Mass Spectrometry Based Personnel Portal Screening System

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Introduction

In this paper we review a new technology for personnel screening of explosives. The detection system consists of an innovative sample collection/concentration portal developed by Sandia National Laboratories and a high-throughput screening, mass spectrometer (MS) system developed by Syagen Technology. The combined personnel screening system is planned for deployment at airports and other high security venues. This paper will focus primarily on the operation of the MS system.

The performance criteria on which aviation security screening technologies are judged are accuracy (high detection and low false positive rate), speed and cost. As terrorists become more sophisticated, there will be a need to detect an increasing variety of threats (new explosives, chemical weapons, etc.). Systems must also be sufficiently automated for non-technical security personnel to operate. Acceptable defenses are now being deployed for baggage scanning, including differential X-ray and X-ray tomography. Swipe methods of sampling are also being used for high-touch areas of baggage and other items. Unfortunately these methods are not appropriate for personnel screening.

Ion mobility spectrometry (IMS) is the most commonly deployed method for trace detection and personnel portals have been developed based on this technology by Barringer and Ion Track. This paper will focus on the unique benefits of MS for achieving effective screening of personnel for explosives.

Detection Method

Background

Fast and accurate screening for trace levels of explosives and other targeted requires a sophisticated combination of components that work together as a system. The three basic functions of the Syagen/Sandia screening system are:

- Sample collection and compound enrichment
- Selective detection of targeted compounds
- Accurate measurement of targeted compounds

The approach being used is portrayed in Figure 1. A large volume of air is collected and sifted to remove the vast majority of air, while retaining particles, residue, and condensable vapors in a step called preconcentration. Following this enrichment process the collected sample is introduced into

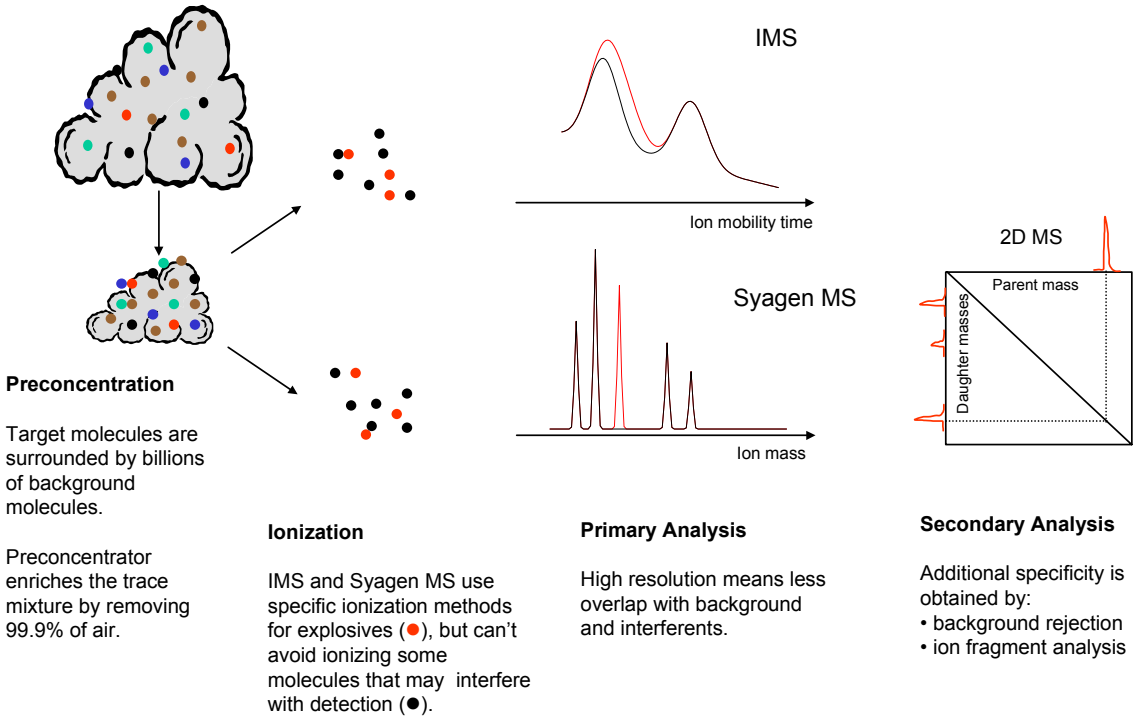


Figure 1. Comparison of ion mobility spectrometry (IMS) and mass spectrometry (MS) methods of detection in an overall high-speed screening system.

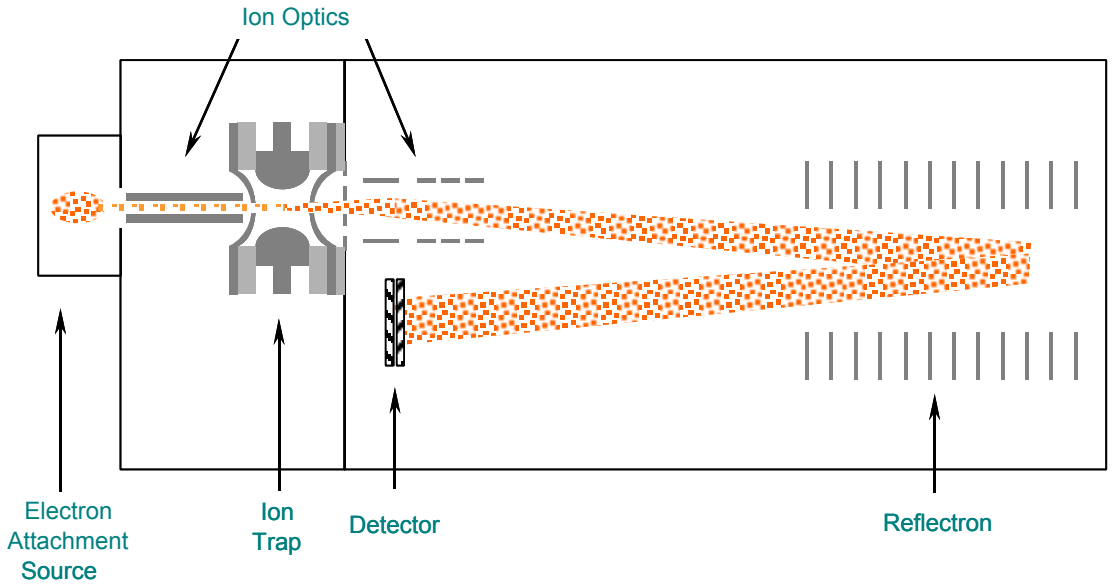
the detection system and the compounds further selected for the targeted compounds using an ionization method that preferentially ionizes the compounds of interest. For example, explosives have properties that make them very reactive to negative ions and electrons. The selectively ionized molecules are then detected by a method that further differentiates different compounds. The two leading detection methods are mass spectrometry (MS) and ion mobility spectrometry (IMS).

Mass Spectrometer

Syagen has developed the QitTof™ MS analyzer, which is coupled to a novel ionizer configuration that is specially tuned for ultrasensitive detection of explosives and chemical agents. QitTof refers to quadrupole ion trap, time-of-flight mass spectrometry (QIT, TOFMS). A schematic of the QitTof configuration is shown in Figure 2. The main benefits of QitTof relative to other MS systems are:

- TOFMS analyzes all ions at once vs. quadrupole mass spectrometry, which can detect only one ion mass at a time
- QitTof enables fast TOF detection compared to QIT MS only
- QitTof enables mass-selective analysis by MS^n analysis compared to TOFMS only

These features translate into exceptional levels of performance in terms of speed, sensitivity, and specificity.



DI source
- Selectivity toward high electron affinity ($-NO_2$)
- Minimum charge competition

Quadrupole Ion Trap (QIT)
- Storage of ions from continuous source
- MS/MS capable
- High duty cycle

TOFMS
- Multichannel detection of all ions at once
- Low noise due to narrow time bins

Figure 2. Schematic of the QitTof MS detection system showing the individual components and their respective advantages.

The principle of TOFMS is very simple and makes use of the energy equation $E=mv^2/2$ where m is mass and v is velocity. As illustrated in Figure 3, all ions are accelerated to constant E. The ions then enter a drift tube where they travel at velocity v. Because each ion mass travels at a different velocity, the ions of different mass separate; the lighter ones run ahead of the heavier ones. This separation means that each ion mass hits the detector at a different time. Ions of the same mass arrive together and give a sharp peak in the TOF mass spectrum. Fast detection methods can measure the arrival times and the simple formula above can be used to transform the times to mass.

IMS is a method that also separates ions in time. Separation is based on the different speeds that ions drift through a viscous gas under the force of an electric field. The drift time depends on both molecular weight and size; they do not give a simple measure of molecular weight. The principal advantages of MS over IMS are higher resolution and molecular identification. As shown in Figure 1, higher resolution minimizes the problem of interference due to overlapping signals from different compounds. The measure of molecular weight by MS is a very strong indicator of what the compound is, unlike the measure of mobility times by IMS. For example, TNT has a molecular weight of 227. The probability of another compound having that molecular weight is very small. However, to positively confirm that a detected signal at molecular weight 227 is actually TNT, Syagen's QitTof MS technology can selectively fragment the molecular ion to determine its struc-

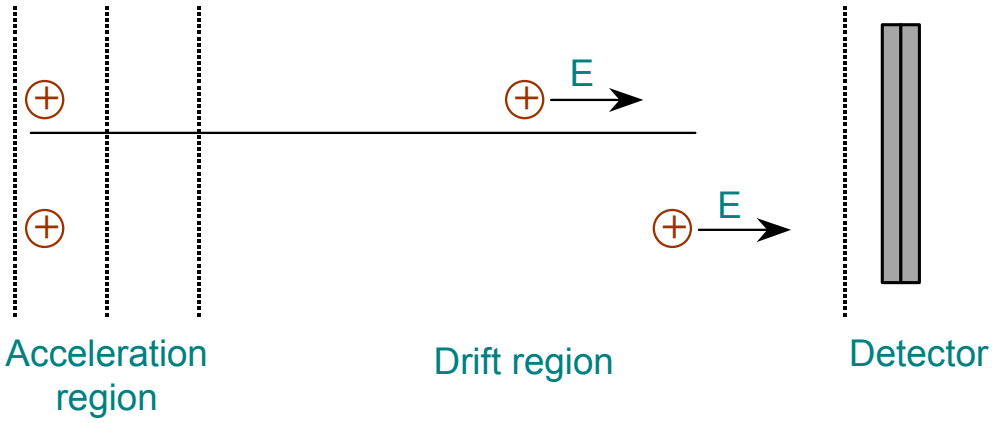


Figure 3. Separation of different ion masses by TOFMS.

ture and definitively identify the detected compound. This secondary analysis shown portrayed in Figure 1 provides an unprecedented level of specificity for positively detecting targeted compounds.

The ionizer is a key component of the detection system. The Syagen detector employs an electron attachment source that forms negative ions for explosives. Explosives are very electronegative compounds that readily attach electrons. Most other common compounds that are likely to be sampled in a portal system are less electronegative, hence the ionization process provides a stage of selectivity in differentiating explosives compounds from common background. However, as portrayed in Figure 1, other compounds besides explosives can be ionized and therefore it is important to have other stages of differentiation. For the Syagen detector, MS^n provides this capability.

The QitTof MS detection system has the following capabilities:

- High resolution
- High sensitivity
- Molecular weight identification
- Secondary confirmation by ion fragment analysis

The detector was designed for automated and unattended operation and for use by non-technical personnel.

Portal System

The portal provides for non-intrusive sampling of individuals on about a 12 s cycle time. An individual is instructed to enter the portal and turn sideways. A series of compressed air jets are pulsed to ruffle clothing and detach particles. Individuals who have handled explosives devices are usually contaminated and some of these particles are likely to be explosives particles. A blower inside the portal structure turns on for 5 s, which pulls the volume of air in the personnel compartment through a duct. This airflow is drawn through a preconcentrator device that “strains” the particles and condensable vapors onto a mesh. This mesh is then shock-heated for 1-2 s to thermally desorb

the explosives compounds, which are then swept toward the detector in a much smaller volume of air. A second preconcentrator further concentrates the explosives compounds, to further promote the detection of explosives compounds.

Results

In this section we present results to illustrate the capabilities of the QitTof MS analyzer coupled to an electron attachment source.

Mass Spectral Signatures

The key to an effective trace explosives detection system is the simultaneous detectability of a broad range of compounds at trace levels in the presence of background compounds at much higher abundance. Achieving this capability is aided by a selective ionization process that maximizes the ion signal of compounds of interest while minimizing the ion signal from the more abundant background compounds. Furthermore it is essential that each compound have distinct and highly resolved molecular signatures to enable positive identification and differentiation from potential interferents. Figure 4 shows electron attachment QitTof mass spectra of common explosives. These compounds are observed to have distinct mass spectral signatures. Because the spectral signals are very sharp, the probability of overlap with other compounds, such as background compounds, is very low relative to lower resolution detection methods such as IMS. Nitroaromatic explosives (e.g.,

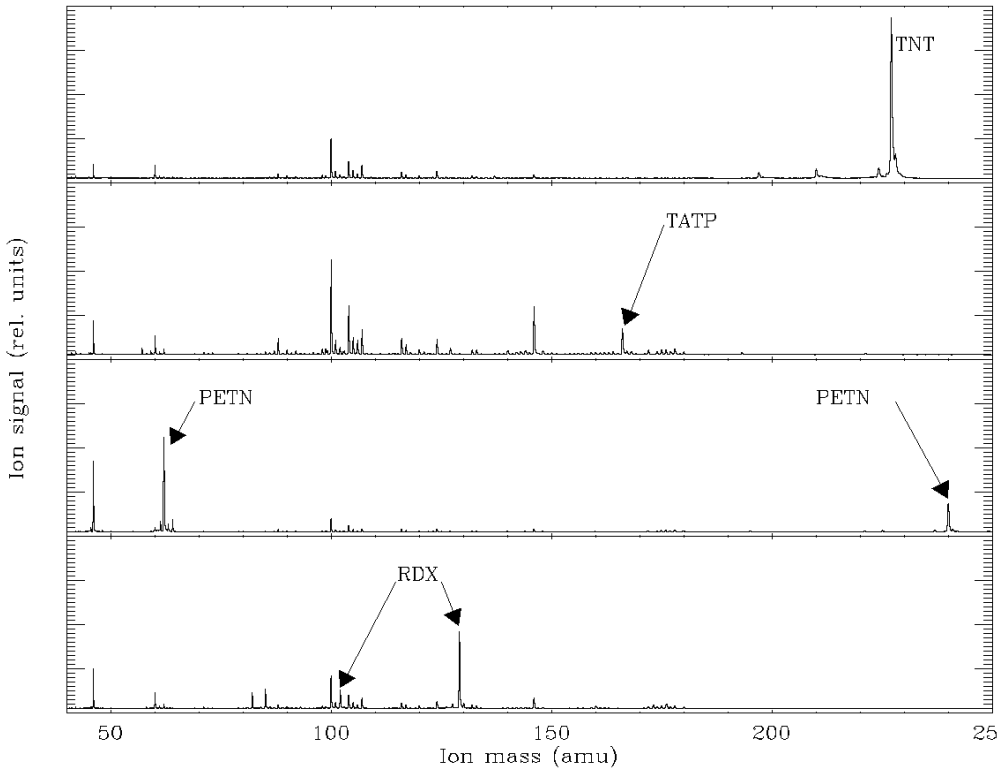


Figure 4. MS spectral signatures for selected explosives. Each compound gives a unique spectrum. Nitrate esters all have a common peak at m/z 62.

TNT, DNT, etc.) generally give molecular ion signal. Nitramines (e.g., RDX and HMX) give distinct peaks at m/z of 176, 129, and 102, but not at the molecular ion. Nitrate esters give the least distinct spectral signatures due to extensive dissociative electron attachment to give a predominant NO_3^- ion at m/z 62. PETN leads to significant signal at m/z 242 under optimized conditions to give the potential to distinguish some nitrate esters.

The spectra in Figure 4 were recorded from headspace vapor either at room temperature (TNT, PETN) or elevated temperature (about 50°C for RDX). For TNT this corresponds to a saturated headspace vapor pressure of less than 10 ppb. At these levels strong signal is observed with relatively weak signal from room air. Explosives compounds that have been detected by the MS detector with high sensitivity include TNT, ADNT, DNT, MNT, TNB, DNB, DMNB, RDX, HMX, EGDN, NG, PETN, and TATP.

MS/MS Analysis

For molecular screening purposes a single stage of MS is usually sufficient to alert to the presence of explosives compounds while maintaining a sufficiently low false positive rate. However, if a more definitive identification is needed the QitTof mass analyzer allows additional stages of ion mass identification through the process of ion mass-selected collision-induced dissociation (CID). In this method the presence of a target ion signal can be used to trigger an excitation waveform in the QIT that excites the target ion to high kinetic energy. When these energetic ions collide with the buffer gas in the trap (typically ambient air), they dissociate to fragment ions. The fragment ion signals are typically very specific to given compounds and greatly increase the confidence in the identification of target compounds.

Figure 5 shows an example of detection of TNT headspace vapor at room temperature in MS mode and in MS/MS mode. In the latter example, the detector is programmed to trigger an excitation waveform when an ion signal at m/z 227 (TNT) is observed. The observation of fragment ions at m/z 210 and 197 is positive identification of TNT.

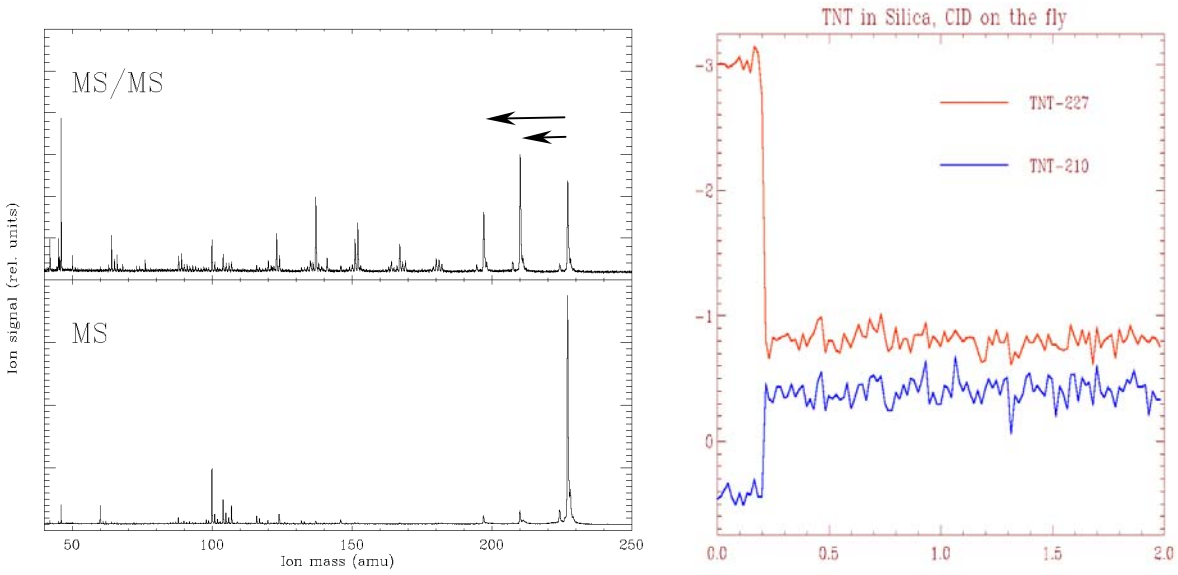


Figure 5. TNT detection using MS/MS. (Left) MS and MS/MS spectra. (Right) molecular and fragment ion signal vs. time showing speed and stability of MS/MS analysis (time in s).

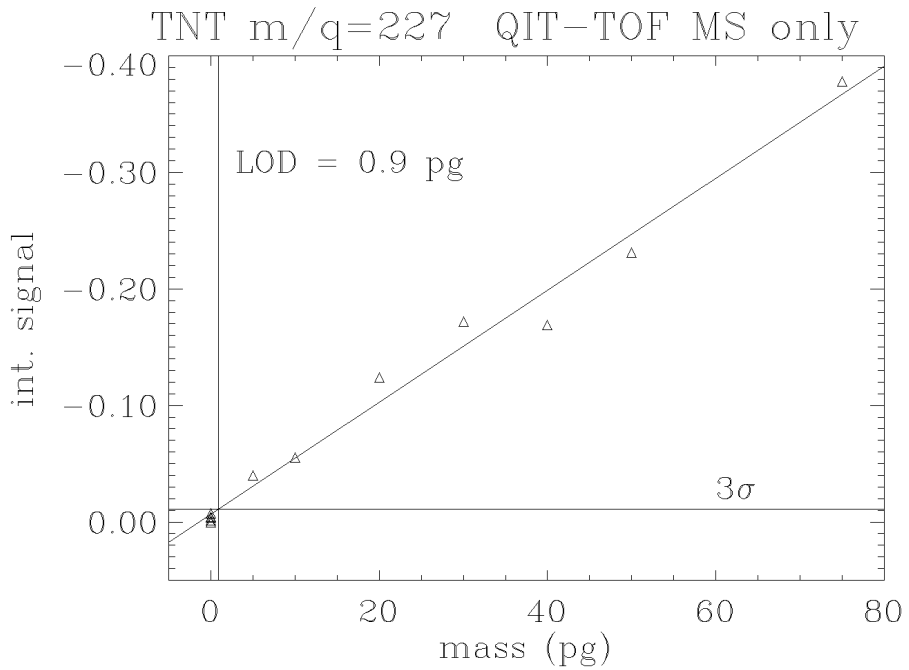


Figure 6. Detector sensitivity. 3σ limits of detection are 1 pg for TNT, 5 pg for RDX, and 20 pg for PETN.

Limits of Detection

The electron attachment source coupled to the QitTof mass analyzer achieves exceptional sensitivity. A limit of detection (LOD) was measured for a wide variety of explosives compounds by depositing known quantities of compound onto a heated tube connected to the inlet of the detection system. The tube was then rapidly heated to desorb the compound, which flowed into the ionizer using room air as a carrier gas. Figure 6 shows a linearity plot for TNT. The LOD is defined as the quantity of compound that gives a signal intensity that is a factor of three greater than the standard deviation of the background signal (i.e., 3σ). The LOD for TNT is about 1 pg. Similar measurements give LODs for RDX and PETN of about 5 pg and 20 pg, respectively. All other compounds tested fall in the LOD range of 2-20 pg, except DMNB and ANFO, which are less sensitive.

Performance when integrated to Portal

Extensive testing has been conducted on the combined MS/portal system at Sandia and at the Federal Aviation Administration (FAA). These results are demonstrating the potential for a highly effective personnel screening capability for a wide range of explosives compounds. However, it should be realized that the LOD at the detector is not the same as the LOD in the portal. The latter is generally about two decades higher owing to several stages where compound can be lost. These include inefficiencies in removing compound from fabric, losses in transferring compound to the preconcentrator, and losses in the preconcentrator desorption. Calibrated samples are being developed to simulate the contamination of individuals who have handled explosives. Results of these tests with the portal system will be presented in a forthcoming paper.

Conclusion

The Syagen MS system is a leading explosives detector offering unprecedented levels of performance with regard to speed, sensitivity, and specificity. In combination with the Sandia personnel portal system, it provides a new line of defense against terrorist acts involving bomb-toting individuals. Compared to current technologies the MS detector offers:

- Greater number of detectable threat compounds
- Higher detection probability (low false negative rate)
- Lower false positive rate
- Software-configurable for specific threat situations

Applications for the MS system in a portal configuration or as a hybrid system with a bulk detector include:

- Airport passenger and baggage screening
- Military force protection
- Prison security and courthouse security
- Public venue security

Acknowledgments

We are very grateful to Dr. Tom Chamberlain and Dr. Richard Lareau of the FAA for their support of the Syagen/Sandia collaboration. We would like to thank the exceptional Sandia team consisting of Kevin Linker, Chuck Rhykerd, and Frank Bouchier for the portal development and for integration of the Syagen detector.