

## TECHNICAL NOTE

Jimmie C. Oxley,<sup>1</sup> Ph.D.; James L. Smith,<sup>1</sup> Ph.D.; Louis J. Kirschenbaum,<sup>1</sup> Ph.D.; Suvarna Marimganti,<sup>1</sup> Ph.D.; and Sravanthi Vadlamannati,<sup>1</sup> B.Sc.

# Detection of Explosives in Hair Using Ion Mobility Spectrometry

**ABSTRACT:** Conventional explosives 2,4,6-trinitrotoluene (TNT), nitroglycerin (NG), and ethylene glycol dinitrate (EGDN) sorbed to hair can be directly detected by an ion mobility spectrometer (IMS) in E-mode (for explosives). Terrorist explosive, triacetone triperoxide (TATP), difficult to detect by IMS in E-mode, was detected in N-mode (for narcotics). Three modes of sample introduction to IMS vapor desorption unit were used: (i) placement of hair directly into the unit, (ii) swabbing of hair and placement of swabs (i.e., paper GE-IMS sample traps) into the unit, and (iii) acetonitrile extracts of hair positioned on sample traps and placed into the unit. TNT, NG, and EGDN were detected in E-mode by all three sample introduction methods. 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 (3.9 µg compared with 0.3 µg). IMS in N-mode detected TATP from hair by all three modes of sample introduction.

**KEYWORDS:** forensic science, ion mobility spectrometer, 2,4,6-trinitrotoluene, nitroglycerine, ethylene glycol dinitrate, triacetone triperoxide, hair, explosive sorption, explosive vapor

Hair analysis has proven to be a relatively noninvasive method for the detection of illicit drug use (1,2). Hair analysis for explosives was pioneered by Wardleworth and Ancient of the Royal Armament Research and Development Establishment in the early 1980s. They examined sorption of ethylene glycol dinitrate (EGDN) and nitroglycerine (NG) to hair (3). Subsequently, our laboratory has developed methods to detect explosives in hair using gas chromatography with electron capture detection (GC/ECD) (4,5). While our methods, using GC/ECD, are quantitative and extremely sensitive, they are relatively time and labor intensive. Hair samples require extraction with solvent (usually hours) and the actual chromatography requires about 30 min per sample. Rapid detection in the field is critical to prevention of terrorist initiatives. A possible field-useable instrument capable of rapid detection (<10 sec) is the ion mobility spectrometer (IMS). The IMS was developed in the early 1970s under the name plasma chromatography and has evolved into an important analytical tool for the detection of explosives, environmental pollutants, and drugs (6,7). Although the IMS has been used for nearly 35 years, relatively few applications have involved analysis of human hair (8). This work reports IMS detection of four explosives from contaminated hair with particular emphasis on triacetone triperoxide (TATP): a peroxide-based explosive used extensively by Middle Eastern terrorists.

Most IMS instruments are limited by sample introduction techniques. Usually, items are swabbed with cloth or paper, and the swab is placed in a heated inlet where air flow and heat drive the constituent vapors or particles into the instrument. Once they enter the instrument, they are ionized by bombardment with beta particles from a nickel 63 source. The ions are allowed to combine with what is referred to as "chemical dopant," usually a halogenated compound such as methylene chloride. These complexes have unique mobilities, which correlate with specific explosives. IMS instruments are

the most frequently used chemical detectors found in airports, government buildings, and border crossings. The primary advantages of IMS include very short analysis time (average response time of 4–10 sec) and detection limits in the nanogram to picogram range; They are robust with a ruggedness of design well suited for field and remote applications. Driven by airport security issues, a number of vendors sell IMS instruments designed to detect all the common military explosives and some peroxide explosives as well.

## Experimental

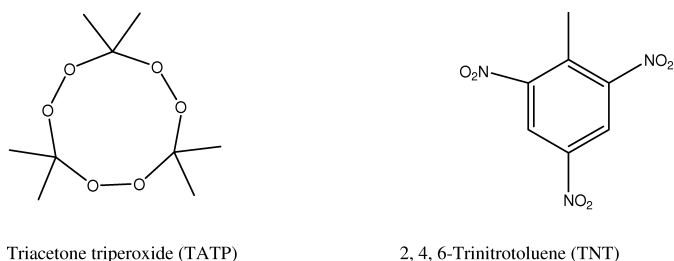
The explosive 2,4,6-trinitrotoluene (TNT) was obtained from military sources. Nitroglycerin (NG) was purchased from Copperhead Chemical Company Inc. (Tamaqua, PA). Both ethylene glycol dinitrate (EGDN) and triacetone triperoxide (TATP) were synthesized in this laboratory (9). Solvents used were spectral grade. The chemical structures are shown in Fig. 1. The IMS was a GE Ion Track (Wilmington, MA) ITEMIZER, generously loaned to us by GE Ion Track. GE E-mode calibration traps were used to calibrate the instrument for TNT.

Hairs of various colors (black, brown, and blond) were obtained from individuals. Most studies used black hair from an Asian female because previous studies showed it to readily sorb explosives (10). Prior to use, hair was washed with 2% sodium laurel sulfate, rinsed with distilled water, and dried on a paper towel at room temperature. Amber-colored jars (10.5 cm diameter × 8.5 cm high) were also carefully cleaned and dried. Approximately 0.5 g of a specific explosive (TNT, NG, TATP, EGDN) was placed into the bottom of a jar. The cut hair samples (~0.5 inch lengths) were placed in aluminum weighing boats, which were stacked three high inside the jar. Care was taken not to let the boats touch the sides of the jar or the explosive.

The IMS instrument was set in the explosives mode (E-mode) for most of the experiments. A dopant of methylene chloride was used to produce negatively charged adduct ions, and the IMS was

<sup>1</sup>Chemistry Department, University of Rhode Island, Kingston, RI 02881.

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Triacetone triperoxide (TATP)

2, 4, 6-Trinitrotoluene (TNT)



Nitroglycerine (NG)

Ethylene glycol dintrate (EGDN)

FIG. 1—Chemical structures of the various explosives.

calibrated daily against TNT using the GE E-mode calibration traps. For TATP, the IMS instrument was also run in narcotics mode (N-mode). In this case, the methylene chloride dopant was replaced with an ammonia dopant and instrument calibration was against GE N-mode calibration traps that contained cocaine. Hair strands, exposed to the explosive vapor, were divided into three portions to allow analysis of hair by three protocols (1). A portion of hair was directly placed in the desorber unit of the IMS (2). A portion of hair was swabbed with a GE E-mode sample trap, and the trap was placed in the vapor desorption unit (3). A portion of the hair was placed in a 16-mL amber vial containing 5 mL of acetonitrile, sonicated for 20 min, and shaken for 2 h (280 shakes per minute). A small portion (100  $\mu$ L) of the acetonitrile extract was added to an E-mode sample trap, dried for 1 min, and placed in the IMS desorber for direct detection. For TATP, GE N-mode sample traps were also used for the IMS in N-mode experiments. The position of the N-mode IMS peak associated with TATP was identified from TATP/acetonitrile standard solutions (peak position about 4.5 msec).

The explosives studied were in the IMS library and detections were recorded as plasmagrams. The IMS was run without sample, with blank hair, and with blank E-mode sample traps, to check for undesirable contaminants. The acetonitrile extracts of TATP, TNT, and NG, taken from the third portion of hair, were transferred to 2-mL wide-mouth gas chromatograph (GC) autosampler vials for GC/ECD analysis (Agilent 6890N GC [Agilent Technologies, Inc., Santa Clara, CA] with micro-electron capture detector [ $\mu$ -ECD] and a DB-5MS [25 m  $\times$  0.25 mm] capillary column [J&W Scientific and Agilent Technologies, Inc.]). Details of the GC/ECD method are given in Ref. (10). Extracts of EGDN were identified with an HP 1100 series liquid chromatography with photo-diode array detector set at 214-nm wavelength. To find IMS minimum detectable amounts of explosives, different volumes ( $\mu$ L) of explosive standards (usually 100 ppm) were introduced onto clean E-mode sample traps. After solvent evaporation (60 sec), the traps were placed in the instrument's vapor de-sorption unit.

## Results and Discussion

The IMS in E-mode easily detected TNT, NG, and EGDN on all colors of hair using all three sampling techniques (direct hair

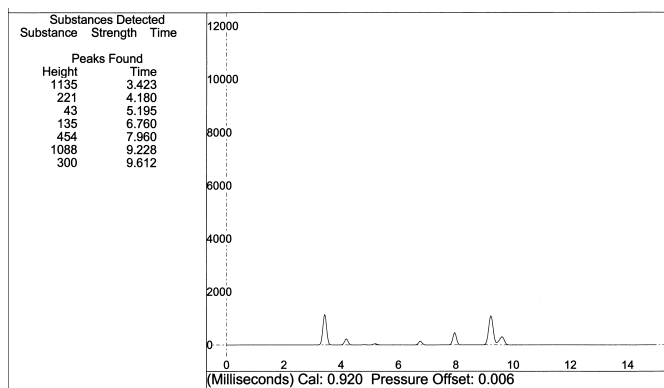


FIG. 2—A plasmagram (E-mode) of a swab from unexposed Asian hair.

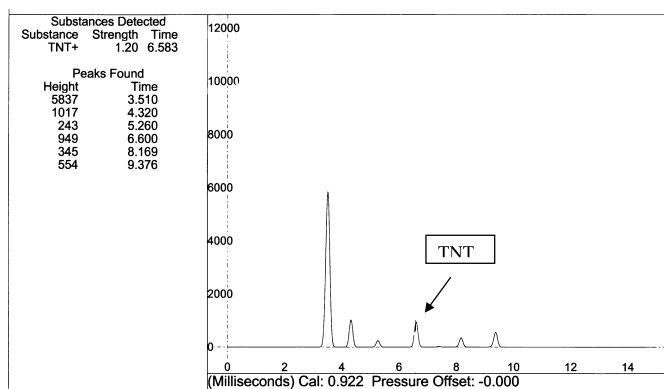


FIG. 3—A plasmagram (E-mode) of a swab from Asian hair exposed to TNT vapor for 2 days.

input, swabs from hair, acetonitrile extracts of hair). Figure 2 shows the E-mode plasmagram of swabbings from unexposed black Asian hair (a blank); no prominent peak, associated with the explosives, was observed. A swabbing of the same black Asian hair ( $\sim$ 0.05 g) following 2 days of exposure to TNT vapor (about 0.02  $\mu$ g TNT sorbed to hair) yielded an IMS plasmagram with a prominent TNT peak (see Fig. 3). Likewise, hair exposed to NG or EGDN for 2 days revealed their characteristic peaks by IMS (set to E-mode) using all three sampling techniques (Figs. 4 and 5).

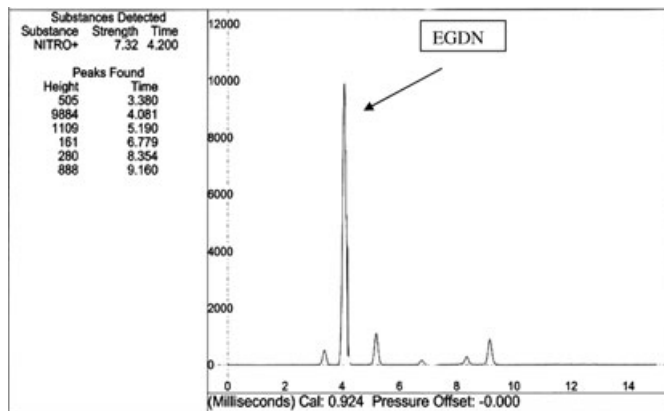


FIG. 4—A plasmagram (E-mode) of a swab from Asian hair exposed to EGDN vapor for 2 days.

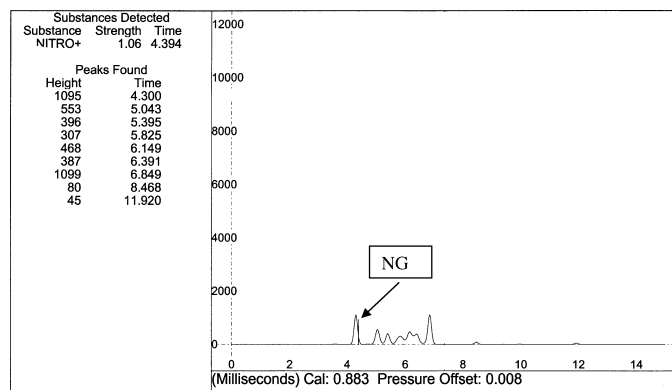


FIG. 5—A plasmagram (E-mode) of a swab from Asian hair exposed to NG vapor for 2 days.

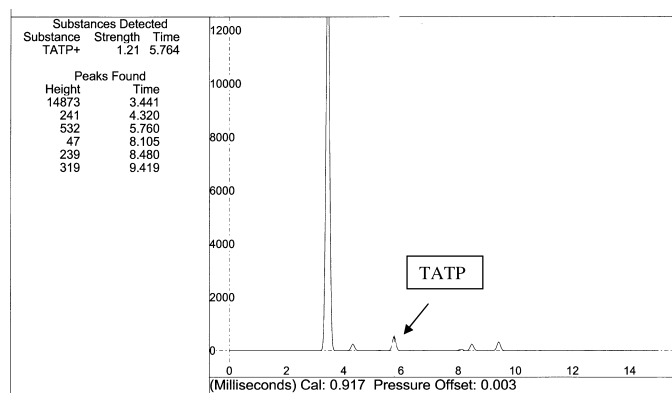


FIG. 6—A plasmagram (E-mode) of 50 µL of 100 ppm TATP (3.9 µg) in acetonitrile on an E-mode sample trap. The pronounced first peak is due to acetonitrile solvent.

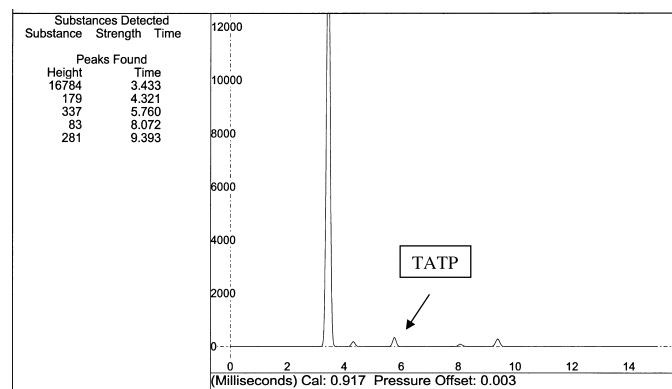


FIG. 7—A plasmagram (E-mode) of 25 µL of 100 ppm TATP (1.9 µg) in acetonitrile on an E-mode sample trap.

The IMS in E-mode did not detect TATP on the Asian hair after 2 days of exposure with any of the three sampling techniques. The minimum amount of TATP detected by our commercial IMS (in E-mode) was between 1.9 and 3.9 µg (Figs. 6 and 7).

The nitro-containing explosives (TNT, EGDN, and NG) were readily detected directly from hair (Table 1) with the IMS in E-mode. However, TATP was not easily detected. Both TATP and EGDN have relatively high vapor pressures at room temperature

TABLE 1—The IMS (E-mode) success rate of sampling techniques on Asian hair exposed for 2 days to explosive vapor.

Explosive	Swab	Hair	Acetonitrile extract
TNT	+	+	+
TATP	—	—	*
EGDN	+	+	+
NG	+	+	+

\*Hair was exposed to TATP for 16 days to achieve positive alarm.

TABLE 2—The minimum amounts of TATP and EGDN explosive necessary for IMS alarm (E-mode).

TATP (µg)	Alarm	EGDN (µg)	Alarm
39	+	7.5	+
31	+	1.5	+
23	+	0.30	+
16	+	0.01	—
7.8	+	0.06	—
3.9	+	0.15	—
1.9	—	0.30	—
3.9	+	1.5	+
1.9	—	0.30	+
		0.60	+
		0.30	+
		0.15	—
		0.30	+
		0.15	—
1.9–3.9		0.15–0.30	Detection limits

Multiple entries (i.e., 0.3 and 3.9 µg) refer to replicate runs.

(0.05–0.07 torr) (5). Although high vapor pressures imply the potential for high vapor densities of the explosives surrounding the hair, it also contributes to a driving force favoring desorption of these explosives from the hair surface. The ability to detect EGDN from the hair surface is mainly because of its greater sensitivity to IMS detection. As shown in Table 2, TATP detection requires about 10 times as much sample as EGDN (3.9 µg vs. 0.3 µg). When hair was exposed to TATP vapors for 16 days, TATP content was estimated to exceed 2000 µg/g hair (5). Hair portions averaged about ~0.05 g which meant that the hair available for IMS analysis contained at least 100 µg of TATP. The TATP was detected in acetonitrile extracts of the ~0.05 g hair specimens. However, swabs from hair and actual hair specimens did not appear to introduce sufficient amounts of TATP into the IMS instrument for detection via E-mode.

Marr and Groves (11) had demonstrated that TATP was detected by an IMS as positive ion adducts (N-mode detection). The IMS was set to N-mode for TATP analysis and, as before for E-mode analysis, blanks were run frequently to check for contamination. When hair was exposed to TATP vapor for 72 h, all three sampling techniques mentioned above produced plasmagrams with the characteristic TATP peak (see Fig. 8).

In conclusion, this study has shown that hair is a viable surface from which explosives may be easily detected using a standard screening instrument, IMS. Analytical protocols for trace detection of explosives from hair can be quite simple. Common military explosives were readily detected by direct insertion of hair, swabbing of hair, or extraction of hair. The peroxide explosive, TATP, required much higher amounts (1.9–3.9 µg) on the hair (~0.05 g) before it was detected by the IMS in E-mode, but was detectable at much lower amounts (<0.8 µg sorbed to ~0.05 g hair) in N-mode. Based on the previous work (5), the total accumulation of

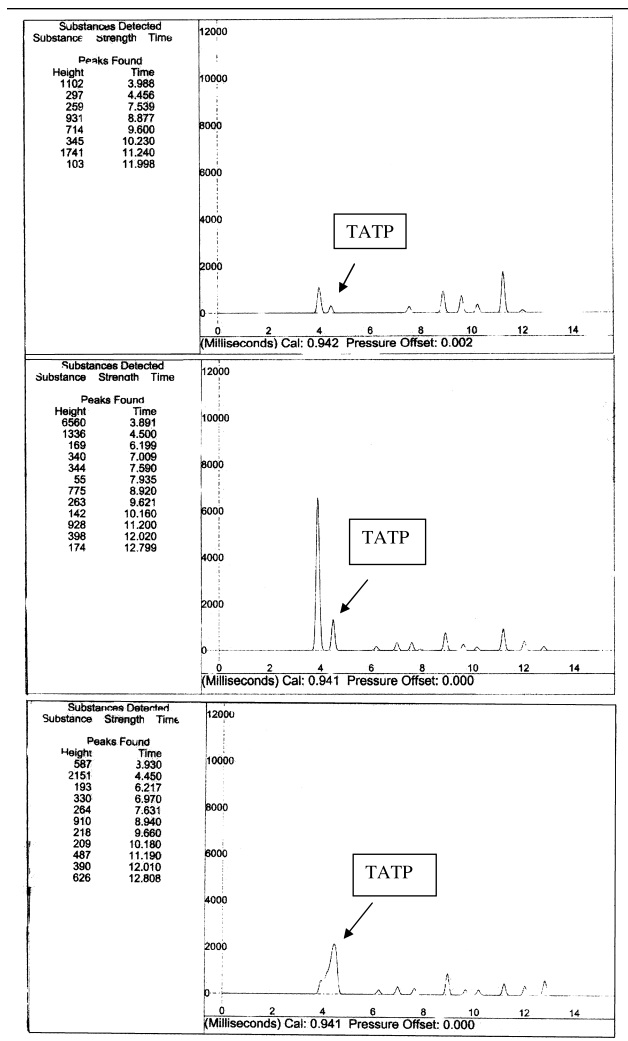


FIG. 8—Plasmagrams (N-mode) from Asian hair exposed to TATP vapor for 3 days. (A) Hair (~0.05 g) placed directly in the vapor desorption unit of the IMS. (B) A swab from the TATP contaminated hair (mg) placed directly in the vapor desorption unit of the IMS. (C) Acetonitrile extract (100 µL) of a portion of TATP contaminated hair (~0.05 g) placed on N-mode sample trap and inserted into vapor desorption unit of IMS.

explosive in ~0.05 g of Asian hair exposed to TNT vapor for 48 h was *c.* 0.35 µg. The direct swabbing of these samples accumulates

only a relatively small amount of the TNT deposited on the hair fibers. A target subject would provide a substantially greater surface area of hair from which much more explosive could be accumulated onto a swab.

[A]

#### Acknowledgments

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Additional information and reprint requests:  
 Jimmie C. Oxley, Ph.D.  
 Chemistry Department  
 University of Rhode Island  
 Kingston, RI 02881  
 E-mail: joxley@chm.uri.edu