Article

Forensic characteristics of organic peroxide explosives (TATP, DADP and HMTD)

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Triacetone triperoxide (TATP), diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD) are sensitive and powerful organic peroxide explosives. They have been encountered by the UK Police, both in terrorist and non-terrorist cases. Initially, in response to the recovery of a substantial quantity of TATP in the UK, it was found that there was a lack of reliable chemical, explosive and analytical data on organic peroxide explosives. Since then, extensive research has been carried out by FEL in order to build up a detailed forensic knowledge of these materials. A systematic study of the physical and chemical properties of these explosives along with methods for qualitative analysis and detection has been undertaken. The research carried out by FEL has found TATP, DADP and HMTD to be powerful primary explosives. They can be prepared in the home from readily available raw materials, although their sensitivity to accidental initiation makes them extremely hazardous materials to handle. Information on their synthesis and properties has been published and is available on the Internet. They exist as white solids which burn rapidly or instantaneously when exposed to a naked flame. Analytical techniques including FT-IR, TLC, GC/MS and LC/MS can be used for their forensic analysis and identification. FEL has also developed a low-hazard TATP training aid for UK Police explosive search dogs.

1. Introduction

The Forensic Explosives Laboratory (FEL) provides a twenty-four hour forensic service to UK Police forces to assist with criminal investigations relating to explosives on the UK mainland. Within FEL there is also a research department which looks at the forensic aspects of new explosive threats.

In 1994, during the investigation of a bombing on the UK mainland, a quantity of white powder was recovered. A sample of this powder was submitted to FEL for analysis. It was positively identified as triacetone triperoxide (TATP), an organic peroxide explosive. As a result of this incident, a full literature search was carried out and it was found that there was a lack of reliable chemical, explosive and analytical data on TATP. The literature search also revealed two other organic peroxide explosives of potential forensic interest, namely diacetone diperoxide (DADP) and hexamethylene triperoxide diamine (HMTD). FEL has since carried out extensive research in order to build up a detailed forensic knowledge of these materials. The emphasis of this work has been on TATP, with parallel studies of DADP and HMTD being carried out where possible.

The research has included: synthesising these explosives from a variety of recipes; studying their physical, chemical and explosive characteristics; looking at methods for the qualitative analysis of bulk quantities of these compounds; investigating

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the forensic recovery and analysis of traces of TATP; as well as looking at the post-blast trace analysis of TATP and developing a low-hazard TATP training aid for use by Police explosive search dogs.

2. Forensic interest

Organic peroxide explosives are of particular forensic interest because they have been encountered by the Police in the UK both in terrorist and non-terrorist cases since the incident in 1994. These explosives can be manufactured easily in the home from readily available and inexpensive raw materials. Details of their synthesis and properties have been published and are available on the Internet.

3. Synthesis

As stated above, the manufacture of these explosives is relatively simple, requiring little chemical knowledge and only basic laboratory equipment. The raw materials used in their synthesis can be easily purchased from a variety of sources. The synthesis of these explosives is, however, extremely hazardous!

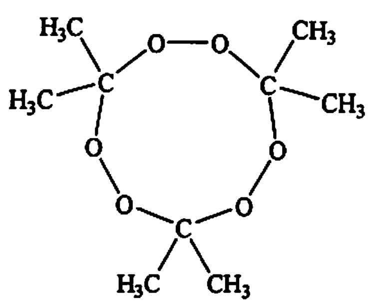
TATP and DADP can be synthesised from acetone, hydrogen peroxide and an acid catalyst. Altering the proportions of these ingredients and the reaction conditions used, determines whether the trimer (TATP) or dimer (DADP) is formed. HMTD can be synthesised from hexamine, hydrogen peroxide and citric acid.

The raw materials used can include laboratory reagents e.g. analar hydrogen peroxide 20%, 30% or 60% and concentrated sulphuric, hydrochloric or nitric acid. "Household" materials can also be used e.g. acetone from nail polish removers and used as a domestic solvent, acids from car batteries, descalers or citric acid used in the preparation of beverages and confectionery, hexamine from fuel tablets and hydrogen peroxide from hair dyes and used as a contact lens cleaner.

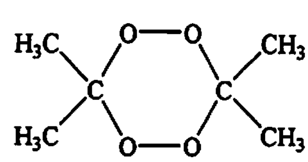
Possible structural formulae and relative molecular masses for TATP, DADP and HMTD are given in Fig. 1.

4. Physical characteristics

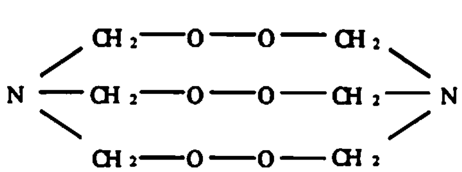
TATP and DADP exist as white crystalline materials. Variations in appearance may be observed between samples synthesised from different raw materials[1]. TATP has a distinctive odour similar to a mixture of bleach and vinegar. This explosive has been found to sublime on storage[1]. HMTD exists as a fine dry white powder. It is thermally labile. When milligram quantities of these explosives were exposed to a naked flame, they burned quickly or instantaneously with an



a) TATP (Relative Molecular Mass = 222)



b) DADP (Relative Molecular Mass = 148)



c) HMTD (Relative Molecular Mass = 208)

Fig. 1 Possible structural formulae and relative molecular masses for a) TATP, b) DADP and c) HMTD.

orange fireball[1].

5. Sensitivity to accidental initiation

To determine the sensitivity of these compounds to accidental initiation by various stimuli, a series of small scale tests were performed on TATP and HMTD. Results of these tests indicated both compounds to be primary explosives which were very sensitive to initiation by various stimuli, including friction, impact and electrical discharge[1]. These materials are, therefore, very hazardous to handle!

6. Forensic analysis and identification

Any item submitted to FEL for examination, which is suspected of containing organic peroxide explosives, may be analysed by one or more of the following techniques. The choice of analytical technique may depend upon the quantity of suspected material available for analysis. Due to the hazards associated with the handling, transport and storage of organic peroxide explosives, only the minimum quantity of suspected material required for analysis would be submitted to FEL.

6.1 Fourier transform infra-red spectroscopy

If a "bulk" quantity (i.e. milligrams) of suspected organic peroxide explosive is available, Fourier Transform Infra-Red Spectroscopy (FT-IR) may be used for forensic identification. The FT-IR spectrum obtained for the suspect sample would be compared to that of reference standards for TATP, DADP or HMTD. Figure 2 illustrates an example of a FT-IR spectrum of TATP. Possible assignments for the absorbance bands shown, include C-H stretching at 3006cm^{-1} and 2947cm^{-1}, symmetric C-H bending of the CH_3 group at 1377cm^{-1}and 1363cm^{-1} (split due to the presence of two CH_3 groups on the carbon atom) with skeletal vibrations and C-O, C-C and O-O stretching at 1275cm^{-1} and below[1,2,3]. If the major absorption bands, their relative intensities and the fingerprint region absorption patterns match between sample and reference standard, then a positive identification may be indicated.

6.2 Thin layer chromatography

If sufficient suspect material is available, it may also be analysed by Thin Layer Chromatography (TLC). Spot visualisation and the Rf value calculated for the suspect sample would be compared to that for TATP, DADP and/or HMTD standards analysed on the same TLC plate. If the Rf values (calculated by dividing the distance travelled by the component by the distance travelled by the eluent) between suspect sample and standard correspond, and the visualisation of the suspect and standard spots are similar, then a positive identification may be indicated.

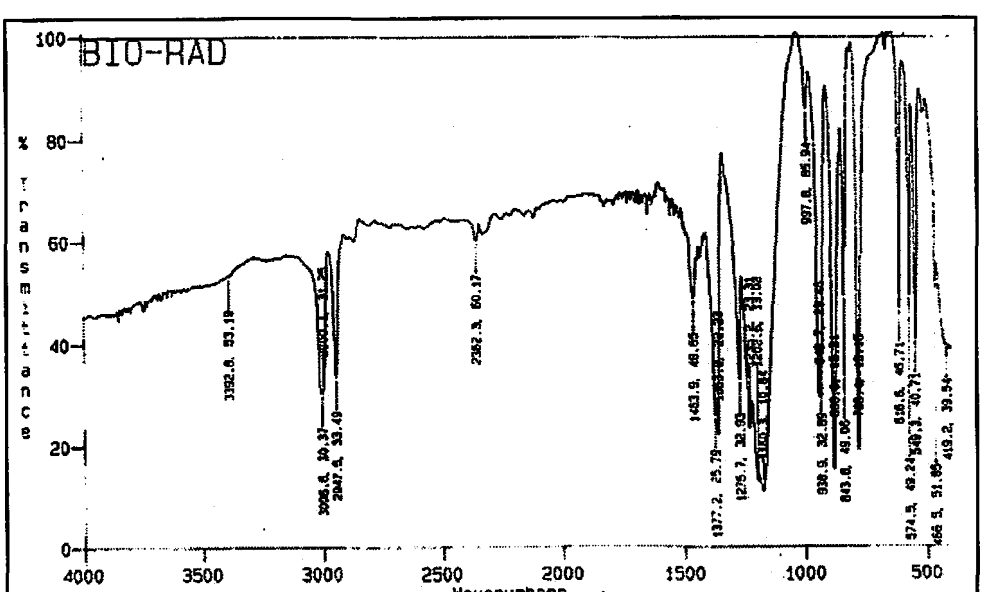


Fig. 2 FT-IR Spectrum of TATP[1].

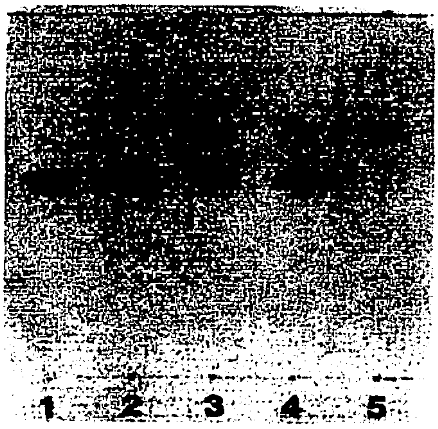


Fig. 3 TLC plate for TATP and DADP. Lanes 1 & 2 contain 20μg TATP, lanes 3 & 4 contain 10μg TATP and 10μg DADP and lane 5 contains 20μg DADP[1].

Figure 3 illustrates an example of a TLC plate for TATP and DADP, using toluene as an eluent and 1% diphenylamine in concentrated sulphuric acid as a visualisation reagent. Lanes 1& 2 contain 20μg TATP, lanes 3 & 4 contain 10μg TATP and 10μg DADP and lane 5 contains 20μg DADP[1].

6.3 Gas chromatography / mass spectrometry

Gas Chromatography combined with Mass Spectrometry (GC/MS) was the first method employed by FEL to obtain direct and structural information on organic peroxide explosives. This method was used for both bulk and trace analysis of items suspected of containing these explosives ("trace" meaning not visible to the naked eye).

Bulk samples were prepared for analysis by simply dissolving some of the suspect material in a suitable solvent and injecting this onto the GC column. If an item was suspected of containing trace quantities of, for example TATP, then a headspace sample may have been taken. This sampling method was also employed for the post-blast trace analysis of TATP. Headspace sampling involved sealing the item in a nylon bag with an adsorbent tube (e.g.Amberlite XAD-7®) inserted halfway into the bag and sealed in place. The bag was then heated at 70°C for fifteen minutes before the air (headspace) in the bag was pumped out through the adsorbent tube. The adsorbent was

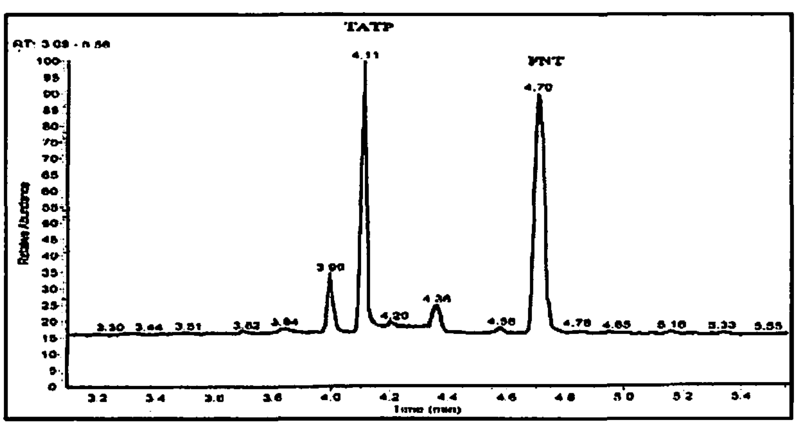


Fig. 4 Total ion chromatogram for TATP headspace sample[5].

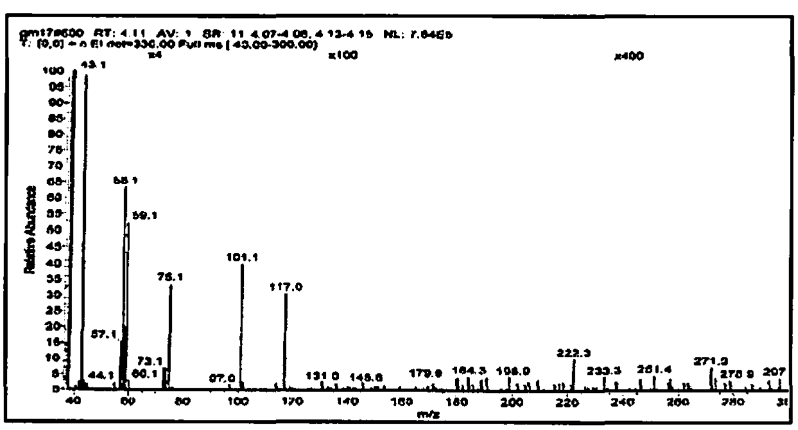


Fig. 5 Mass spectrum for TATP headspace sample[5].

then emptied into ethyl acetate to desorb any substances, before the resulting solution was injected onto the GC column[1]. Figure 4 illustrates an example of a total ion chromatogram obtained for a headspace sample of TATP[5]. This includes the retention time marker, 2-fluoro-5-nitrotoluene (FNT). Fiure 5 illustrates an example of the corresponding mass spectrum for the TATP headspace sample[5]. This spectrum was collected using electron impact mass spectrometry, in full scan mode.

The relative retention time for the suspected TATP peak on the chromatogram would be compared to that for a TATP standard. The mass spectral data for the sample would also be compared to that for the standard. The mass spectrum for TATP shows most of the fragments in the low mass region. This part of the spectrum (with peaks at mass/charge ratio (m/z) 43, 58, 59 and 75) is similar to that for acetone. The two peaks at m/z 101 and 117, differ by 16 mass units, indicating the possible loss of an oxygen atom which may be indicative of the presence of a peroxide. The peak at m/z 222 corresponds to the molecular ion of TATP[6]. If the relative retention times and mass spectral data between the suspected sample and standard correspond (within acceptable limits) then a positive identification may be recorded.

Problems, however, have been encountered analysing organic peroxide explosives by gas chromatography. FEL has found that with repeated analysis, various polar GC columns have

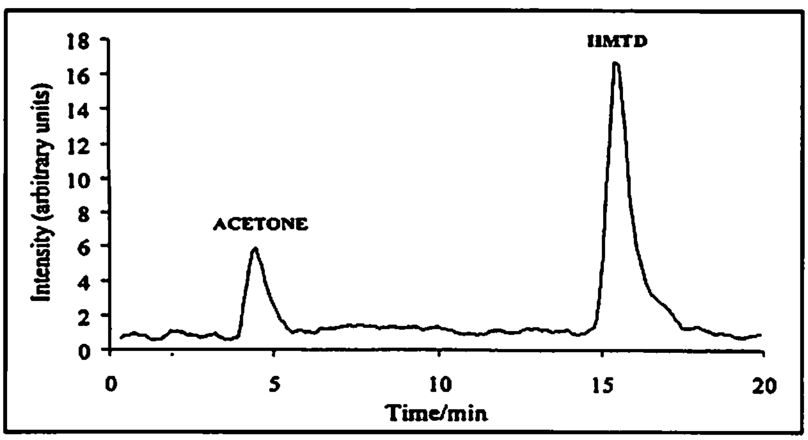


Fig. 6 Composite ion chromatogram for HMTD[7].

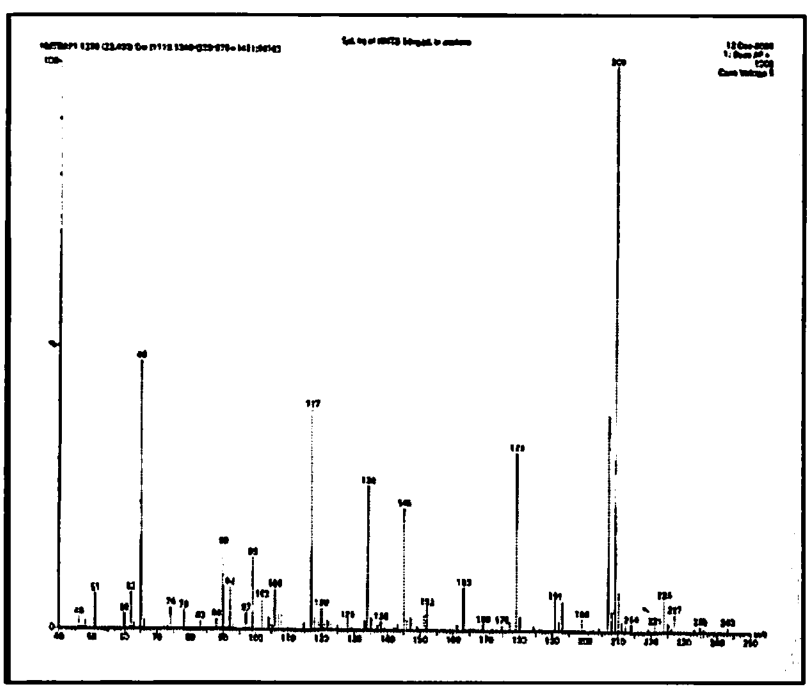


Fig. 7 Mass spectrum for HMTD

become activated by these materials, resulting in very broad, asymmetrical chromatographic peaks. Gas chromatography has posed particular problems for the analysis of HMTD, which is thermally labile[7].

6.4 Liquid chromatography / mass spectrometry

As a result of these problems, FEL has investigated the use of Liquid Chromatography with Mass Spectrometry (LC/MS) as an alternative technique. With liquid chromatography being performed close to room temperature, the thermal decomposition of HMTD is avoided.

Due to the submission of a large number of items to FEL suspected of containing HMTD traces in the year 2000, the rapid development of a LC/MS method for HMTD became a priority. A method for the analysis of HMTD traces has now been developed by FEL and methods for the analysis of TATP and DADP traces are currently under development.

Figure 6 illustrates an example of a composite ion chromatogram for HMTD[7]. This also includes a peak arising from acetone (the solvent used to dissolve HMTD). Figure 7 illustrates an example of a mass spectrum obtained for HMTD. The mass spectrum was collected using atmospheric pressure chemical ionisation in positive ion mode (APCI+) and using full scan mode[8].

As for GC/MS, the retention time for the suspected HMTD peak on the chromatogram would be compared to that for a HMTD standard. The mass spectral data for the sample would also be compared to that for the standard. The mass spectrum for HMTD shows the strongest peak at m/z 209 (assigned to the $[HMTD + H]^+$ ion). Other peaks assigned to HMTD fragments shown on the mass spectrum are m/z 62, 90, 106, 179 and 207. (Several additional ion peaks shown in the mass spectrum were also found in the acetone solvent used to prepare the HMTD solution and were assigned to an impurity, not yet identified)[7]. If the retention times and mass spectral data correspond between sample and standard (within acceptable limits) then a positive identification for HMTD may be recorded.

In summary, FEL has developed a range of analytical methods that may be used for the forensic identification of organic peroxide explosives. These developments have been in response to the emerging threat posed by the criminal misuse of these explosives in the UK.

7. TATP training aid for police dogs

Due to the continuing threat from these explosives in the UK, it has become desirable to train Police explosive search dogs to detect them. Conventional dog training involves the use of threat quantities of live explosives. It is not possible however, to provide large quantities of organic peroxide explosives for training, because of their particular sensitivity to accidental initiation. A low hazard TATP dog training aid has been developed by FEL. This has been achieved by incorporating milligram quantities of TATP onto filter paper carriers. Trial results have indicated that dogs can reliably detect TATP odour from these training aids[5].

8. Conclusions

The research carried out by FEL has found TATP, DADP and HMTD to be powerful primary explosives. They can be prepared in the home from readily available raw materials, although their sensitivity to accidental initiation makes them extremely hazardous materials to handle. Information on their synthesis and properties has been published and is available on the Internet. They exist as white solids which burn rapidly or instantaneously when exposed to a naked flame. Analytical techniques including FT-IR, TLC, GC/MS and LC/MS can be used for their forensic analysis and identification. FEL has also developed a low-hazard TATP training aid for UK Police explosive search dogs.

References

1) Ritchie K., Warren D.C., Forensic Explosives Laboratory, Dstl, Fort Halstead, DERA/CES/FEL/CR9704 internal report (unpublished work).
2) Pouchert, C. J., The Aldrich library of infrared spectra, 2nd Edition, Aldrich Chemical Company, 1975.

3) Bellamy, L. J., The infra-red spectra of complex molecules, Methuen & Co. Ltd, 1996, pp.120-122.
4) Lancaster S., Forensic Explosives Laboratory, Dstl, Fort Halstead, DERA/CES/CS/CR990083 internal report (unpublished work).
5) McKay G. J., Forensic Explosives Laboratory, Dstl, Fort Halstead, DERA/DSTL/CR00824 internal report (unpublished work).
6) Leppard, Major M. W. S., Forensic Trace Analysis of Triacetone Triperoxide, The Royal Military College of Science, Shrivenham, 1997.
7) Crowson, A., Beardah, M. S., Development of an LC/MS method for the trace analysis of hexamethylenetriperoxidediamine (HMTD), The Analyst, 2001, 126, pp1689-1693.