sensing device requires just a few components, all of which can be easily miniaturized.

IMS has been known as an analytical technique [19,20] since the late 1960s and early 1970s. The technique was then referred to as plasma chromatography. To date, it has been successfully utilized for the detection of environmental pollutants, warfare agents, explosives, herbicides, pesticides, petroleum products as well as for the detection of prescription and illicit drugs. In this article we depict the use of the IMS technology in cases of forensic interest in India. The proven experience, both in the field and in the laboratory, of IMSs for forensic science applications is also described, and the merits and shortcomings of present-day IMS technology, and future trends have been discussed.

One specific technique, which has seen growing use in airports in recent years, is IMS, a mass spectrometry technique for the gas phase which relies on the mobility of ions in a carrier gas. Differential Mobility Spectroscopy (DMS) is a slight variation on this concept, where high electric fields are used to filter out certain types of ions. In both of these techniques, the choice of carrier gas is crucial for an effective analysis. One reason that mass spectrometry based techniques is popular for explosive detection is their speed and accuracy. They can measure trace amounts of material, as low as picograms (10-15 kg), putting them on a par with optical techniques such as LIBS. However, proximity is an issue; they require samples of materials to be inserted into the spectrometer unit. This limits the applications to more controlled situations, such as airport security, rather than broader field applications where detection at a distance is highly desirable.

Principle of operation and design of IMS

The principle of IMS is that a sample is being introduced in the instrument, brought into the vapor phase by flash heating, the vapor is ionized and the resulting ions are introduced into a drift tube (Figure 1). Ion mobilities are determined from ion velocities measured in the drift tube at ambient pressure and are characteristic for the analyte. Therefore, they can be used for the identification of substances. Around 1975 the limitations of IMS became clear and the number of publications decreased. However, it is a potentially useful technique in some specific areas and developments went on mainly in military institutions.

In this article an introduction to IMS is given, followed by a description of the instrument used for the experiments. In any IMS system, ionized gas molecules are separated according to their mobility as they drift through gas at atmospheric pressure whilst under the influence of an electric field. The principles of operation of IMS systems have been described thoroughly elsewhere therefore only a brief description of the construction and principles of operation have been presented in literature [21,22].

There are several designs of mobility spectrometers [23], but here we have focused on the two main types: low electric field linear IMS and differential mobility spectrometers (DMS). The design of an IMS is very simple as shown in the schematic (Figure 1). Vapors of the sample are introduced into a tube that comprises an ionization sector, where some of the vapors are ionized, and a drift sector, where ions are separated according to the time that is required to reach a detector plate that depends on their mobility (drift velocity). A pulsed electronic shutter separates the two sectors and allows a discrete package of ions to enter the drift sector. Ions with high mobility, generally small ions, travel faster than large ions and cover the distance between the shutter and detector in a shorter time.

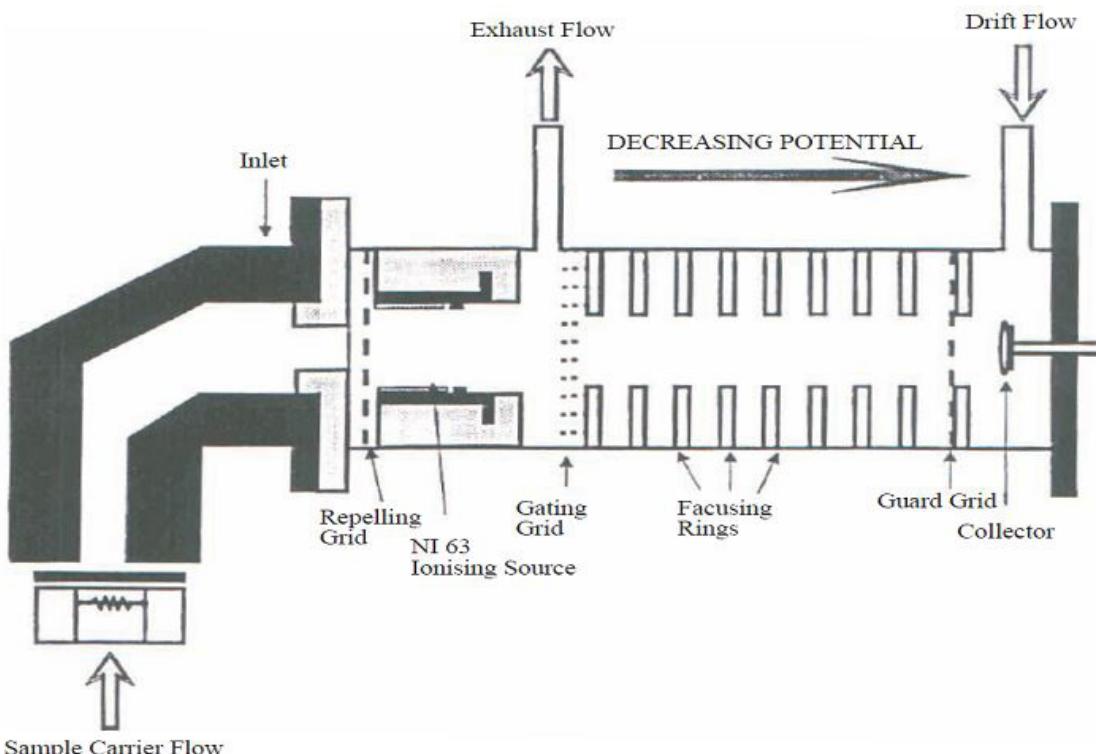


Figure 1: Schematic diagram of a linear ion mobility spectrometer

The common ionization sources are radio-active β emission (most commonly Ni^{63}), corona discharge and photo-ionization. The description presented above pertains to the classic, linear IMS where a relatively low electric field ($\sim 250 \text{ V cm}^{-1}$) is used to transport the ions along a drift tube. During the last 18 years the concept of differential mobility spectrometry (DMS) [24], also known as field asymmetric ion mobility spectrometry (FAIMS), was developed, and is gaining popularity among practitioners of mobility measurements.

Ions that are carried by a stream of air through a strong perpendicular electric field are displaced by the field at a velocity, V_{\perp} , that is proportional to the field strength, $E(t)$ and the field dependent mobility of the ion, $K(E)$:

$$V_{\perp} = K(E) \cdot E(t)$$

If the strength of the electric field is changed periodically by an asymmetric rectangular shaped waveform, between for example $20,000 \text{ V cm}^{-1}$ to 1000 V cm^{-1} , the motion of the ions would follow the waveform, as shown schematically in Figure 2.

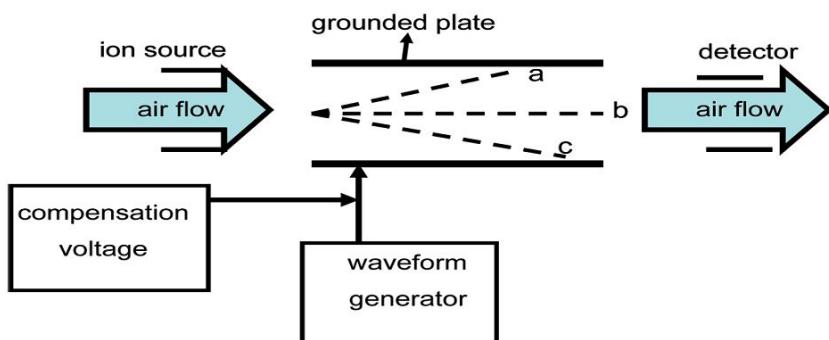
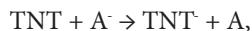


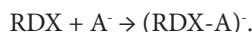
Figure 2: Schematic Diagram of a Differential Mobility Spectrometer (DMS)

The mobility of a given ion under high field conditions would differ from its mobility under low field conditions and different ions would be affected and displaced to a different extent. Thus, under given conditions only ions with the appropriate mobility would pass through the plates and reach the detector. A mobility spectrum is obtained by sweeping the compensation voltage setting on one of the plates. More details about DMS and its applications have reviewed by kolakaowski and Mester [24]. The main advantages of DMS compared with IMS are the possibility of miniaturization and of using micro-fabrication techniques for less expensive production of sensors. The first requirement of an IMS system is a suitable ion source. The source is typically a β emitter (most commonly Ni^{63}). In a dry air system the ionic species generated are pre-dominantly N_2 or O_2^+ positive ions and O_2^- negative ions. These ions are referred to as reactant ions. When molecules of the sample species are introduced into the ion source region these molecules will interact with the reactant ions and, assuming they have a greater affinity for the associated charge, a charge transfer will take place creating ions of the sample species. Other mechanisms are also possible to create characteristic product ions [25], such as the formation of adduct ions.

These ions will, to varying degrees, cluster with water molecules, creating more complex cluster ions, depending on temperature and humidity levels. Thus $O_2(H_2O)$; $O(H_2O)^-$ and perhaps some NO_2^- ions are formed, and these interact with the sample ions. For example, TNT will undergo charge transfer reactions,



RDX gives ion-molecule reactions with the reactant ions,



The reduced ion mobility times correspond to the molecular weights of the addition compounds [$RDX-O(H_2O)$], [$RDX-O_2^-$] etc. These ionic species will then move toward the ion gate under the influence of the extracting electric field. The polarity of the latter controls, whether positive or negative ions, is detected. Explosive substances form negative ions, while most narcotics, like heroin and cocaine, form positive ions.

In the drift region the sample ions move under the influence of the applied electric field. Due to the collision between the sample ions and the drift gas molecules, separation takes place depending on the mobility of the sample ions. Ions with a higher mobility traverse the length of the drift region in a shorter time than ions with a lower mobility. The mobility of the ions will depend on their size, mass and shape. Hence, for each opening of the electronic gate, a pulse of electronic charge representing different ionic species in the sample will arrive at the ion collector separated in time. This ion current spectrum is referred to as a plasmagram.

The detailed theory of mobility has been discussed by Rivercomb & Mason and Karpas [26,27]. It should be noted here that the mobility of ionic species is defined by

$$V_d = KE \quad (1)$$

Where V_d : drift velocity, K: the mobility of the species and E: electric field gradient.

$$K = d/E_t \quad (2)$$

d: Drift Region Length (cm) and E_t : Drift Time (s).

The mobility of an ion will be to a first order approximation, a linear function of temperature and pressure. The reduced mobility K_0 is defined as follows, being the first order contributions of pressure and temperature normalized out:

$$K_0 = K(273/T)(P/760) \quad (3)$$

Where T: Absolute Temperature and P: Pressure in Torr.

For known temperature and pressure characteristics in the IMS system, sample ions can be identified through measurement of their drift time in a drift tube of known length and electric field [27].

Identification of the type of explosive involved in terrorist bombings is often a vital clue for police forces trying to capture the perpetrators. Post-detonation debris contains residues of unexploded materials which have to be sorted out from innocent debris. The analysis may provide the link between a suspect and the type of explosive used. From the various literature the experimental data showed measurable differences in the K_0 values for most of the compounds which are given below (Table 1).

Compounds	m/z	Species	K_0 ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)*					
TNT	226	(M-H) ⁻	1.54 [N ₂]	Ref:28	1.45 [air]	Ref: 29	1.48 [N ₂]	Ref:30
2-ADNT	196	(M-H) ⁻	1.57 [N ₂]	Ref:30	---	---	---	--
2,4-DNT	181	(M-H) ⁻	1.67 [N ₂]	Ref:28	1.57 [air]	Ref:29	1.62[N ₂]	Ref:30
4-NT	136	(M-H) ⁻	1.81 [air]	Ref:28	1.79[N ₂]	Ref:30	---	---
TNB	244	(M+CH ₃ O) ⁻	1.42 [N ₂]	Ref:30	---	---	---	---
RDX	257	(M+Cl) ⁻	1.39 [air]	Ref:29	1.40[N ₂]	Ref:30	1.39 [air]	Ref:31
HMX	331	(M+Cl) ⁻	1.25 [N ₂]	Ref:30	1.25[air]	Ref:29	---	---
EGDN	152	M ⁻	1.57 [N ₂]	Ref:30	---	----	---	---
NG	226	(M-H) ⁻	1.45 [air]	Ref:29	1.47[N ₂]	Ref:15	1.45[air]	Ref:31

Table 1: K_0 Values of Different Product Ions Given in the Literature

*Drift Gas Given in Parentheses; Ref: References

To date, all ion mobility measurements made for CW agents have been direct mobility measurements made under low electric field conditions in which the ion mobility is directly proportional to the electric field strength. However [28-31], a new and promising method for using ion mobility for monitoring gas phase ions takes advantage of the nonlinear behavior of ion mobilities under high electric field strength conditions [32]. Unfortunately, the resolving power of this novel approach is currently too low to provide adequate selectivity for CW agent detection, but the absence of an ion gate promises improved sensitivity over traditional IMS instruments.

A third type of IMS that is used for the detection of CW agents is called aspiration IMS. In this system [33], the ions travel through an orthogonal electric field in which the ions are deflected to multichannel located on the collecting electrode. Ions with higher mobilities are deflected to electrodes faster than ions with lower mobilities. Although these types of detectors also suffer from low resolving power, they also have the advantage of not requiring an ion gate.

Sample Preparation and Screening

Forensic chemists face a daunting variety of target analytes; therefore, the scope and variety of sample preparation methods available are just as large. In the area of explosives analysis, drug analysis (solid dose and forensic toxicology), the typical organic extraction methods are the workhorses of the laboratory. These methods include LLE and micro-LLE, solid-phase extraction (SPE), solid-phase micro extraction (SPME) and headspace methods.

When attempting to characterize explosives or explosive residues at low to trace levels, the most critical step in the analysis is the location, whether at the scene or in the laboratory, of materials likely to contain either intact residual explosive or residues characteristic of a particular explosive material. Once collected at the scene, the sample must be packaged so that its evidentiary value is not lost and that it does not contribute to contamination of other samples.

When the sample arrives in the laboratory, separation, and concentration of the target analytes becomes crucial. The objectives of this step are separation of the analyte from the sample matrix and potential interferants and, if feasible, at the same time, concentrating the material of interest for analysis. Efficient sample collection, whether involving vapors or particulates, is essential to detection of materials present at low levels. Trace detection captures and analyzes the microscopic particles and vapors naturally emitted by organic substances. Trace samples are collected by wiping surfaces suspected of contamination or by “sniffing” concentrated vapors trapped within a sealed container.

Two promising techniques for the removal and concentration of an analyte in a matrix are SPME and Supercritical Fluid Extraction (SFE). SPME utilizes a coated fiber housed inside a syringe needle as an adsorbent. The needle is inserted directly into the aqueous or organic extract of the sample and the fiber then exposed for collection. Once collected, the sample can be desorbed either thermally or by solvent extraction. A number of articles [34-36] on this technique have been reported and SPME appears to have considerable potential for the analysis of explosives, combining speed and simplicity.

SPME is an effective extraction technique that has been successfully employed in the field for the pre-concentration of a variety of compounds. Many organic high explosives do not have a high enough vapor pressure for effective vapor sampling. However, these explosives and their commercial explosive mixtures have characteristic volatile components detectable in their headspace. In addition, taggants are added to explosives to aid in detection through headspace sampling. SPME can easily extract these compounds from the headspace for IMS vapor detection. An interface that couples SPME to IMS was constructed and evaluated

for the detection of the following detection taggants: 2-nitrotoluene (2-NT), 4-nitrotoluene (4-NT), and 2,3-dimethyl-2,3-dinitrobutane (DMNB). The interface was also evaluated for the following common explosives: smokeless powder (nitrocellulose, NC), 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 2,4,6-trinitrotoluene (2,4,6-TNT), hexahydro-1,3,5-trinitro-s-triazine (RDX), and pentaerythritol tetranitrate (PETN). At first, Furton *et al.*, [37] have reviewed briefly and reported on SPME-IMS system that is shown to extract volatile constituent chemicals and detection taggants in explosives from a headspace for subsequent detection in a simple, rapid, sensitive, and inexpensive manner.

Explosives detectors can play a role in locating evidence at the scene and improving the quality of evidence submitted for examination, or for screening bomb scene debris in the laboratory. A great deal of the work with explosive detectors has been directed toward aviation security. The Canadians have carried out a study of five different trace explosive detectors, both in the laboratory and in place at airport security locations. Malotky provided a discussion of current technology for explosive detection in luggage [38,39].

In related work, Phares and co-workers used an IMS to determine if explosives could be detected on fingerprints left by an individual who had handled explosives [40]. They reported that less than 1 ng of RDX was collected from fingerprint transfers. The above explosives detector work, while not having significant laboratory applications at present, could result in simpler and more specific laboratory instruments in the future. And a wider application for using these instruments for screening of bomb debris in the laboratory is encouraged.

The use of effectively trained dogs as explosive detectors continues to expand throughout the world. Overall, canines represent the fastest, most versatile and reliable real-time explosive detection device available. Furton and Meyers have reviewed the use of dogs as chemical detectors [41], their reliability in this regard, and a comparison with analytical instrumental techniques. Atkinson *et al.*, combined IMS with multivariate chemometric data methods to enhance the quantitative performance of IMS needed for detailed explosive analyses [42].

Detection and Identification of Explosives and Residues

Most commercial explosives have several nitro groups and relatively low vapor pressures. There are several explosives, mainly improvised explosive devices (IED) that do not confirm with this, like the organic peroxides that do not have nitro groups but may have high vapor pressures and inorganic compounds like perchlorates that do not contain nitro groups and have a low vapor pressure. Detection of such compounds requires non-standard techniques and operating conditions, so adaptation of the sensor is necessary.

Presence of nitro groups renders the compounds highly electro-negative thus making them suitable for detection by mobility spectrometers operating in the negative ion mode. Negative ions may be formed in the ionization sector directly by electron capture (eq.1) or by dissociative electron capture (eq.2).



Where Z is a neutral molecule that does not participate directly in the reactions (third body) and X^- is an ion like Cl^- , NO_2^- , Br^- , NO_3^- . Sometimes several negative ions from the explosive compounds and their adduct ions may be observed simultaneously in the mobility spectrum.

Positive ions originating from explosive compounds may also be formed under APCI conditions, but usually with lower efficiencies and with more interference from other chemicals present in the sample. For explosive compounds that do not contain electronegative groups, like the peroxide molecules, detection in the positive ion mode may be preferable, especially if they tend to form adduct ions with suitable reagents. For example, there have been reports [43] that triacetone triperoxide (TATP), a favorite improvised explosive among terrorists due the ease of its production, can be detected by IMS as it may form an adduct ion with ammonium ions (NH_4^+) [44].

A number of different methods for analyzing explosives from complex environmental matrices using LC and GC separations have been reported so far. The separation capabilities of ESI-IMS-MS demonstrating [45] a resolving power similar to LC have already been demonstrated. As the IMS also shows high sensitivity for many of the explosives, the use of ESI/IMS for analyzing environmental samples were taken into consideration. The extent to which even a protocol involving use of sophisticated instrumentation "identifies" an explosive depends on the rigor of the protocol and conduct of all tests required.

For purposes of discussion, a further distinction will be made between detection/identification and characterization. The detection will encompass an alert indicative of a "target-type material" such as an explosive or a presumptive "group-type" analysis. Identification will be considered as incorporating the results of additional confirmatory testing beyond the initial tests. Typically, subsequent testing would involve a conceptually different approach to the test conduct than that used in prior testing. Identification thus requires independent confirmation of the preliminary results.

Conventional explosives TNT, NG, and EGDN absorbed to hair can be directly detected by an IMS in E-mode (for explosives) were studied by Oxley *et al.*, [46] have studied Ionscan IMS for the detection of drugs in hair. Terrorist explosive, TATP difficult to detect by IMS in E-mode, but it was detected in N-mode (for narcotics). TATP could only be detected by the acetonitrile extraction method after exposure of the hair to vapor for 16 days because of lower sensitivity. With standard solutions, TATP detection in E-mode required about 10 times as much sample as EGDN.

In recent years, explosive examination schemes or protocols are becoming much more formalized. For a variety of reasons, TLC techniques remain attractive both in the laboratory and in the field. One reason is that, in some instances they can be inexpensively and readily performed at a scene as, for example, to demonstrate explosive product contamination of soil at a site with greater validity than that offered by other simple presumptive tests [47]. HPTLC offers improved performance and is an integral part of some laboratory protocols [48].

New instrument designs have greatly improved spectral quality and the analysis is non-destructive so re examination of the sample by another sensitive technique is feasible. If a portable version could be developed, it would be useful in processing the bomb scene or in searches of a suspect's vehicle, premises, etc. IMS, once considered a technique of great promise for both field and laboratory [49], continues to receive moderate attention. Mass spectrometry has been used for identification of low levels of explosives for many years, but its applications continue to increase with new spectrometer designs and improved interfaces with either gas or liquid chromatographs. Yinon have described the appropriate conditions for obtaining good mass spectra for thermally labile nitrate ester explosives using both electron impact and chemical ionization techniques [50].

Chih-Wu Su and Kim Babcock [51] have studied on the use of Solid Phase Desorption/GC/IMS (SPD/GC/IMS) for Explosives Detection. These tests included the use of Barringer Teflon discs and Schleicher and Schuell filter paper grade 404 (S & S404) as sample holding materials and the explosives RDX and HMX. The criteria for an RDX alarm on the Ionscan included the detection of any two of the following RDX cluster ions: RDX chloride cluster (RDX-C), RDX nitrate cluster (RDX-N) and RDX dimer chloride cluster (RDX-D). Since this SPD/GC/IMS technology did not require the use of extra laboratory procedures and simulated Ionscan operational conditions, it was selected as a tool to further investigate the extra RDX-N/HMX generated on S & S404.

IMS has become the most successful and widely used technology for the detection of trace levels of nitro-organic explosives on handbags and carry on-luggage in airports throughout the US and other countries. The low detection limits are provided by the efficient ionization process, namely, APCI reactions in negative polarity. An additional level of confidence in a measurement is imparted by characterization of ions for mobilities in weak electric fields of a drift tube at ambient pressure. Findings from over 65 years of investigations [49] into IMS response to these explosives have been collected and assessed to allow a comprehensive view of the APCI reactions characteristic of nitro-organic explosives. Also, the drift tube conditions needed to obtain particular mobility spectra have been summarized. During the past decade, improvements have occurred in IMS on the understanding of reagent gas chemistries, the influence of temperature on ion stability, and sampling methods. In addition, commercial instruments have been refined to provide fast and reliable measurements for on-site detection of explosives.

There have been many advances in the application of IMS over the past 50 years [23]. IMS is a valued field detection technology because of its speed and high sensitivity, but IMS cannot easily resolve analytes of interest within mixtures. Coupling GC to IMS adds a separation capability to resolve complex matrices [51,52]. Maggie Tam and Herbert have studied the unique capability of secondary electrospray ionization (SESI) as a nonradioactive ionization source to detect analytes in both liquid and gaseous samples was evaluated using aqueous solutions of three common military explosives: RDX, NG and PETN [53].

Fetterolf and Clark have determined the limits of detection for most common explosives to be approximately 200 pg [54]. The vacuum sampling method permits the collection of trace physical evidence transferred to hands or surfaces through contact or post blast residue. The persistence of explosives on hands and transfer to other surfaces has been examined. Post-blast residue of NG was detected on fragments of improvised explosive devices constructed with double-based smokeless powder. Post-blast residues from C-4, Deta Sheet, SEMTEX, and ammonium nitrate explosives have also been detected on items of forensic and evidentiary value.

Huang *et al.*, in their study they have used laser desorption to volatilize explosive materials for analysis by IMS measurements [55]. The laser desorption is performed at relatively low power ($<10^7$ W/cm²) so that mainly neutrals are produced, which are subsequently ionized by ⁶³Ni-β-source induced ion-molecule reactions at atmospheric pressure. Atmospheric pressure ionization, together with the soft vaporization method, produces relatively simple spectra of the explosives investigated, yielding ions that are very characteristic of each molecule for identification. The technique has great potential for high sensitivity based upon the combination of complete laser vaporization of the sample and the API method, which is an extremely efficient form of ionization for these molecules with high electron affinities.

The analysis of explosives with IMS directly from aqueous solutions was shown for the first time using an electrospray ionization technique by Hill and Tam [56]. They have operated IMS in the negative mode at 250°C and coupled with a quadrupole mass spectrometer (QMS) to identify the observed IMS peaks. The IMS response characteristics of TNT, 2,4-DNT, 2-ADNT, 4-NT, TNB, RDX, HMX, EGDN and NG were investigated. Several breakdown products, predominantly NO₂⁻ and NO₃⁻, were observed in the low-mass region.

Nevertheless, all compounds with the exception of NG produced at least one ion related to the intact molecule and could therefore be selectively detected. For RDX and HMX the $[M^+ Cl^-]$ cluster ion was the main peak and the signal intensities could be greatly enhanced by the addition of small amounts of sodium chloride to the sprayed solutions. The reduced mobility constants (K_r) were in good agreement with literature data obtained from experiments where the explosives were introduced into the IMS from the vapor phase. The detection limits were in the range of 15-190 $\mu\text{g l}^{-1}$ and all calibration curves showed good linearity. A mixture of TNT, RDX and HMX was used to demonstrate the high separation potential of the IMS system.

The increase in terrorist activities committed using explosives in recent years has generated the need for improved analytical methods that can accurately and rapidly identify explosives and their residues. Hulya Koyuncu *et al.*, were studied such an analytical method is evaluated [31]. They have analyzed in the three phases, in the first phase of the study, standard solutions and a standard mixture solution of TNT, RDX, PETN and Tetryl were examined using IMS. In the second phase, qualitative analysis of a real explosion residue was carried out and the explosive material used in the bomb was identified by analyzing the acetone extract. In the third phase, a hand swab sample taken from a suspect was analyzed for trace explosive residues. Some advantages of using IMS for the detection of explosives and their residues were determined.

Tam and Hill have demonstrated a novel analytical method [56], called Liquid Phase Ion Mobility Spectrometry (LiPIMS), where aqueous phase analytes were ionized and introduced into non-aqueous liquids, transported by an external electric field from the point of generation to a collection electrode. Ions were produced from a unique liquid phase ionization process, called Electro dispersion Ionization. Spectra of analyte ions illustrated the potential of LiPIMS as a new separation technique. Experimental data showed that electro dispersion ionization was effective in generating nano ampere level of ion current in hexane and benzene from aqueous samples. By controlling the ionization voltage in relation to the sample flow rate, it was possible to operate the electro dispersion ionization source in both continuous and pulsed ionization modes.

As with MS, the development of ESI has enabled the introduction of nonvolatile compounds into the IMS. Using the IMS as a pre separation device, IMS serves as a rapid replacement for LC prior to the introduction into a mass spectrometer. CW degradation products have been separated and detected from water samples by using an IMS coupled to a QMS [57]. Not only do IMS separations have a greater resolving power than LC separations, they are also faster. Complete ion mobility spectra can be obtained within 20 ms. Even when several spectra are averaged to improve signal- to-noise ratio, separations occur in less than 10s compared with 10-30 min for LC. With IMS/QMS separation and detection, the IMS is scanned continuously while the QMS is scanned slowly to produce the mobility-mass spectrum in about 10 min.

However, IMS have been interfaced to a time-off-light mass spectrometer, and complete mobility-mass spectra can be obtained in a few seconds. In both IM/MS instruments, the detection limit for the CW degradation products is similar at about 100 ppb. The primary advantage of adding an IMS to the front of a mass spectrometer is to keep the mass spectrometer clean and to reduce the noise from that electrospray process in the mass spectrum. IM/MS data can also be collected for volatile CW simulants using a Ni ionization source or a secondary ESI source.

Ion mobility-based separation methods can be combined with mass spectrometry (IMS-MS) in order to minimize chemical suppression caused by interference and the use of chromatography separations to targeted applications [58]. The interface has only a few centimeters in length and operates in seconds; besides, it can be adapted to any MS system using atmospheric-pressure ionization-targeted applications. In this analysis, a miniature differential ion mobility filter is used and placed in front of the entrance of the mass spectrometer, and a solution of 10 ng/mL of the sample was introduced using infusion introduction of ions created by electrospray ionization source coupled with ion trap MS/MS. This method allowed the characterization of samples in 30 seconds, reducing case backlogs in the targeted analysis of analytes of interest.

Recent Developments of IMS

Two general developments can be observed in IMS: (i) The application of Ion mobility Spectrometers as standalone instruments, sometimes in combination with selective sample preparation techniques and (ii) The application of IMS as pre-separation technique in combination with MS. Due to the availability of "structural information" from ion mobility spectra, IMS can become an important sensor technique for on-site monitoring. However, this requires the development of new ion sources for ionizing complex mixtures. Perhaps the coupling of IMS with other sensor techniques can permits more comprehensive or detailed analytical information about samples. Noteworthy is comparatively brief period where IMS has been under active development as pre-separation technique for MS. Considering the impressive results obtained in this short period of time, further capabilities of IMS can be expected promising an exciting future in measurement and analytical sciences.

Recently, paper spray ionization coupled with mass spectrometry has been reported [59-62], as a method for directly analyzing complex biological fluid samples [63-66]. In these paper spray ionization measurements, chromatographic grade paper or other porous substrates have played important roles for solvent transport based on the capillary action through their micro-channels. The paper is cut into triangular-shaped pieces; then, solutions containing the analytes are added onto the paper. A field-assisted evaporation spray occurs at the tip of the paper, which can be analyzed via mass spectrometry IMS [67].

Paper spray (PS) ionization is a recently developed ion source that has been used to analyze samples in their native environments at ambient pressure without requiring sample preparation or pre-separation. The design of an IMS coupled with PS ionization can help expand IMS applications to on-site detection of complex liquid samples, Jiang Jie *et al.*, have reported a paper spray ionization ion mobility spectrometer prototype that consists of a PS source and an ion mobility spectrometer optimized using a numerical simulation [68].

PS ionization consists of three analytical steps: sample collection, analyte separation, and analyte ionization. Compared with ESI, paper spray ionization does not have the four previously mentioned drawbacks. In addition, PS ionization can be used with non-polar solvents that are not allowed by ESI [69]. Therefore, a paper spray ionization source coupled with a proper detector has great potential for achieving on-site detection of liquid samples.

Many major breakthroughs in IMS have occurred over the last decades [70]. The large number of flavors (e.g., DT-IMS, PFIMS, DIMS/FAIMS, TWIMS, and TIMS) and operating condition (low pressure to atmospheric) has allowed the IMS community to solved problems in a broad range of fields (e.g., biomedical, forensic, environmental, out-of-space, and basic science). Initially, IMS-MS developments were mainly restricted to research groups that focused on the development of IMS instrumentation and potential applications. With the recent increase of commercially available IMS-MS variants, there will be an exponential growth in number of IMS-MS users and it will soon become a required analysis for most MS service laboratories.

Advantages and Limitations

The applications of IMS have grown exponentially beyond its uses for explosive, illicit drug and chemical warfare agent monitoring in recent years. Instrumental developments including new drift tube materials and ionization sources have enabled the manufacturing of more sophisticated and affordable IMS equipment for the advantageous analysis of samples with no pretreatment. The most recent applications of IMS include quality control and cleaning validation procedures in the pharmaceutical industry; determinations of contaminants in food samples; clinical analyses of biological fluids; environmental analyses of contaminants in gaseous, liquid and solid samples; and (bio) process quality control monitoring.

The qualitative and quantitative capabilities of IMS act as a comprehensive and powerful tool in explosives residue analysis. IMS is a useful analytical technique for the determination of volatile and semi volatile compounds based on the gas-phase separation of the resulting ions under a weak electric field at ambient pressure. The analytical potential of IMS, particularly as regards operational speed, atmospheric pressure operation, simplicity, and sensitivity, offers viable alternatives in the determination of workplace air exposure with their own associated benefits which have not been fully exploited. Sensitivity, in the ng-pg range, selectivity, possibly to provide results in near real time, and reduction of analysis costs are the most important properties that ratify IMS as a serious alternative in post detonation and explosives residue analysis.

One of the advantages of IMS is its rapid analysis time, typically six to eight seconds. One of the initial advantages of IMS was its ability to give a response to a wide range of compounds. However, this is not such an advantage when required to analyze for a target analyte within a mixture. The selectivity and sensitivity of IMS to explosives can be improved by a number of modifications the use of the chlorinated reagent gas, the detection of multiple species, optimization of operating temperatures and the use of an internal calibrant.

Analysis of complex mixtures is unrealistic by IMS unless coupled to a pre-separation technique. Matrix effects can be overcome by the use of improved reagent ion chemistry or by a pre separation of the mixture, by either clean up or by the use of a chromatographic technique such as GC. Matrix effects will also affect the linearity of response and quantitation. IMS has not really been used as a quantitative instrument favoring applications that require positive or negative response such as explosives detectors.

The stand-alone IMS explosives detectors were designed with speed, reliability and ease of use in mind. There are no analytical columns that need to be replaced. The air purification system will need replacing periodically to keep the air carrier gas clean and dry. The instruments recover well from moderately dirty or overloaded samples. Heavily overloaded or dirty samples may require repeated blanking to clear the system or cleaning of the inlet liner and system bake-out. The instruments are easy to operate and require little training for simple operation. Operators can be trained to operate the instrument and carry out routine maintenance in one week. Although the instruments give a positive or negative response, interpretation of spectra should be carried out by persons with an understanding of the ionization process.

IMS is generally not useful for the characterization of mixtures, because components present in high concentrations or components with a high proton affinity will dominate the spectrum. Similarly, matrix components present together with the analyte in the sample may cause problems during analysis. Three approaches have been developed to minimize matrix effects: Alternate reagent ion chemistry, standard addition methods, and pre-separation of complex samples with a GC [71]. In alternate-reagent ion chemistry a dopant is added to the reagent gas. As a result, molecules with a lower proton affinity than the dopant are not ionized and the appearance of the plasmagram is improved. The first two approaches may be useful for mixtures with four or fewer components, but for mixtures that are more complex a GC pre separation is necessary.

Other fields of applications are the semi-conductor industry (detection of surface contaminants), the identification of trees after stripping of the bark, the monitoring of microbiotics in water, the monitoring of anaesthetics in operating rooms and the sensing of petrochemical fuels in soils (using headspace analysis). The coupling of GC and IMS has several advantages: GC can separate the analyte from other substances in the mixture or from the matrix and brings it into the vapor phase. The IMS functions as a detector with very low detection limits and provides some degree of identification. The IMS has to be adapted and a special interface has to be designed to allow its use as a detector for the GC. Several environmental applications of GC-IMS have been published [72].

IMS can be used for direct analysis [21,73] of samples and as a chromatographic detector. It is currently used for the direct analysis of explosives, drugs of abuse, chemical warfare agents and atmospheric and workplace pollutants. Major advantages of IMS are its sensitivity in the sub ppb or pg range, its continuous real time monitoring capability, its reasonable price due to instrumental simplicity, and the easy automation. A major disadvantage of the IMS is its limited linear range [21], which seems to be related to the limited number of reactant ions available for ion-molecule reactions. It is relatively easy to overload the IMS and therefore sample size must be controlled with care [72]. Another weakness is the response variation that occurs with different background gas compositions and with different sample compositions.

New techniques for the field detection of inorganic improvised explosive devices (IEDs) are urgently developed. Although ion mobility spectrometry (IMS) has been proved to be the most effective method for screening organic explosives, it still faces a major challenge to detect inorganic explosives owing to their low volatilities. Herein, Haiyang Li *et al.*, proposed a strategy for detecting trace inorganic explosives by thermal desorption ion mobility spectrometry (TD-IMS) with sample-to-sample analysis time less than 5 second based on in-situ acidification on the sampling swabs [72]. The responses for typical oxidizers in inorganic explosives, such as KNO_3 , KClO_3 and KCLO_4 were at least enhanced by a factor of 3000 and their limits of detection were found to be sub nanogram. The common organic explosives and their mixtures with inorganic oxidizers were detected, indicating that the acidification process did not affect the detection of organic explosives. Moreover, the typical inorganic explosives such as black powders, firecrackers and match head could be sensitively detected as well. These results demonstrated that this method could be easily employed in the current deployed IMS for on-site sensitive detection of either inorganic explosives or organic ones.

The common organic explosives and their mixtures with inorganic oxidizers were detected, indicating that the acidification process did not affect the detection of organic explosives. Moreover, the common nitro-explosives and its mixture with the inorganic oxidizers and the frequently-used inorganic explosives such as black powder, firecracker and match head were sensitively detected. The influence of acidification process on the detection of organic explosives was also investigated. These results demonstrated that this method could be easily employed in the current deployed IMS for on-site sensitive detection of either inorganic explosives or organic ones.

The excellent mass detection limits, rapid analysis time, superior resolution, and extremely small sample requirements of IMS method is attractive for the forensic analysis of the explosive material especially in post blast residue analysis. The IMS technique also requires the only limited consumption of inexpensive and nonhazardous reagents.

Conclusion

The expanding threat, illegal behavior and illicit activities utilizing energetic explosive materials for criminal and terrorism activities have urged the need for a reliable, rapid but also an accurate investigation technique for analyzing vital trace evidence at the scene of the crime. Analysis of explosive residues become more difficult since the residues of origin material from post-blast samples are usually trapped and fused into surrounding. To identify unknown explosive samples, it demands a competency technique to determine an extensive number of organic and inorganic explosive materials. It is of great importance for the explosive and their post-blast residues analysis to assist forensic scientist in determining the origin of explosive material used in the bombing and eventually help the law enforcement in narrowing down the investigation. Therefore, this review article emphasizes on steps to track traces of evidence and the use of IMS for explosive residue analysis.

IMS is an analytical technique that has primarily been used as a trace chemical monitor in the field. Therefore, the potential sensitivity of an IMS system to these compounds is quite high. It is clear that IMS technology will integrate into many different fields in the future. We should also expect to see pocket size miniature detectors of chemicals warfare agents widely distributed to soldiers or first responder personnel to give a timely and sensitive alert as well as sensors mounted on drones flying ahead and above armed forces. Another future trend will be monitoring of central air supplies in buildings and crowded areas for chemical and biological warfare agents.

In forensic sciences the IMS methodology is mainly used as a detection device to prove the presence of latent traces of illicit drugs or explosives on surfaces of suspicious or confiscated material of evidence [74,75]. IMS supports a wide variety of search and detection scenarios and is of great value in the support of police and custom authorities all over the world. This technology enables its user to swiftly detect and identify microscopic traces of the most common drugs and explosives on any surface.

The benefits of IMS as a field detector are its simplicity, sensitivity, fast analysis times, portability, ruggedness, and its operation at ambient pressures. IMS has successfully been used for many years to detect traces of explosives at airports and other security

checkpoints; illicit drugs in prisons, cargo, and in border security. The military have long used IMS for detection of chemical warfare agents. Innovations in drift tubes, nonradioactive ion sources, and hyphenated IMS techniques in recent years have expanded the range of forensic applications.

However, a major disadvantage of IMS has been its limited selectivity, such that some interferent ions have the same low- field mobility as the analyte ion, and thus can result in a false positive. During the last decade, IMS research has exploded and, as such, has experienced much progress in the selectivity and resolution of explosives detection. Prospective methods to improve the selectivity, sensitivity, and resolution of IMS will make certain its continued success in the monitoring and detection of energetic materials.

Much research work can be improved in order to cope with the advancement in terrorism. For the sake of global security, other than enrichment of law enforcement and military strength, attention should be paid to the importance of research and development on the analysis of scientific evidence, particularly on explosive post detonation residue analysis. There is a growing necessity to develop more innovative methodologies to reduce time consumption in the analyses, enhance sensitivity, and finally move forward towards greener chemistry.

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