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Surface-sampling and analysis of TATP by swabbing and gas chromatography/mass spectrometry

Francesco Saverio Romolo [a,b,*], Luigi Cassioli [c], Silvana Grossi [c], Giuseppe Cinelli [d], Mario Vincenzo Russo [d]

[a] *Dipartimento SAIMLAL, SAPIENZA Universita di Roma, Viale Regina Elena 336, 00161 Rome, Italy*
[b] *Institut de Police Scientifique, Université de Lausanne, Batiment Batochimie, 1015 Lausanne, Switzerland*
[c] *Italian Air Force, Flight Test Center, Armament Division, Aeroporto M. De Bernardi, Pratica di Mare, 00040 Pomezia, Rome, Italy*
[d] *Facoltà di Agraria (DISTAAM), Università del Molise, Via De Sanctis, 86100 Campobasso (CB), Italy*

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ABSTRACT

The method of sample recovery for trace detection and identification of explosives plays a critical role in several criminal investigations. After bombing, there can be difficulties in sending big objects to a laboratory for analysis. Traces can also be searched for on large surfaces, on hands of suspects or on surfaces where the explosive was placed during preparatory phases (e.g. places where an IED was assembled, vehicles used for transportation, etc.).

In this work, triacetone triperoxide (TATP) was synthesized from commercial precursors following reported methods. Several portions of about 6 mg of TATP were then spread on different surfaces (e.g. floors, tables, etc.) or used in handling tests. Three different swabbing systems were used: a commercial swab, pre-wetted with propan-2-ol (isopropanol) and water (7:3), dry paper swabs, and cotton swabs wetted with propan-2-ol. Paper and commercial swabs were also used to sample a metal plate, where a small charge of about 4 g of TATP was detonated. Swabs were sealed in small glass jars with screw caps and Parafilm® M and sent to the laboratory for analysis. Swabs were extracted and analysed several weeks later by gas chromatography/mass spectrometry. All the three systems gave positive results, but wetted swabs collected higher amounts of TATP. The developed procedure showed its suitability for use in real cases, allowing TATP detection in several simulations, including a situation in which people wash their hands after handling the explosive.

1. Introduction

Improvised explosives are nowadays considered a major threat by police forces and security administrations, because their use by terrorists and criminals has increased in the last decades. 3,3,6,6,9,9-Hexamethyl-1,2,4,5,7,8-hexaoxacyclononane, better known as triacetone triperoxide (TATP), is an improvised explosive which has been used in terrorist attacks in the last years. TATP is an organic peroxide, having the properties of a primary explosive, with a value of 250 cm^3/10 g obtained by the lead block test, to be compared with the value of 300 obtained by 2,4,6-trinitrotoluene (TNT). It is a very dangerous compound, due to its tendency to sublimation and its sensitivity to impact, friction and heating, especially if stored as a dry product [1,2]. TATP has never found practical application as a commercial or military explosive, but the instructions to synthesize it, the acid catalyser and the reactants needed for its preparation (acetone, hydrogen peroxide) are easily available. In 1983 Zitrin et al. reported an analytical procedure to identify TATP [3]. In 1986 Evans et al. published the first paper about forensic analysis of TATP in the Journal of Forensic Science [4], followed by White in 1992 [5].

Several methods can be used for trace analysis of TATP [6], including gas chromatography/mass spectrometry (GC/MS) [3–5,7–10] and high performance liquid chromatography/mass spectrometry (HPLC/MS) [11–15].

To sample traces from smooth surfaces, a piece of material can be soaked in a solvent and rubbed over the surface being examined. This procedure, called swabbing, is the method of choice for skin, work surfaces, floors and smooth fabrics such as leather or plastic. For porous surfaces such as clothes, the vacuum sampling might be more effective than swabbing. Several papers were published in the past about swabbing explosive traces [16–21], but in the opinion of the authors, the surface-sampling by swabbing of TATP traces was a field deserving more research. The present paper reports an evaluation of the applicability of different swabbing systems for trace detection of TATP using GC/MS. Two of the swabbing systems evaluated here were already studied for organic gunshot residue [22] and for other explosives [23].

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[*] Corresponding author at: Dipartimento SAIMLAL, SAPIENZA Universita di Roma, Viale Regina Elena 336, 00161 Rome, Italy.
E-mail addresses: FrancescoSaverio.Romolo@uniroma1.it, FrancescoSaverio.Romolo@unil.ch (F.S. Romolo).

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2. Materials and methods

2.1. Safety note

Organic peroxides, and particularly TATP, are extremely dangerous materials which may lead to severe explosions, even if not confined, under various stimuli like friction, impact, heating, electric discharge and direct sunlight exposure.

The synthesis and handling of these substances may only be carried out by authorised and highly qualified personnel, using appropriate safety measures (reinforced goggles and gloves, splinter-proof vessels, protective shield, etc.) and in small quantities. In Italy "It is forbidden to manufacture, to hold at home or elsewhere, to transport or to sell. . .explosives that has not been recognized and classified by the Minister of the Interior" [24], such as TATP.

The risk of treating these materials increases with mass. Therefore they should be handled in small quantities with all possible precautions. Contact of these materials with metals must also be avoided and static charges must be prevented by operating on antistatic mats with antistatic tools. For no reasons TATP should be kept into sealed containers. Possibly all the material prepared should be used as soon as possible. If necessary, small amounts of material can be stored under water at low temperature (5 °C) inside open splinter proof containers (plastic beakers), but it is important to know that even if the presence of water decreases the sensitivity to friction, this compound is still able to detonate under water. Where the compound is kept in solution to prevent detonation, evaporation of solvent must be avoided, as this can cause formation of highly sensitive crystals. Every effort must be made, during preparation of this substance, to keep the size of crystals as small as possible because crystals larger than few mm tend to detonate spontaneously due to internal tensions [25].

2.2. Chemicals and sampling materials

The 0.1 mg/mL standard solutions of TATP in acetonitrile (ACN) were purchased from AccuStandard (New Haven, CT, USA) and stored at 2 °C as all the solutions used in this work. Bulk samples of TATP were synthesized in the laboratories of the Technical Investigation Group of the Armament Division of the Flight Test Centre of the Italian Air Force.

Three different swabbing systems for surface sampling were tested. The first type of swab was Alco-Prep® kindly provided by H&W (Glabbeek, Belgium). These swabs contained a mixture called "isopropyl rubbing alcohol" made with Isopropyl Alcohol USP (United States Pharmacopeia) and Purified Water USP (7:3). Each swab was 2.5 cm × 6.0 cm and was sealed in a sachet made of printed aluminium foil laminated. The second type of swab was made of dry paper obtained by cutting rectangular portions of handkerchiefs Tempo® (Sca Hygiene Products, S.r.l. Lucca, Italy) which were of the same dimensions of the Alco-Prep® swabs. The third type of swab was prepared using cotton round pads DEMAK-UP from Fort James Italia (Genova, Italy) cut in four, wetted with isopropyl alcohol (propan-2-ol) RS for HPLC from Carlo Erba (Milano, Italy). Diethylether RPE, dichloromethane RPE, n-pentane RPE, and acetonitrile HPLC grade were also from Carlo Erba. Carbon disulphide RPE grade was from JT Backer (Deventer, Holland). The small glass jars were NEMI 15 mL, produced by Eurovetrocap (Milano, Italy). The flexible film used to seal the NEMI glass jars was the Parafilm® M from Pechiney Plastic Packaging Company (Menasha, WI, USA). Internal standard (IS) was 1-nitronaphthalene, 99% from Acros Organics (Geel, Belgium). The I.S. solution was prepared by dissolving 1-nitronaphthalene in acetonitrile. All other chemicals and organic solvents were of reagent grade. A mercury thermometer (range from −10 °C to +250 °C) was used for the synthesis.

2.3. Sampling procedures

The surfaces tested were a surface of ply wood, the upper surface of a laminated desk, a tile from an office floor, an external concrete floor, the steering wheel of a car, the hands of volunteers who handled TATP and a metal plate where a charge of TATP was detonated by means of an electrically activated hot wire. The amount of solid TATP in crystal form distributed on the surfaces to be tested was 6 mg. The charge detonated was made of 4.3 g TATP in crystal form.

Three sampling procedures were used, always using disposable gloves to touch the swabs. The sachet of the Alco-Prep® swab was torn just before using. The dry paper swabs were prepared in advance by cutting rectangular portions of Tempo® handkerchiefs. The swabs from cotton round pads were also prepared in advance by cutting the pad into four pieces to prepare four cotton swabs. Each swab was closed in a glass jar with a screw cap immediately after cutting and it was enclosed into the same glass jar immediately after sampling. The large neck of the NEMI glass jars 15 mL allowed easy handling of swabs with gloved hands. Swabs from cotton pads were dampened with 1.0 mL propan-2-ol and then shaken to remove the excess solvent. The swab was firmly rubbed numerous times over the entire surface to be sampled (e.g. for hands palm, fingers, thumb, back and wrist). One swab was used to sample each hand. After sampling, each swab was immediately enclosed into a small glass jar with a screw cap, sealed with Parafilm® M. Samples were sent to the laboratory for analysis, where they were stored at −20 °C before the extraction.

2.4. Extraction procedure

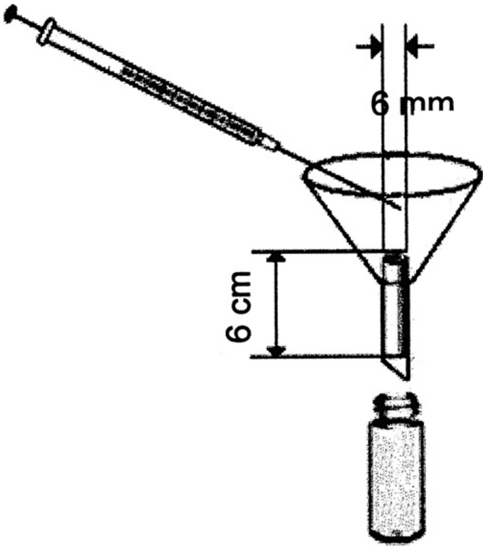

Fig. 1. Swabs rolled and inserted into the cylindrical lower part of a glass funnel to carry out extraction and recovery tests.

In the first set of extraction and recovery tests, 1000 ng of TATP were distributed on dry paper swabs having an area of 1 cm^2. The swabs were rolled and inserted in vials containing 0.5 mL of solvent. After shaking the vials, 1 μL of solution was analysed by GC/MS. In the following extraction and recovery tests, the swabs were rolled to make a small cylinder and inserted into the cylindrical lower part of a glass funnel, having an internal diameter of 6 mm, leaving about 1 cm of the rolled swab sticking out in the conical upper part of the funnel (see Fig. 1). Extraction of 1000 ng of TATP was performed by adding different solvents in one or more aliquots. The solvents tested were diethyl ether, carbon disulphide, n-pentane and dichloromethane.

2.5. GC/MS analysis

A Trace GC Ultra (Thermo Scientific, Austin, TX, USA) equipped with a Polaris Q ion trap mass spectrometer (Thermo Scientific, Austin, TX, USA) was used in electron impact (EI) ionization mode. The software was the Xcalibur™ ver. 1.4 SR1. The injector was a Programmed Temperature Vaporizer (PTV) and operated in splitless mode, opening after 1.5 min. A fused-silica capillary column with chemically bonded phase (SE 54, 5% phenyl–95% dimethylpolysiloxane) was prepared in the laboratory [26,27] with the following characteristics: 30 m × 250 μm i.d., *N* (theoretical plate number) 115,000 for *n*-dodecane at 90 °C; *K* (capacity factor) 6.7; d_f (film thickness) 0.25 μm; U_{opt} (optimum linear velocity of carrier gas, hydrogen) 38.5 cm/s, and *UTE*% (utilization of theoretical efficiency) 97%.

Conditions were as follows: injection volume, 1 μL; injection port temperature, 60 °C for 10 s; then programmed 800 °C/min to 130 °C, after 30 s programmed 130 °C/min to 300 °C, final time, 3 min; carrier gas, helium, 99.9995% purity; flow, 1 mL/min; column temperature, 40 °C for 1.5 min; then programmed 3 °C/min to 60 °C, after 1 min programmed 15 °C/min to 300 °C, final time, 3 min; transfer line temperature, 130 °C. The Damping Gas was helium 99.9995% purity; flow 0.3 mL/min; the source was set at 150 °C; the scan range of the mass spectrometer was between m/z 41 and 350.

3. Results and discussion

The synthesis made with 50 mL of acetone, 110 mL of hydrogen peroxide and 10 mL of sulphuric acid produced 9.6 g of material, which represents a yield of 49%. According to Matyas and Pachman [28], the prepared TATP contained a negligible amount of DADP. The TATP cost referred to reagents resulted to be 32.00 €/kg.

The obtained MS spectra of TATP contained a low abundant molecular ion at m/z 222 only when the most concentrated standard solution was analysed, as already referred by Tamiri [29]. The base peak was always at m/z 43.0 (C_2H_3O), followed in order of abundance by the peak at m/z 59.1 (C_3H_7O), and 75.1 ($C_3H_7O_2$), in agreement with Sigman et al. [10]. It was interesting to see in the analysis of samples from tests that the main peak of TATP was followed by a small peak (see Fig. 2) attributed to the conformer [30,31].

A method based on selected ion monitoring of the peak at m/z 43 of the TATP and of the ion 115 of the internal standard 1-