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Improved Method for the Detection of TATP After Explosion*

ABSTRACT: TATP in post explosion exhibits was reported earlier to be best recovered from vapor phase. A typical procedure includes its adsorption on Amberlite XAD-7, elution with acetonitrile and analysis by GC/MS. In this work, improved recovery of TATP from the vapor phase was achieved by SPME using PDMS/DVB fiber and immediate sampling to GC/MS. The recovery of TATP by SPME was compared with headspace and with adsorption on Amberlite XAD-7 by spiking onto filter paper put in a 100 mL beaker. The limit of detection of TATP was 6.4 ng in these conditions, few orders magnitude more than in the other tested methods. Recovery of TATP in the presence of various solvents was also studied. Acetone, water, and mixtures of water:alcohols (1:1) were found to reduce the recovery of TATP. Using SPME, TATP has been identified in dozens of post-explosion cases.

KEYWORDS: forensic science, post-explosion analysis, triacetone triperoxide, solid-phase microextraction, gas chromatography-mass spectrometry, headspace, adsorption

3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxocyclononane (triacetonetriperoxide, TATP) is a powerful explosive, extremely sensitive to flame, heat, impact and friction (1). Since its first preparation in 1895 (2), it has never been used as a military or commercial explosive due to its sensitivity. The simplicity of its synthesis from easily available raw materials often made TATP an explosive of choice for terrorists and youngsters in prank activity. Its first reported use in terrorist activity was in Israel in 1980, where a pipe bomb was found (3). TATP has been reported in other countries by law enforcement agencies (4–6). It was also reported to be the cause of an accidental explosion in an industrial plant (7). In some major explosions perpetrated by terrorists in 1996 in Israel, no explosive had been identified. Later on it was found from other sources that TATP was used in some of these devices. As a result, we concluded that TATP “disappeared” during the routine analytical procedure used in our laboratory (extraction of the exhibits in hot acetone and then evaporation of the solvent). In order to avoid sublimation of TATP during the process, direct headspace of the exhibits was sampled prior to any extraction procedure. Headspace is a widely used method for the analysis of volatile explosives (8). It is also used for the analysis of fire accelerants (9) and flavors (10). Using this procedure, TATP was successfully recovered and identified in some post-explosion cases.

In order to improve the recovery of TATP from the vapor phase, adsorption of volatile explosives on various solid resins were performed using the following resins: activated charcoal, Tenax, RDX[®], Amberlite XAD-2, XAD-4 and XAD-7 (11). In addition, solid phase microextraction (SPME) was tested using polyacrylate (PA) fiber. The best recovery was achieved using Amberlite XAD-7. This resin was reported to adsorb successfully other

volatile explosives such as ethylene glycol dinitrate (EGDN), glycerine trinitrate (NG), dinitrotoluene (2,4-DNT) and trinitrotoluene (2,4,6-TNT) (12).

SPME was reported to be successfully used in the analysis of some standard explosives (13), drugs (14), fire accelerants (15) and environmental pollutants (16,17). In this work, we studied the recovery of TATP by SPME using polydimethylsiloxane and polydimethylsiloxane/divinylbenzene fibers (PDMS and PDMS/DVB). Recovery of TATP by SPME was carried out on two GC/MS instruments operated in our laboratory in order to compare limits of detection in both instruments. In addition, comparison of the recovery of TATP from the vapor phase by three methods (headspace, adsorption on Amberlite XAD-7 resin and SPME) was carried out.

Solvents present in post-explosion scenes (e.g., water) or used as wetting agents for swabs (e.g., acetone, alcohol), may interfere with the analysis of TATP using SPME. Therefore, recoveries of TATP by SPME were tested in the presence of various solvents such as acetone and water/alcohol (methanol and ethanol) mixtures.

Methods

Materials

TATP was prepared according to the procedure described previously (1). Amberlite XAD-7, SPME holder and PDMS and PDMS/DVB fibers were purchased from Sigma-Aldrich Supelco, Bellefonte, PA. Acetonitrile CHROMASOLV[®] was purchased from Riedel-de Haen company (Germany). Acetone, methanol, ethanol, ethyl acetate and chloroform AR were purchased from Frutarom and BioLab, Israel. Round filter paper n° 3, 42.5 mm diameter was obtained from Whatman. Bags (Polyamide 66) were obtained from M&Q Packaging Ltd., Ireland. For headspace samples, disposable plastic syringes were used to prevent sample contamination. The syringes from Becton Dickinson, Spain, were assembled with needles from Alltech. After each injection the needles were rinsed with chloroform or ethyl acetate and dried overnight in an oven at 130°C.

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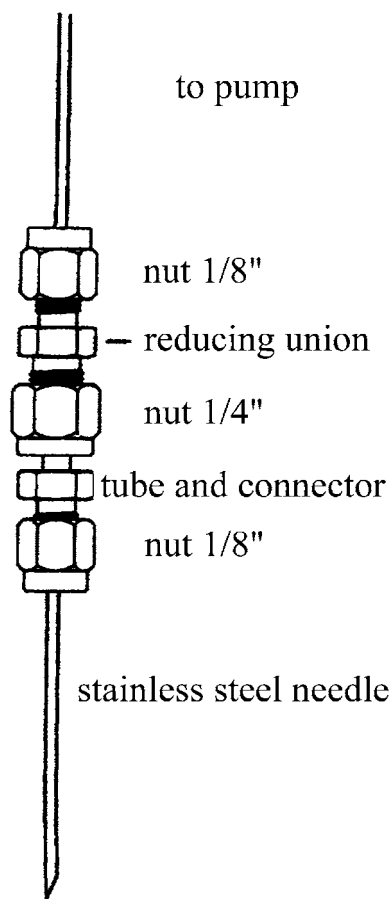


FIG. 1—Device for the adsorption of vapor onto a resin.

Procedures and Sample Preparations

Experiments were done in triplicate. A known amount of TATP dissolved in chloroform was spiked on a round filter paper placed in an empty 100 mL beaker. The beaker was tightly enclosed using a nylon bag. The bag was placed in an oven for 10 min (130°C for headspace and SPME experiments, 80°C for adsorptions on XAD-7) and then sampled as described below:

Headspace—The beaker was removed from the oven and 400 μ L of vapor were directly injected into the GC/MS.

Adsorption on Amberlite XAD-7—The XAD-7 resin (ca. 30 mg) was put in a 2.5 cm glass tube (1.6 mm i.d.; 3 mm o.d) and plugged at the two ends by glass wool. The glass tube was then inserted into a stainless steel tube connected through a pipe to water vacuum. The adsorption was carried out by putting the bag with the beaker in an oven (80°C) while gently pumping the air (4 mL/min) from the bag for 10 min through the glass tube as shown in Fig. 1. The amberlite XAD-7 was removed from the tube and put into a conical vial. Fifty μ L acetonitrile was added to the resin (the minimum amount necessary to cover the resin). Three μ L of the solvent was injected into the GC/MS.

SPME—The beaker was removed from the oven and the fiber was immediately exposed to the vapor phase for 10 min. Desorption from the fiber into the injector of the GC/MS was carried out for 2 min.

SPME of Real Case Exhibits—The exhibit was enclosed in a suitable size nylon bag. The bag was placed in an oven at 80°C for

ten min. The bag was removed from the oven and the SPME fiber was exposed to the vapor phase for ten min. Desorption from the fiber into the injector of the GC/MS was carried out for 2 min.

Solvents Effect—i. TATP (1 μ g) dissolved in 10 μ L chloroform was put on round filter paper and left for 5 min to dry. ii. Recovery of TATP was carried out using SPME adsorption as described above and analyzed by GC/MS. The peak area measured was determined as 100% recovery. iii. Step i. was repeated and followed by adding 0.5 mL of various solvents. SPME adsorption was then carried out. The yield was determined as percentage of the peak area from that measured in step ii. The solvents tested were: acetone, water, water/methanol (1:1), water/ethanol (1:1).

Equipment

A Varian Star 3400CX gas chromatograph coupled with a Varian Saturn 2000 Ion Trap Detector (ITD). The GC column was an Alltech fused silica capillary column 30 m \times 0.25 mm (i.d.) coated with BP-1 (0.25 μ m film). Injector temperature was 250°C. Column temperature was held at 50°C for 3 min, then heated to 230°C at a rate of 5°C/min and held for 5 min at 230°C. Transfer line was held at 170°C. Ion trap temperature was 120°C. Scan range was 20–250 daltons. Scan rate was 3.4 scans/sec. Ionization times were set using automatic gain control. The carrier gas was helium. Injections were carried out in splitless mode.

An Agilent 6890 PLUS gas chromatograph, coupled with an Agilent MSD 5973N. The GC column was a J&W fused silica capillary column, 15 m \times 0.25 mm (i.d.) coated with DB-5MS (0.25 μ m film). Injector temperature was 180°C. Column temperature was programmed from 60°C to 280°C at a rate of 25°C/min. Transfer line was held at 180°C. Ion source temperature was 230°C and quadrupole temperature was 150°C. Scan range was 40–500 daltons. Scan rate was 3.11 scans/sec. Electron energy was 70 eV, the carrier gas was helium. Injections were carried out in splitless mode.

Results and Discussion

The limit of detection (LOD) of TATP dissolved in chloroform by direct injection was 1.6 ng using Saturn ITD and 10 ng by Agilent MSD 5973N. The recovery by SPME was tested using two fibers: 100 μ m PDMS and 60 μ m PDMS/DVB coated fibers. The latter was found to be 3.5 times more efficient than the PDMS fiber. Thus, further experiments were carried out using the PDMS/DVB fiber.

The limit of detection of TATP vapors in the Saturn ITD using headspace, adsorption on Amberlite XAD-7 and SPME were:

- 10,000 ng (10 μ g)/100 mL by headspace
- 320 ng/100 mL by adsorption on the amberlite XAD-7
- 6.4 ng/100mL by SPME

The results show that from the three tested methods, SPME using PDMS/DVB fiber, is the method of choice for the recovery of TATP. It is about 1500 times more efficient than headspace and 50 times more efficient than the adsorption on amberlite XAD-7.

A curve describing the recovery of TATP by SPME using PDMS/DVB in the Saturn Ion Trap is shown in Fig. 2.

It is shown that the recovery of TATP is linear in the range between 6.4–200 ng/100 mL. Above 200 ng, recovery of TATP reached a “plateau” which could be possibly explained by the saturation of the SPME fiber. The recovery of TATP using SPME was evaluated by comparison to calibration curve of TATP obtained by

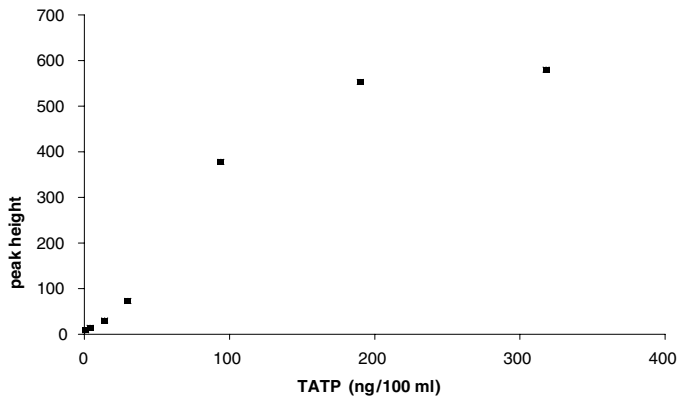


FIG. 2—Recovery of TATP by SPME using PDMS/DVB.

direct injections to the GC/MS. The recovery of TATP using SPME, was 22% in the linear range (6.4–200 ng).

A mass spectrum of an authentic sample of TATP obtained using the Agilent MSD is shown in Fig. 3.

The molecular ion of TATP (m/z 222) appears with very low relative abundance (RA < 1%). When amounts of TATP were close to the limit of detection, the molecular ion was not seen.

Figure 4 shows a gas chromatogram (A) and a mass spectrum (B) of TATP in a real case. The data were obtained with SPME adsorption using the PDMS/DVB fiber.

Solvent Effects

Large exhibits from an explosion scene, which cannot be taken to the laboratory, are swabbed using cotton wetted with acetone or water. These swabs are sent to the laboratory for analysis. During the SPME analysis of acetone wetted swabs, we sometimes failed to recover any explosive, although later on, explosives (e.g., TNT)

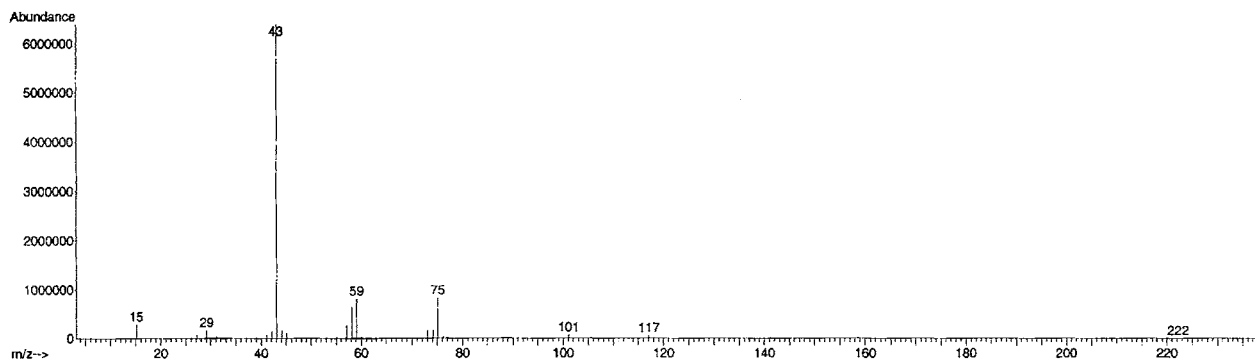


FIG. 3—Mass spectrum of an authentic sample of TATP.

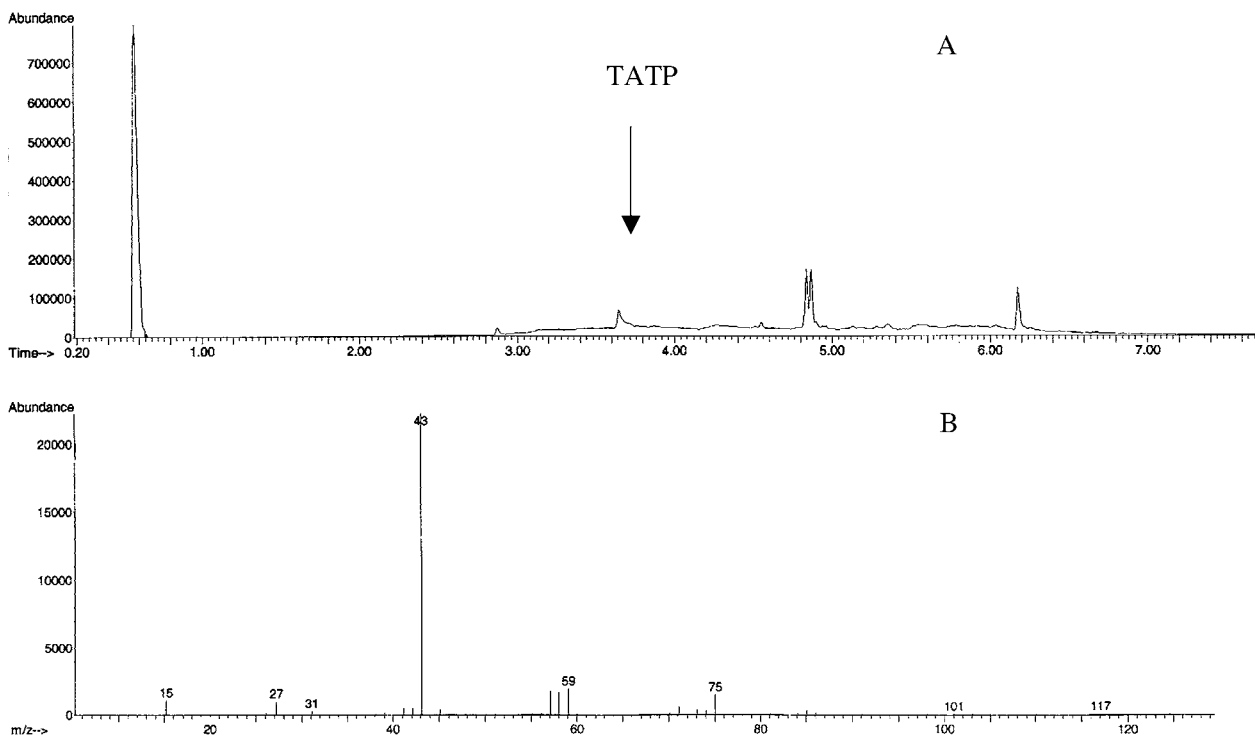


FIG. 4—A total ion current (TIC) (A) and the mass spectrum (B) of TATP identified by SPME using PDMS/DVB in a real case.

TABLE 1—Recovery of TATP from vapor phase using SPME in the presence of various solvents.

Solvent	Recovery (%)
Water	14
Acetone	6
Water:methanol (1:1)	6
Water:ethanol (1:1)	6
Methanol	3
Ethanol	1

were identified by GC/MS in the acetone extract. It was suspected that the fiber was saturated by the acetone present in the vapor phase of the cotton swab. Therefore, we studied the recovery of TATP by SPME, in the presence of various solvents which may be present in the exhibits: water (which is used to extinguish fire after explosion), acetone which is used as wetting solvent for swabbing exhibits and suspects' hands. In addition, mixtures of water and alcohol, which recently was reported to be suitable for the recovery of organic and inorganic explosives [18], were tested.

The results in Table 1 show that all solvents tested in this experiment significantly reduce the recovery of TATP by SPME. The recovery of TATP in the presence of acetone, alcohols and mixture of alcohol and water was lower than 10%. Water was the least interfering solvent (14% recovery). However, water is not a suitable solvent for organic explosives. Dry swabbing might be the best option. However, it is necessary to investigate the recovery of TATP and other explosives on dry swabs.

Conclusion

SPME has been shown to be a suitable method for the detection of TATP from vapors of post-explosion exhibits. It has been found to be less efficient in the detection of TATP in vapors of wetted swabs. Further work should be carried out to find a suitable method for the detection of TATP in the presence of water and acetone vapors. Using SPME, we identified TATP in 54 exhibits of real post-explosion cases during the years 2002–2003.

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