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Novel Optimization of HMTD Traces Detection by HS-SPME-GC/MS and HS-SPME-GC/µECD

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Abstract

HMTD is known for its decomposition at low temperatures. The use of common techniques such as GC/MS and GC/µECD for its detection in liquid solutions or solid traces requires the control of analytical conditions. The present work proposes two sensitive methods using GC/MS and GC/µECD where the injector temperature is set at 150°C to analyse successfully the concentrations of 0.1 ng (10-4 mg/mL) and 0.05 ng (0.5-10.4 mg/mL) of HMTD in acetone solutions. The analysis of solid traces of HMTD was performed with the same methods by adopting the headspace mode using the SPME fibre. The exposure the fibre in the headspace during 10 min at ambient temperature (22°C) and the desorption in the injector at 150°C, allow the detection of HMTD without degradation. In addition, to simulate crater sample, 3 mg of HMTD are mixed to 150 g of soil (0.002%). In this case, HMTD was also successfully detected by HS-SPME-GC/MS and HS-SPMEGC/µECD after 1 h exposure of the fibre at 22°C. These results demonstrate the performance of these optimized methods for trace analysis of HMTD.

Keywords: Forensic science; Explosive peroxide; Hexamethylenetriperoxidediamine; Post-blast; Vapour pressure; Headspace solid phase microextraction; Gas chromatography-mass spectrometry; Gas chromatography-electron capture detector

Introduction

The detection and identification of peroxide explosives has recently become very important for forensic purposes due to their increasing prevalence in terrorist Improvised Explosive Devices (IEDs) [1]. The most common home-made peroxide explosives is tri-acetone-tri-peroxide (TATP) and hexamethylenetriperoxidediamine (HMTD), due to their simple synthesis from available starting materials. The latter is classified as a primary explosive, but was soon superseded by more stable compounds such as tetryl. It has become a popular homemade explosive because it is relatively inexpensive, easy to synthesize and can be produced from common ingredients. It is readily manufactured by amateurs and used in unlawful circumstances. His main precursor, and also of two other explosives: HMX and RDX, is hexamethylenetetramine (HMTA) or hexamine (Figures 1 and 2) [2]. This substance is used as fuel and could be found in stores selling camping equipment.

Although no longer used in any official application, HMTD has been identified in several cases of terrorist activity as suicide bombings and terrorist attacks throughout the world [3]. It was cited for example by law enforcement in the 2000 millennium attack plots of Los Angeles International Airport, the 2005 London bombings, the planned explosive in the 2006 transatlantic aircraft plot and the 2016 New York and New Jersey bombings.

HMTD is known to be very unstable and especially sensitive to initiation by friction, impact and electrical discharge [4]. Due to his blast power and high brisance, it is effective as initiator for the detonation of other explosives. This compound is amine peroxide chemically reactive [5] that starts to decompose at ambient temperature and begins to break up at 40°C into volatile pungent compounds, including tri-methylamine [6].

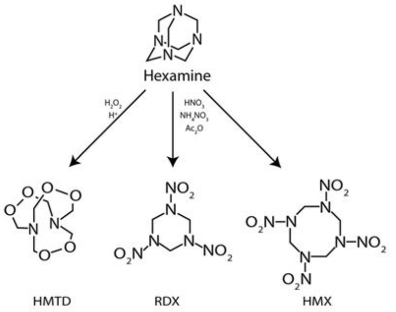

Figure 1: Scheme of obtaining the three explosives RDX, HMX and HMTD from Hexamine.

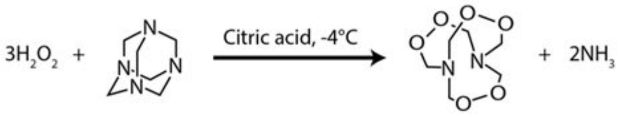

Figure 2: Chemical reaction for the HMTD synthesis.

On the analytical aspect, because of low volatility, HMTD detection is much harder compared to TATP solid explosives for example. With longer extractions and elevated temperatures, more volatile compounds were released into the headspace. Moreover, HMTD explosive has very low vapour pressure in the headspace and the pre-concentration was not a success using SPME. At least 16 hours was needed to accumulate two unidentified decomposition products over the headspace of 100 mg of solid HMTD at 40°C [7].

These properties explain the difficulty to detect this substance in post blast analysis by common techniques requiring heating such as gas chromatography coupled with mass spectrometry (GC/MS). GC/MS analysis of HMTD was first done in 1981, using quantities of explosive above trace amounts and using both chemical and electron ionization. More recently, a study of Peña-Quevedo et al. [8] states that the low vapour pressure of HMTD impedes a determination of its purity by GC methods, which are overcome using a direct insertion probe. The molecule showed a strong molecular ion at m/z 208 and compares well with literature results [9,10].

On the other hand, a method using liquid chromatography-atmospheric pressure chemical ionization-mass spectrometry (LC/APCI-MS) has been developed and validated for the identification of HMTD trace using three structurally-specific ions. Residues were extracted with de-ionized water (DI) and identified using a gradient mobile phase program and positive ion full scan mode on Ion trap mass spectrometer. In addition, an HPLC-APCI-MS(/MS) method for the trace analysis of HMTD and TATP in the same run, has been applied successfully for the identification of peroxides in the bulk solid state (powder sample), as well as in post-blast extracts originating from a forensic case [11].

In a previous work conducted after the terrorist acts of May 16th 2003 in Morocco (Casablanca), we proposed an easy headspace-GC/MS method to detect TATP traces in post-explosion debris [12]. In the present study, we determine the stables conditions for analyzing the second well-known peroxide explosive HMTD by solid phase micro-extraction SPME-GC/MS and gas chromatography-electron capture detector (GC/µECD). The chosen SPME method is fast, solvent free and avail the analyte equilibrium established among the matrix, the headspace above the sample, and the polymer-coated fused fibre. Then, the analyte is directly desorbed from the fibre to the chromatography column. So, it should be beneficial for peroxides trace analysis in post blast debris.

In order to conduct this work, we synthesized HMTD from its main precursor hexamine (camp stove fuel tablet) and confirmed the chemical structure by analyzing its solution in acetone with GC/MS and GC/µECD in dedicated chromatographic and spectrometric conditions. The detection of the limits about the two techniques was determined. The same run allows the simultaneous detection of other explosives TATP, Nitroglycerin NG, Trinitrotoluene TNT, Penthrite PETN and Cyclotrimethylenetrinitramine RDX.

These protocols make it possible to treat various situations, in particular after the discovery of the raw products or HMTD traces, and also in post-blast investigations. Indeed, this explosive can be analyzed in acetone extract after the collection of residues by cotton swabs (liquid GC/MS or GC/µECD) or even from debris taken directly from the post-blast crater (HS-SPME-GC/MS or GC/µECD).

Materials and Methods

The chemicals used for HMTD synthesis from hexamine tablets (camp stove fuel) are analytical grade purchased from VWR: hydrogen peroxide 30%, citric acid; and acetone for organic extraction. For SPME sampling, we used a Polydimethylsiloxane (PDMS-100 µm) fiber from Supelco. It was placed in headspace of 10 ml glass vial containing 0.2 mg of synthesized HMTD. The device is kept at a temperature of 22°C for 10 min. For post-blast tests, the fiber is placed in headspace of 720 ml sampling glass bottle containing 150 mg of soil doped with 3 mg of synthesized HMTD (0.002%) and stabilized for 2 h. The device is kept at 22°C for 1 hour. Thereafter, the desorption is made directly from the fiber to the chromatography column, in an injector (Splitless mode) at temperature of 150°C for 5 min with a constant flow (8 mL/min).

For GC/MS analysis, we used an Agilent GC 6890N, MS 5975B, equipped with a capillary column HP-5 (30 m × 0.25 mm × 0.32 µm) and helium gas carrier. The GC oven program is held at 80°C for 0 min, ramped at 16°C/min to 240°C (0 min). The temperatures adopted for transfer line, MS source and MS Quad, are respectively 170°C, 230°C and 150°C. The MS is operated in electron ionization mode (-70 eV) with a scan range of m/z 40-500. For the SIM mode, the selected ions are (42, 176, 208 uma). For GC/µECD analysis, we use an Agilent GC 6890N equipped with a capillary column Restek RTx® - TNT, (6 m × 0.53 mm × 1.5 µm) and helium gas carrier. The GC oven program is held at 80°C for 0 min, ramped at 10°C/min to 150°C (0 min) and 18°C/min to 250°C (5 min). The temperature detector is 230°C.

Results

In the present study, HMTD was prepared according to an established procedure from HMTA, 30% hydrogen peroxide and citric acid [13]. The product was obtained with 62% yield and to avoid HMTD decomposing, it was stored in a freezer at -16°C. So, the molecule was synthesized as follows: 0.93 g of HMTA (MW 140.19) was dissolved in 4.91 g of a 30% hydrogen peroxide solution. 1.31 g of citric acid was then added to the solution slowly over a total period of about 10 min. This solution was mechanically stirred for 3 hours in an ice-NaCl bath (-4°C), removed from this bath and allowed to warm to room temperature and precipitate for about 3 hours. Following filtration, the white crystals obtained were rinsed thoroughly with water and methanol. This preparation produced about 0.86 g of HMTD (MW 208.17) thus a yield of 62%.

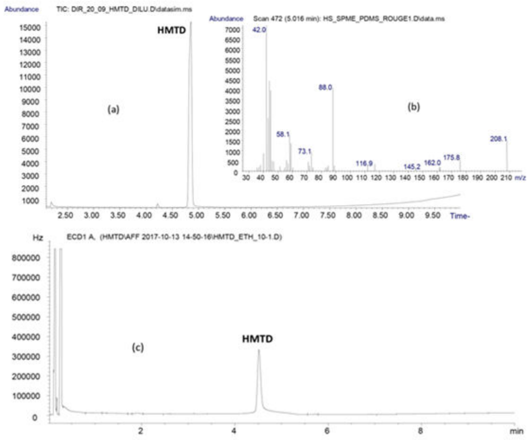

Figure 3: (a) GC/MS total ion chromatogram of HMTD traces in acetone (b) Mass spectra of HMTD (c) GC/µECD chromatogram of HMTD traces in acetone.

The GC/MS chromatogram obtained from injecting 1 µL of HMTD solution in acetone shows the HMTD peak at 5.016 min (Figure 3a) without any additional compound, as the low temperatures of injector (150°C) and transfer line (170°C) avoid the degradation of this peroxide. The mass spectrum is characterized by a molecular ion m/z [M] 208[$C_6H_{12}N_2O_6$]+, a base peak 42[C_2H_2N]+, and other fragments were seen at m/z 176[$C_5H_8N_2O_5$]+, 88[$C_3H_6O_2N$]+, 73[$C_2H_3NO_2$]+ and 45[CHNO]+, confirming the molecular structure of this explosive (Figure 3b). The GC/μECD chromatogram shows the HMTD peak at 4.51 min (Figure 3c).

At the conditions described above, limit of the detection of HMTD traces is evaluated at 0.1 ng for the GC/MS technique and 0.05 ng for the GC/μECD. With the same conditions, it was possible to detect a mixture of HMTD, TATP, nitroglycerin NG, trinitrotoluene TNT, penthrite PETN and cyclotrimethylenetrinitramine RDx (Figure 4).

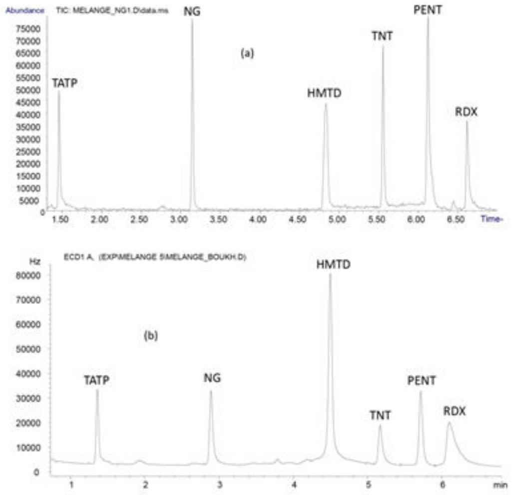

Figure 4: Chromatogram of explosives mixture in acetone obtained by (a) GC/MS (b) GC/μECD.

In forensic cases, the characterization of HMTD in post-explosion debris requires the use of suitable sampling and analysis procedures. The SPME fibers have several advantages compared to other pre-concentration techniques which include quantitative results from very low concentrations of analytes and almost no sample losses during extraction, concentration and desorption. So, we experiment this technique in our study, by determining through several tests under different conditions of temperature (5°C, 22°C, 30°C) and SPME fiber time exposure above the headspace sample (10 min, 30 min, 1 h, 2 h) in a glass vial (10 mL), the optimal situation allowing the adsorption of HMTD. The fibre coating selected (PDMS-100 μm) is commonly dedicated for adsorption of non-polar volatiles. A time exposure of the fiber in the headspace at 22°C for only 10 min load to detect HMTD by GC/MS (Figure 5a). The peak of HMTD is reconstituted in GC/MS with ions m/z 42, 176 and 208 (Figure 5b).

Finally, to simulate the conditions of post-blast crater sampling, we use a 720 mL conventional glass bottle containing 150 mg of soil doped with 3 mg of synthesized HMTD (0.002%). The mixture is left for 2 hours (delay of transportation to the lab) at ambient temperature (22°C) for stabilization. The best result is obtained with 1 hour exposure of the fibre in the headspace at 22°C. The detection of this explosive was validated by GC/MS (Figure 6a) and GC/μECD (Figure 6b). The GC/μECD offers better sensitivity since 30 min is sufficient to detect HMTD traces (0.05 ng).

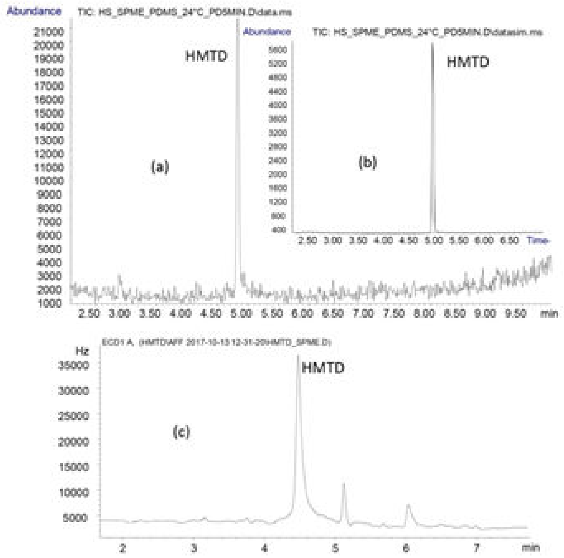

Figure 5: Chromatogram of HMTD traces obtained by (a) HS-SPME-GC/MS with SCAN mode, (b) with SIM mode, ions 42, 176 and 208 (c) HS-SPME-GC/μECD. Exposure time of the SPME-PDMS fiber at ambient temperature (22°C): 10 min, desorption time in injector: 5 min at 150°C.

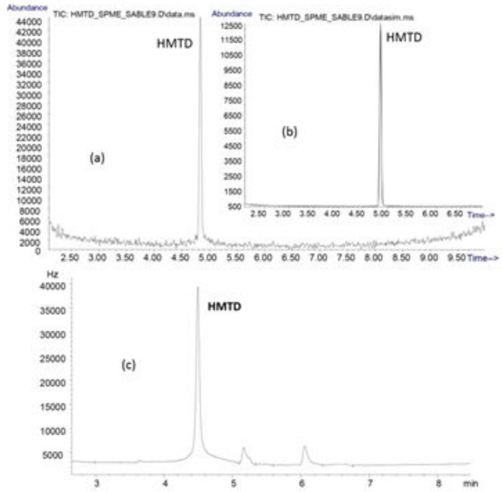

Figure 6: Analysis of HMTD traces in soil (3 mg /150 g) (a) HS-SPME-GC/MS chromatogram with SCAN mode (b) chromatogram with SIM mode (c) HS-SPME-GC/μECD chromatogram. Stabilization time of glass container (750 mL): 1 h, desorption time in injector: 5 min at 150°C.

These sampling conditions are sufficient as HMTD has very low vapor pressure, and working at more elevated temperature (40°C) is not successful and might accumulate decomposition products over the headspace. It is in concordance with a study about estimation of

HMTD vapor pressure using secondary electro-spray ionization mass spectrometry over the temperature range from 28°C to 80°C [14]. The value obtained was so low approximately 60 pptv (parts per trillion by volume) at 20°C, and this temperature allowed direct detection of HMTD vapor through an intact [M + H] +ion in real time.

Conclusion

The present study permitted to determine the best GC/MS and GC/μECD analytical conditions to detect and identify HMTD traces. A low injector temperature (150°C) allows avoiding degradation of this peroxide explosive both for the analysis of liquid solutions or headspace SPME. The GC/μECD was proved to be more sensitive (0.05 ng) than GC/MS with scan mode (0.1 ng).

On the other hand, SPME fiber was also successfully applied to sample traces of this explosive in simulated post-explosion residue. Despite the low vapor pressure of the HMTD, working with SPME mode at ambient temperature (22°C) during 1 hour exposure of the fiber in the headspace of the sample, proved to be adequate for fixing the HMTD without any risks of degradation losses during organic solvent extraction and concentration of aliquots.

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