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Detection of Trace Explosive Evidence by Ion Mobility Spectrometry

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ABSTRACT: The continuing threat of worldwide terrorism has prompted the need for new and innovative explosives detection systems. As part of an ongoing research effort, the FBI Laboratory has been evaluating new technology and the innovative adaptation of existing technology for use in counterterrorism and counternarcotics investigations. We have been examining the application of ion mobility spectrometry (IMS), for its role in explosives detection.

The explosives residue is collected on a membrane filter by a special attachment on a household vacuum. Subsequent thermal desorption and analysis requires 5 s. Experimental results have determined the limits of detection for most common explosives to be approximately 200 pg. 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 residue from C-4, Deta Sheet, SEMTEX, and ammonium nitrate explosives have also been detected on items of forensic and evidentiary value.

KEYWORDS: criminalistics, trace explosive evidence, explosives, ion mobility spectrometry

Many nations, including the United States, have been prime targets of international terrorism for many years. The bombings of the U.S. Embassy and the U.S. Marine Barracks in Beirut in 1983, and the destruction of Pan American Flight 103 over Lockerbie, Scotland in December, 1988 are grim reminders of terrorism in recent years. These criminal acts have prompted the need for the development of new and innovative methods of explosives detection. As part of an ongoing research effort, the FBI Laboratory has been evaluating new technology and the innovative adaptation of existing technology for use in counterterrorism and counternarcotics investigations.

Ion mobility spectrometry (IMS) was first introduced by Cohen and Karasek in 1970 [1]. Much of the earlier work on the applications of IMS technology focused on funda-

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mental studies and laboratory feasibility. In a recent review it was pointed out that IMS technology is experiencing a resurgence of interest in specific purpose detection systems because of its analytical flexibility [2].

We have been examining the application of IMS to explosives detection in a variety of scenarios of forensic interest by collecting the trace physical evidence transferred to hands or surfaces through contact or post blast residue. The exceedingly low vapor pressure of explosives (ppm to ppt) [3], makes their detection by vapor methods alone difficult.

In general, IMS possess many of the desirable analytical figures of merit of conventional laboratory-based instruments such as good sensitivity, selectivity, and speed of analysis. They are often small and simple to operate. This ease of use and portability permit operation in real world scenarios not only as a forensic tool but also as an investigative tool.

The value of IMS as an investigative tool (rather than purely a laboratory tool) is exemplified in recent applications, which have included the detection of drug microparticulates on hands [4,5], determining cocaine in injection molded plastic [6,7] and use in customs scenarios [8]. Forensic applications of IMS technology from 1970 to 1989 have been thoroughly reviewed by Karpas [9]. We present here our results demonstrating the application of IMS to the detection of trace physical evidence from explosives.

Technique

The instrument used in these experiments was the Barringer IONSCAN Model 200 (Barringer Instruments, Inc., South Plainfield, NJ). The system consists of the IMS analyzer and a briefcase-sized pumping unit. A separate portable computer is used for data storage, display and adjusting the detector operating conditions and detection alarms.

The IMS block diagram in Fig. 1 consists of two main areas: the reaction region and the drift region. In the reaction region, atmospheric pressure carrier gas (purified air), hexachloroethane (C_2Cl_6), the reactant gas and 4-nitrobenzotrile, an internal calibrant

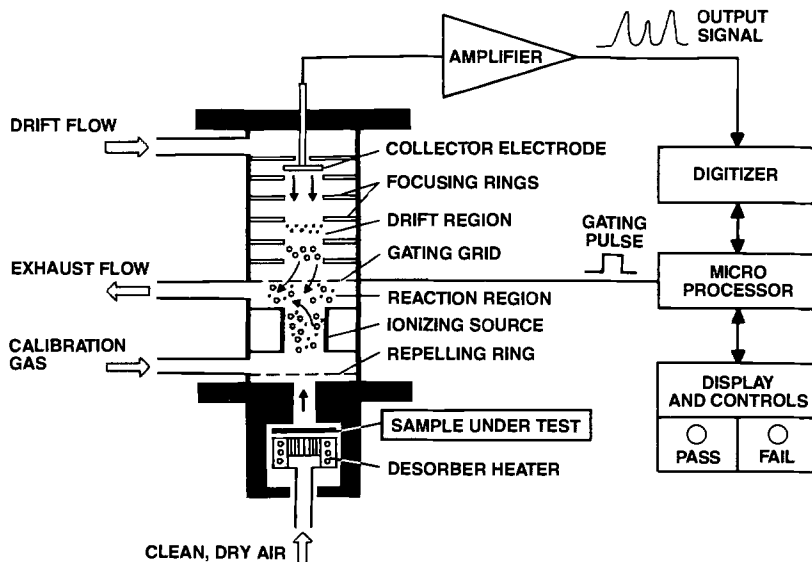
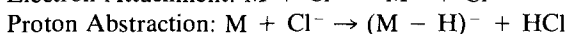
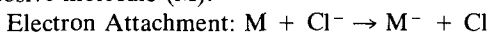


FIG. 1—Block diagram of the Barringer IONSCAN Model 200 ion mobility spectrometer.

are ionized by a ^{63}Ni beta emitter to form Cl^- ions. The use of modified ion chemistry to improve the sensitivity and selectivity of detection by IMS is quite common.

The reactant ions can then undergo one or more ion/molecule reactions with an explosive molecule (M):



The neutral explosive molecules can also undergo other ion-forming reactions such as adduct formation and dissociation reactions. The exact nature of the species formed in the IMS can be decisively determined using an IMS/MS combination. Karpas has reviewed the ionization of explosives in IMS under a variety of operating conditions [9]. In general, negative ionization provides a high degree of selectivity because only highly electronegative compounds such as explosives are ionized.

Under the influence of an electric field, the mixture of reactant and product ions reaches a shutter grid that separates the reaction region and the drift region. The shutter grid is made of sets of thin mesh wires with a voltage bias between them. When the shutter grid is "on" (with bias voltage applied), the ions are attracted to the gating grid and lose their charge. For a brief amount of time the grid is turned "off." Ions are then transmitted into the drift region of the cell. In the drift region an electric field gradient is applied. The ions migrate through the electric field, but at the same time are hindered by the countercurrent drift gas. The smaller, compact ions have a higher mobility than the heavier ions, and therefore traverse the region and collide with the electrometer plate in a shorter time. With the aid of a microprocessor, a plot of ion current intensity versus the time elapsed from the opening of the shutter grid gives the mobility spectrum or plasmagram.

Theory

The drift velocity, v_d , (cm/s) of an ion traversing through an electric field gradient, E , (V/cm) is proportional as follows:

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

where the proportionality constant, K , is the mobility of the ion in $\text{cm}^2\text{V}^{-1}\text{S}^{-1}$.

If t is the required time (s) for the ion to travel the drift region length (cm), d , at this velocity, and the drift velocity is the drift length divided by the drift time, then

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

in general, for a given temperature, T (Kelvin) of the drift gas and pressure, P (torr) the mobility is given as reduced mobility, K_o , in the form of

$$K_o = [d/(Et)] (273/T) (P/760) \quad (3)$$

With a given set of electric field gradient, temperature, and pressure conditions, the product of the reduced mobility and the drift time of an ion, $K_o t$, is a constant.

From the above equation, it can be seen that the ratio of the reduced mobility of any two species is independent of operating conditions and allows for the use of the calibrant as an internal standard. The ratio of the sample ion mobility to the mobility of the calibrant corrects for any drift and provides for identification and alarm triggering. The audible IMS alarms were calibrated by analyzing standard samples of the explosives of interest.

Ion behavior can also be derived from the fundamental relationships between ion mobility and collision processes at the molecular level as expressed by McDaniel [10]:

$$K = (3e/16N) (2\pi/kT)^{1/2} \times (m + M/mM)^{1/2} (1/\Omega) \quad (4)$$

where e is the charge on the ion, N is number density of the drift gas, k is the Boltzmann's constant, T is the absolute temperature, m is the ion mass, M is the mass of the drift gas, and Ω is the average collision cross section which is determined by ion size, shape, and polarizability.

From this equation a nonlinear relationship exists between the ion mobility and mass. A semilogarithmic plot of reduced mobility vs mass should produce a straight line. Comparing equations (2) and (4) also suggests that a plot of drift time vs mass should also be linear. These relationships can be helpful in determining the mass of an unknown species in the IMS as will be demonstrated in the following section.

Results and Discussion

IMS Spectra and Limits of Detection

Standards with concentrations of 1 ng/ μ L and 100 pg/ μ L were prepared of TNT, RDX, PETN, NG, and NH_4NO_3 , and placed on the teflon membrane filter with a microliter syringe. The instrument conditions for our experiments are shown in Table 1. The drift times, ion mobility (referenced to TNT, $K_0 = 1.451$) and the limit of detection for these five common explosive components are shown in Table 2. The detection of a specific

TABLE 1—Operating conditions for explosives detection.

Parameter	Setting
Drift temperature	95°C
Inlet temperature	215°C
Desorber temperature	235°C
Desorption time	4.3 s
Shutter grid pulse	200 μ s
Scan cycle time	24 ms
Drift flow	350 mL/min
Sample flow	300 mL/min
Exhaust flow	650 mL/min

TABLE 2—Characteristic ions for some common explosives.

Peak	Proposed Species (-)	Mass	Drift Time (ms)	K_0 ($\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)	L.O.D.
TNT	TNT - H	227	14.52	1.451	200 pg
RDX - 1	RDX + Cl	257	15.19	1.387	200 pg
RDX - 2	RDX + NO_3	284	16.03	1.314	800 pg
RDX - 3	RDX + (RDX + Cl)	479	22.22	0.948	1 ng
PETN - 1	PETN - H	316	17.37	1.213	80 ng
PETN - 2	PETN + Cl	351	18.40	1.145	200 pg
PETN - 3	PETN + NO_3	378	19.08	1.104	1 ng
NG - 1	NG + Cl	262	15.73	1.339	50 pg
NG - 2	NG + NO_3	289	16.50	1.275	200 pg
NO_3	$\text{H}_2\text{O} + \text{NO}_3$	100	10.93	1.927	200 pg

ionic species on the computer displayed plasmagram was found to range from 200 pg to 80 ng.

It can be seen in Table 2 that more than one species is generated for some of the explosives depending upon the amount of explosive present. For example, three species labeled RDX-1, RDX-2, and RDX-3 are formed for RDX. It is theorized that these species are the chloride adduct $(\text{RDX} + \text{Cl})^-$, the nitrate adduct $(\text{RDX} + \text{NO}_3)^-$, and an adduct between a neutral RDX molecule and the chloride adduct $(\text{RDX} + (\text{RDX} + \text{Cl}))^-$. At 200 pg of RDX in the ionization region only the chloride adduct is formed. As the concentration increases to 1 ng more free neutral RDX molecules are present, which can undergo ion molecule reactions with the chloride adduct. Proposed ionic species for the other explosives are presented as well. The plasmagram for RDX and PETN are shown in Figs. 2 and 3, respectively.

The ionic species formed from the desorption of ammonium nitrate is believed to be $(\text{NO}_3 + \text{H}_2\text{O})^-$. Experimental results have verified that at the thermal desorption conditions used the relatively involatile nitrates such as sodium and potassium are not detected even when samples are placed on the desorption filter. Material containing potassium nitrate such as Pyrodex or black powder is not detected either.

The exact nature of the species formed in the IMS under these conditions can only be decisively determined using an IMS/MS combination. A good deal of confidence can be gained in the assignment of the species by applying equations (2) and (4) to the data. As shown in Fig. 4 an excellent agreement between the theoretical and observed behavior for the constant product of $(t \times K)$, drift time (t) vs mass, and a semilog plot of reduced mobility vs mass is observed as discussed in the theory section.

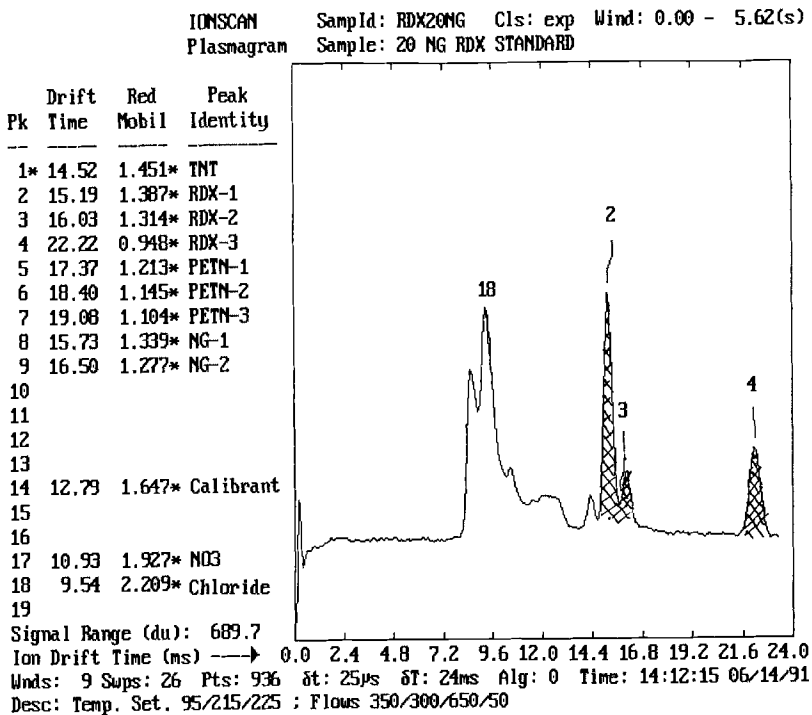


FIG. 2—Computer displayed plasmagram for 20 ng of RDX standard. The table on the left of the display shows the current target explosives programmed into detector. The plasmagram (plotted as intensity vs. drift time (ms)) is the average spectrum recorded over the thermal desorption cycle.

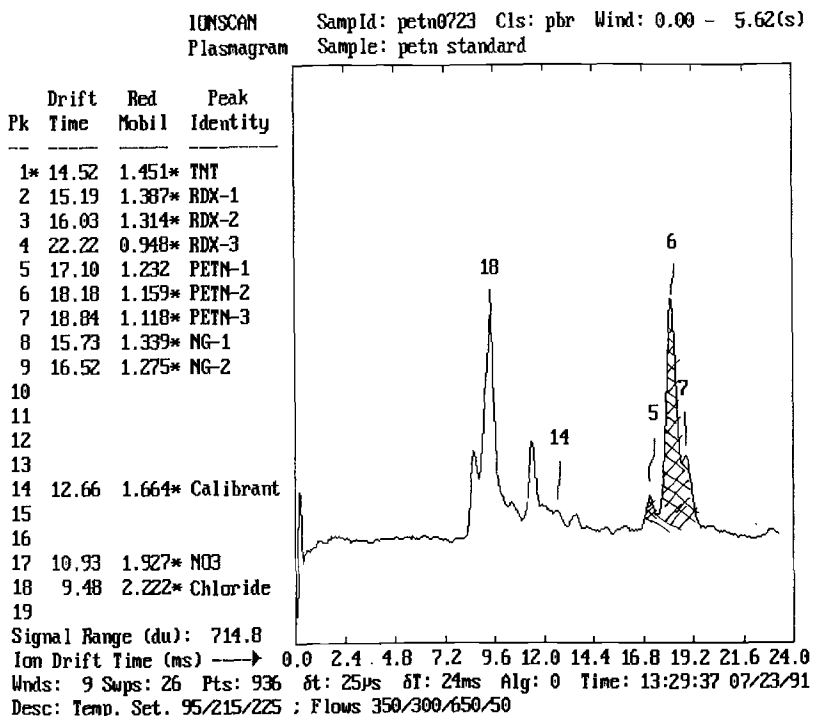


FIG. 3—Computer displayed plasmagram for 20 ng of PETN standard.

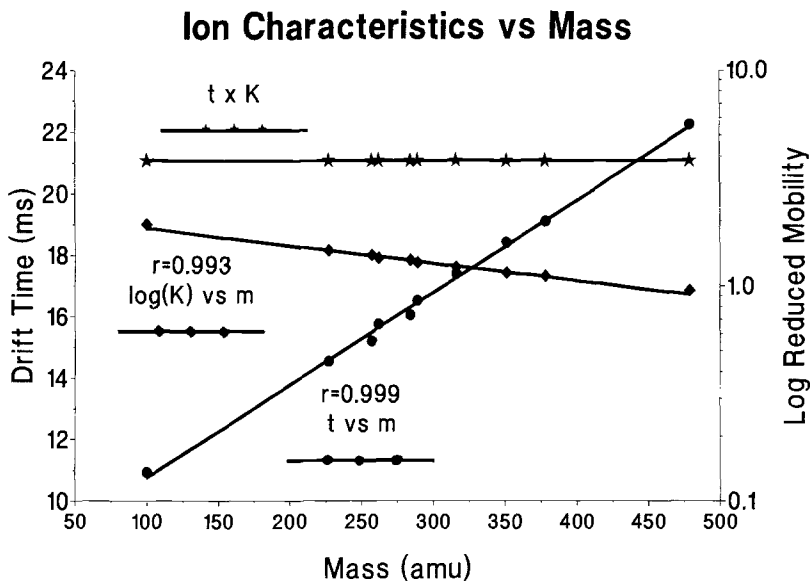


FIG. 4—Characteristic ion behavior as a function of mass.

The formation of multiple species greatly increases the specificity. As an aid to the analyst and to reduce the chance of false alarms, the peak detection algorithms in the detector unit are designed by the manufacturer to recognize two of the three peaks for RDX and PETN before the audible detector alarm will sound. The alarm threshold, (that is, how large a signal is required before the alarm sounds) is user programmable. Irregardless of an audible alarm, the trained operator will carefully examine the plasmagram following each sample.

Hand and Surface Contamination

Contamination of the hands has been shown to occur after handling commercial [11] and military explosives [12]. The persistence of these explosives on hands and evidence of contact transfer is well documented in forensic sciences [13,14]. IMS can be used to identify explosives on suspects or on their belongings. This evidence can provide probable cause for a search warrant, help identify a potential terrorist, and locate concealed explosives.

To demonstrate this, a subject touched C-4 (RDX). The subject then enacted several normal stages in operating a car, including opening and closing the hood, the driver side door, the trunk and handling the steering wheel, gearshift, and keys. Samples were collected before and after the contact transfer from each of the touched areas of the car and from the subject's hands by vacuuming onto the 1.25" diameter membrane filter disk. Each disk was then placed over the desorption heater (Fig. 1) and thermally desorbed into the IMS for analysis. An alternative sampling method that has also proven successful is to simply wipe the suspected surface with the sample collector. Careful procedures were followed to ensure that no cross contamination occurred by verifying that the sample disks and the IMS were clear of explosives before sample collection.

As shown in Table 3 the car surfaces and hands were negative for RDX prior to touching the explosive. After contact, all touched areas showed easily detectable RDX residue. In a separate experiment, after handling C-4, eight consecutive hand washings with soap and water were required before the IMS could no longer detect the RDX.

Post-Blast Residue

Following a terrorist attack, rapid and accurate analysis of post-blast residues plays a vital role in the bombing investigation. The first question often posed by an investigator following a blast is, "What was the explosive?" The analysis may provide the link between a suspect and the type of explosive used. Yelverton has demonstrated the detection of post-blast RDX vapor using a quartz tube preconcentrator and IMS [15]. Because of its

TABLE 3—Contact transfer of C-4 from hands to automobile surface.

Car Area	Before Touching	After C-4 Transfer
Hands	—	+
Hood	—	+
Door handle	—	+
Hatch back	—	+
Steering wheel	—	+
Gear shift	—	+
Keys	—	+

portability, the IMS can be taken to a bombing crime scene for preliminary analysis to aid law enforcement investigators.

We conducted a series of post-blast residue experiments the results of which are summarized in Table 4. Samples were collected on the teflon membrane filters by vacuum, and the IMS was cleared between samples by running a blank.

A number of improvised explosive devices (pipe bombs), were prepared. The pipes contained Hercules Green Dot, Royal Scott, Hercules Red Dot and Winchester Ball double-based smokeless powder, Pyrodex (a black powder substitute), and black powder. Following detonation, fragments of the pipes were recovered for analysis. A single fragment, just a few square inches in size was vacuumed. Fragments from the four pipes containing the double based smokeless powder alarmed positive for nitroglycerine. Figure 5 shows the NG plasmagram from a segment of the pipe which contained Green Dot double-based smokeless powder. Post-blast NG residue on pipe fragments can still be detected six months later by reanalyzing the fragments.

It can be seen that a third peak with a drift time of 14.52 ms (same as TNT) is also observed. This third peak from NG is only observed in the IMS under conditions in which high concentrations of NG are present. It is only found in the presence of the other two NG peaks. This peak was tentatively identified as dinitroglycerine through the analysis of standards of dinitroglycerine.

Nitroglycerine vapors have also been observed to be collected on nearby surfaces. For example, NG residue has been detected on wipe samples taken from a night deposit box following an explosion. Vacuum samples from the inside, outside and handles of a gym bag believed to be used to transport the explosives to the bank, were also positive for NG. The bag acted as a preconcentrator.

Finally, it should be noted as shown in Table 4 the fragments of pipe from the Pyrodex and black powder devices were negative for nitroglycerine, nitrate or any other explosive. Only the more volatile ammonium nitrate is detected as described above.

The second experiment involved post-blast steel plates. Semtex (PETN and RDX),

TABLE 4—*Postblast residue analysis results.*

Item and Explosive	Explosive Detected
Pipe Bombs	
Green Dot double based smokeless powder	NG
Royal Scott	NG
Red Dot	NG
Winchester Ball	NG
Pyrodex	—
Black Powder	—
Steel Plates	
Data Sheet	PETN
C-4	—
Semtex	—
Trenchrite	NO ₃
Powermax	—
Suitcase (C-4)	
10 individual items of clothing	RDX
Cardboard liner	RDX
Metal rim	RDX
Cassette/Radio (SEMTEX)	
Speaker magnet	RDX/PETN
Plastic piece	RDX
Metal nameplate	RDX

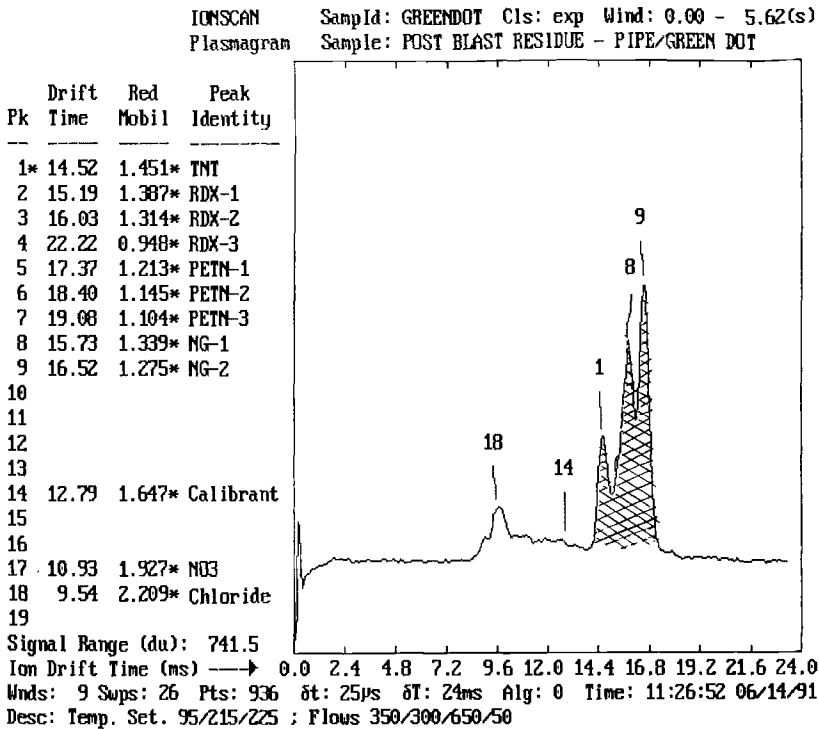


FIG. 5—Detection of postblast NG residue on a pipe fragment.

C-4 (RDX), Deta Sheet (PETN), Powermax (an Atlas Powder emulsion explosive), and Trenchrite (an Explosives Technologies Industries explosive) were placed on top of five clean steel plates on the ground and detonated in the open atmosphere. Samples were collected by vacuuming the plates.

The IMS alarmed for PETN from the Deta-Sheet steel plate, and for ammonium nitrate on the Trenchrite plate. The lack of detectable explosive residue on the other plates could have been because of the high heat of the blast and the lack of available material in the immediate environment for condensation of explosives vapor or trapping of particles. The use of wipe samples and solvent extraction is being further explored for sample collection. It should be noted that the IMS is only another tool that can be used as a part of an analytical scheme for the analysis of pre and post-blast explosives. Confirmation by other analytical methods should be employed.

In a third experiment a demolition block (1.25 lbs) of C-4 was placed in a suitcase containing 10 clothing items. Before the blast, the clothing and suitcase were clear of explosives. The C-4 was detonated and the post blast debris was collected. Post-blast RDX residue was detected on all articles of clothing using the vacuum sample method. Figure 6 shows the plasmagram for the detection of RDX on pieces of a pair of blue jeans. RDX was also detected on pieces of cardboard liner and metal trim from the suitcase.

The terrorist access to and the use of SEMTEX is a major concern to law enforcement officials. In our final experiment, a portable cassette/radio containing a small amount of SEMTEX was detonated. The remaining fragments and components were collected following the blast. Figure 7 shows the post-blast RDX and PETN residue on a speaker magnet. RDX was also detected on a piece of plastic and the metal nameplate.

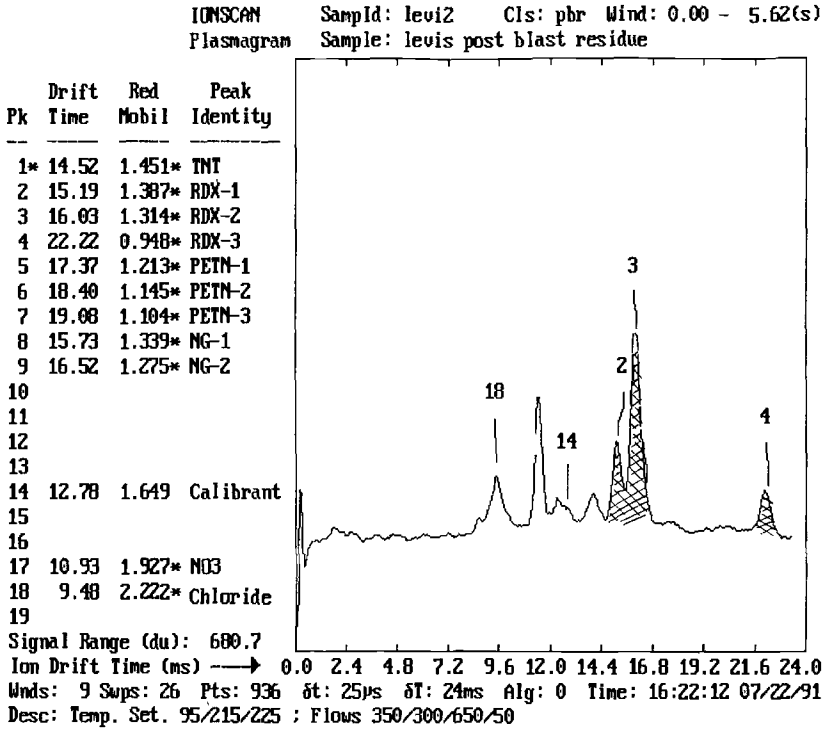


FIG. 6—Detection of postblast RDX residue on an item of clothing.

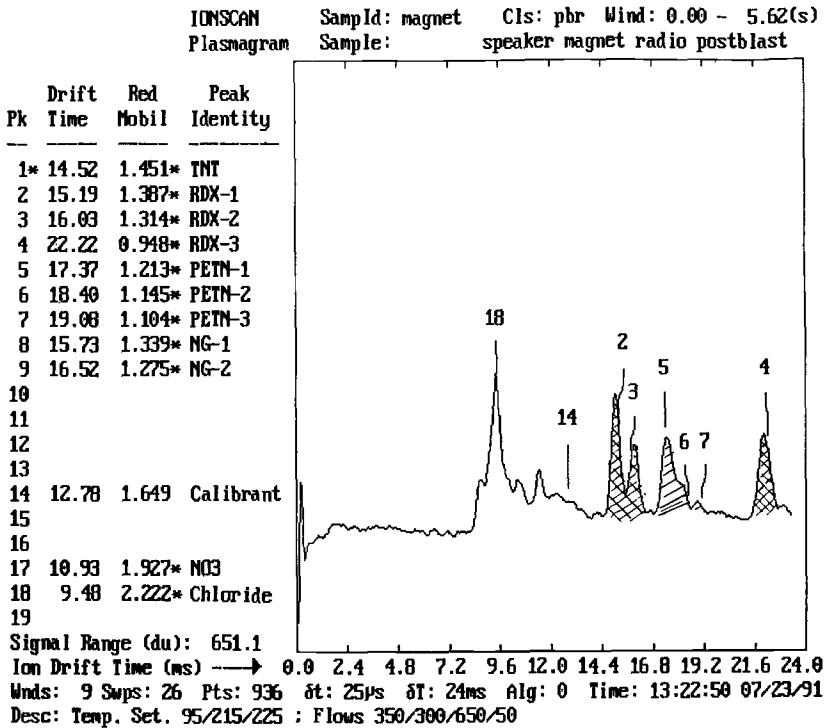


FIG. 7—Detection of postblast PETN and RDX residue on a speaker magnet.

Conclusion

Ion mobility spectrometry offers forensic scientists, law enforcement investigators, and security personnel a new tool in trace explosives detection. Laboratory measurements of the sensitivity and specificity of the IMS showed detection as low as 200 pg for common explosives. In addition, results of experiments involving the detection of trace physical evidence from explosives in practical law enforcement scenarios have been presented.

The demonstrated retention of explosives on hands and the contact transfer to other surfaces provides the law enforcement investigator potential new sources for the collection of trace physical evidence when dealing with suspected terrorists or bombers.

The detection of post-blast residue from improvised explosive devices can aid the investigator at a bombing crime scene by providing a rapid means of screening evidence for further laboratory evaluation.

The ease of sample collection with a vacuum, a rapid 5 s analysis, sensitivity of 200 pg for most explosives, selectivity (lack of false alarms in real world scenarios), and the capability for crime scene detection of trace physical evidence from explosives provides a new tool for forensic and law enforcement use.

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References

- [1] Cohen, M. J. and Karasek, F. W., "Plasma Chromatography—A New Dimension for Gas Chromatography and Mass Spectrometry," *Journal of Chromatographic Science*, Vol. 8, 1970, pp. 330–337.
- [2] Hill, H. H., Siems, W. F., and St. Louis, R. H., "Ion Mobility Spectrometry," *Analytical Chemistry*, Vol. 62, 1990, pp. 1201–1209.
- [3] Dionne, B. C., Rounbehler, D. P., Achter, E. K., Hobbs, J. R., and Fine, D. H., "Vapor Pressure of Explosives," *Journal of Energetic Materials*, Vol. 4, 1986, pp. 447–472.
- [4] Lawrence, A. H., "Detection of Drug Residue on the Hands of Subjects by Surface Sampling and Ion Mobility Spectrometry," *Forensic Science International*, Vol. 34, 1987, pp. 73–83.
- [5] Nanji, A. A., Lawrence, A. H., and Mikhael, N. Z., "Use of Skin Sampling and Ion Mobility Spectrometry as a Preliminary Screening Method for Drug Detection in an Emergency Room," *Clinical Toxicology*, Vol. 25, 1987, pp. 501–515.
- [6] Fetterolf, D. D., Donnelly, B., and Lasswell, L., "Detection of Heroin and Cocaine Residue by Ion Mobility Spectrometry," presented at the International Symposium on the Forensic Aspects of Trace Evidence, Quantico, Virginia, June 24–28, 1991.
- [7] "Cocaine Smuggled as Ingredient in Plastic," *Chemical and Engineering News*, July 8, 1991.
- [8] Chauhan, M., Harnois, J., Kovar, J., and Pilon, P., "Trace Analysis of Cocaine and Heroin in Different Customs Scenarios Using a Custom-Built Ion Mobility Spectrometer," *Canadian Society of Forensic Science Journal*, Vol. 24, 1991, pp. 43–49.
- [9] Karpas, Z., "Forensic Applications of Ion Mobility Spectrometry," *Forensic Science Review*, Vol. 1, 1989, pp. 104–119.
- [10] McDaniel, E. W., *Collision Phenomena in Ionization Gases*, John Wiley, New York 1964, p. 426.
- [11] Twibell, J. D., Home, J. M., Smalldon, K. W., and Higgs, D. G., "Transfer of Nitroglycerine to Hands During Contact with Commercial Explosives," *Journal of Forensic Sciences*, Vol. 27, No. 4, Oct. 1982, pp. 783–791.
- [12] Lloyd, J. F. B. and King, R. M., "Detection and Persistence of Military Explosives on the Hands," *Journal of Forensic Sciences*, Vol. 29, No. 1, Jan. 1984, pp. 284–290.
- [13] Lloyd, J. F. B. and King, R. M., "Detection and Persistence of Semtex and Some other Explosives on Skin Surfaces," presented at the 3rd International Symposium on Analysis and Detection of Explosives, Mannheim-Neustheim, Federal Republic of Germany, July 1989.
- [14] Lloyd, J. B. F., "Glycerol Dinitrates in the Detection of Skin-Contact with Explosives and Related Materials of Forensic Science Interest," *Journal of Forensic Science Society*, Vol. 26, 1986, pp. 341–348.

- [15] Yelverton, B. J., "Analysis of RDX Vapors on Pre- and Postdetonations Using the Ion Mobility Spectrometer Under Field Conditions," *Journal of Energetic Materials*, Vol. 6, 1988, pp. 73-79.

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