THE ANALYST
FULL PAPER
www.rsc.org/analyst

Development of an LC/MS method for the trace analysis of hexamethylenetriperoxidediamine (HMTD)†

Andrew Crowson* and Matthew S. Beardah

Forensic Explosives Laboratory, Dstl, Fort Halstead, Sevenoaks, Kent, UK TN14 7BP. E-mail: acrowson@dstl.gov.uk

Received 14th August 2001, Accepted 23rd August 2001
First published as an Advance Article on the web 21st September 2001

The detection and quantification of trace amounts of hexamethylenetriperoxidediamine (HMTD), a primary organic peroxide explosive, is investigated by LC/MS. LC/MS is well suited to the analysis of explosive compounds, such as HMTD, that are thermally labile. This property of HMTD has prevented other chromatography separation techniques, such as GC/MS, from being successfully employed for the analysis of HMTD. In this paper, the development of an LC/MS method capable of detecting trace quantities of HMTD is described. Potentially, the method is capable of being used to detect a lower detection limit of 20 pg μl^{-1} (2 ng per 100 µl) of HMTD. In comparison to other chromatography separation techniques that are used for analysis of explosives and explosive mixtures, *e.g.* GC/MS and GC/TEA, this represents an extremely valuable technique.

Introduction

In recent years, the development of analytical methods which are capable of detecting ultra-low trace quantities of explosives has become increasingly important in the field of forensic science.[1] In broad terms, bulk explosive quantities can be defined as amounts that can be visually observed, while trace explosive quantities are amounts that cannot. In quantitative terms, a trace quantity may be considered as a milligram, or less. At the present time, two of the most useful and sensitive techniques for analysing traces of explosives and explosive mixtures are gas chromatography combined with thermal energy analysis (GC/TEA), or mass spectrometry (GC/MS).[1] Indeed, both techniques can be used to detect low nanogram quantities of explosives.

Important advances in the state of GC/MS technology have revolutionised the analysis of organic compounds and multi-component mixtures and have also led to a significant broadening in the applicability of the technique.[2] This technique is especially important, since it combines the separation power of gas chromatography with a detection method that yields direct, structural information. In general, the application of GC/MS for explosives analysis is limited to volatile explosives that are not thermally labile and can be eluted from a GC column. Nevertheless, the range of explosives that can be successfully analysed is extensive.[3]

In terms of general organic analysis, GC/TEA is a considerably less versatile technique than GC/MS. TEA relies on a highly selective detection mechanism that has been commercially developed to carry out specific detection of nitro-containing (NO_2) compounds.[1] Since a large proportion of explosives contain nitro-groups, TEA is well suited to explosives analysis. The thermal energy analyser operates on the principle that nitric oxide (NO) is produced following pyrolysis of nitro-containing explosives. Reaction between NO and ozone (O_3) results in the formation of electronically excited nitrogen dioxide (NO_2) which relaxes *via* red emission that can be detected *via* a photomultiplier tube (PMT). Once again, the chromatography component of the technique does limit the number of nitro-containing explosives that can be detected using GC/TEA. However, these are relatively few and do not seriously compromise the overall effectiveness of the technique.

Clearly, although GC/TEA is an extremely important method for the detection of nitro-containing explosives, the extreme selectivity excludes other important *non* nitro-containing explosives from TEA detection. One family of compounds that do not usually fall into the category of nitro-containing are organic peroxides.[4] In general, compounds that contain one, or more, R–O–O–R functional groups can be described as organic peroxides. The number of compounds that fall into this family is substantial and usually organic peroxides can be broken down into two distinct classes, namely alkyl/acyl peroxides and cyclic peroxides. Cyclic peroxides normally consist of 5-, 6-, or 9-membered rings, although larger ring sizes are possible.[4] Although the reactions, properties and chemistry of alkyl/acyl peroxides are well known,[4] information pertaining to the characterisation of cyclic peroxides is less well established. One of the characteristic properties of cyclic peroxides is their tendency to detonate with relative ease. Indeed, a number of cyclic peroxides fall into the class of primary explosive. As a result, experimental work with cyclic peroxides is often extremely hazardous[4,5] and is the likely explanation for the relative scarcity of experimental data.

Hexamethylenetriperoxidediamine (HMTD) is one such cyclic peroxide primary explosive that has been partially characterised in recent years. It is a white solid that is exceptionally sensitive to initiation by impact, friction and electrical discharge.[6] Two molecular structures have been proposed for HMTD. Fig. 1 illustrates the two proposed molecular structures. Fig. 1(a) illustrates the structure that was

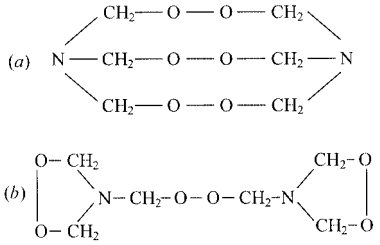

Fig. 1 Molecular structures for HMTD proposed by (a) Baeyer and Villiger (1900) and (b) Grisewald and Siegens (1921).

first proposed by Baeyer and Villiger in 1900,[7] while Fig. 1(b) shows an alternative structure proposed by Grisewald and Siegens in 1921.[8] The majority of experimental evidence, collected from studies of HMTD using conventional structural characterisation techniques, such as infrared (IR) spectroscopy,[9] nuclear magnetic resonance (NMR) spectroscopy[9] and both chemical[9,10] and electron[9] ionisation mass spectrometry, points to the most probable structure of HMTD as that shown in Fig. 1(a).

In addition to the standard structural techniques mentioned above, a number of separation-based analytical methods have been used in recent years for the identification of HMTD. Some of these include thin layer chromatography (TLC)[11,12] and gas chromatography combined with mass spectrometry (GC/MS).[13] As mentioned above, GC/TEA is suitable for the analysis of nitro-containing explosives and, consequently, HMTD cannot be detected using this method. GC/MS was first used to analyse HMTD by Gielsdorf[13] in 1981 using both chemical and electron ionisation, although not using trace quantities. EI and CI mass spectra of HMTD were also published by Zitrin and co-workers in 1984.[9] Both ionisation techniques yielded relatively simple mass spectra with *m*/*z* peaks at 208 (for EI), corresponding to the molecular ion $[HMTD]^+$, and 209 (for CI), corresponding to $[HMTD + H]^+$. A subsequent GC/EI/MS study, using ~500 ng of HMTD, was carried out within the Forensic Explosives Laboratory (Dstl).[14] The results showed that EI mass spectra, similar to those published by Zitrin, could be obtained at levels corresponding to trace quantities. However, a serious problem was encountered during this GC/MS study. It was found, during repeated analysis of HMTD, that the solid phases of a number of standard polar GC capillary columns became activated after an extremely short length of time. This activation resulted in extremely broad, asymmetrical chromatographic peaks.

Over the past four years, the Forensic Explosives Laboratory (FEL) has conducted an ongoing research programme involving the use of high-performance liquid chromatography, combined with mass spectrometry (LC/MS), for the detection of trace quantities (low nanogram) of explosives.[15] A number of explosive compounds are insufficiently volatile, or too thermally labile, to undergo chromatographic analysis using a GC capillary column and, generally, HPLC is more suited for the analysis of these types of compounds.

It is highly improbable that, under the milder conditions employed in HPLC, analysis of HMTD will cause any damage to the LC column solid phase, unlike analysis *via* GC. Additionally, thermal decomposition of HMTD using the milder conditions of HPLC is likely to be significantly reduced, in comparison to analysis *via* GC. The decomposition temperature of HMTD is 150 °C.[6] Following this line of reasoning, the possibility of employing LC/MS for the analysis of trace quantities of HMTD has been investigated at the Forensic Explosives Laboratory. In this paper, preliminary findings from the study are described which show that at the current stage of development the method is suitable for low nanogram detection of HMTD.

Experimental

Apparatus

Historically, one of the major difficulties with combining an HPLC system to a mass spectrometer has involved efficiently interfacing a liquid, at high pressure, with the high vacuum of the mass spectrometer. It is only within the last two decades that developments in atmospheric pressure ionisation (API) techniques, such as atmospheric pressure chemical ionisation (APCI) and electrospray chemical ionisation (ESI), have occurred and led to significant advances in the versatility of LC/MS.[1] Until the development of soft, atmospheric pressure ionisation techniques, the types of sample amenable to analysis by LC/MS were severely limited by, for example, their thermal lability, volatility, polarity and molecular weight. In general, samples which are now routinely analysed by APCI, are likely to have been previously analysed by thermospray LC/MS.

The HPLC system used in the current study consisted of an HP1100 quarternary pump system with a membrane degasser, autosampler, thermostatically controlled column oven and UV/Vis photodiode array detector. A Thermo-Finnigan (Manchester UK) 'Navigator' (bench-top, quadrupole mass spectrometer) was coupled to the HPLC system *via* an atmospheric pressure chemical ionisation (APCI) interface which could be used in positive, or negative, ion mode. In the current study, APCI in positive ion mode (APCI+) was employed as the ion source in all experiments.

Data acquisition

Data was collected and stored using the data system, MassLab, using either full scan, or selected ion monitoring (SIM). In full scan mode, data was collected across a range of masses (40–350 *m*/*z*), with a scan time of ~2 s and an inter-scan delay of 0.10 s, using the centroid mode of acquisition. In SIM mode, single ion masses were monitored, using an inter-channel delay of 0.02 s (the time between scanning each channel), a span of 0.5 amu (width of acquisition window centred on selected *m*/*z* value) and a dwell time of 0.2 s (time required to obtain a well-defined chromatographic peak).

HMTD solutions

Solid hexamethylenetriperoxidediamine (HMTD) was manufactured at the Forensic Explosives Laboratory, Fort Halstead. Due to the dangers associated with handling HMTD, purification of the final product was not attempted. However, the method used to synthesise HMTD is known to produce a 70–80% yield of the product.[16] Consequently, the concentrations of HMTD solutions used in this study could not be accurately quoted and an estimated error of ~20–30% is likely to be associated with all solution concentrations. All of the HMTD solutions were prepared in acetone (Fisher Scientific, HPLC grade) because of the relatively high solubility of HMTD in acetone (2.6 g l^{-1}). HMTD is virtually insoluble in water (0.1 g l^{-1}).[6] An approximate 500 mg l^{-1} (≡500 ng μl^{-1}) solution of HMTD/acetone was used as a stock solution, from which appropriate dilutions could be made.

Preliminary experiments

The first stage of the method development process involved carrying out preliminary experiments using a ProC18 method development HPLC column (YMC, Europe GmbH). No guard column was used. The ProC18 method development column consisted of 5 μm ultrapure spherical silica bead packing (120 Å pore size), with dimensions of 50 mm length and 4.0 mm internal diameter (stainless steel). The HPLC oven temperature was set to 20 °C. For these experiments the mobile phase was chosen to be a 95:5 water–methanol mixture, without the addition of a buffer. A flow rate of 0.2 ml min^{-1} was used and the injection volumes varied between 0.1 and 5 μl. All experiments involved data acquisition over a period of 30 min.

In order to optimise the mass spectrometer for detection of HMTD, the majority of experiments using the method development column involved varying a number of parameters relating to the APCI ionisation source. Details of the APCI conditions

relating to specific experiments, along with a discussion of the results obtained from each, can be found in the appropriate results section.

Analytical experiments

Following preliminary experiments using the ProC18 method development column, all subsequent experiments were carried out using a YMC ProC18 analytical column (150 mm × 2.0 mm id), with a YMC ProC18 guard column (10 mm × 2.0 mm). All of the HPLC operating conditions were the same as those used in the preliminary experiments, except where stated. The flow rate of 0.2 ml min^{-1} corresponded to a mobile phase pressure of ~150–200 bar. Additionally, data acquisition was reduced to 20 min with a non-acquisition post-run time of 10 min. Again, the majority of work with this column involved varying different parameters in the APCI source, along with a number of HPLC conditions, in order to obtain an increased response for HMTD detection. A discussion of the experiments carried out in order to refine HMTD detection can be found in the appropriate results section.

Results and discussion

A. Investigative experiments using a Pro C18 method development column

Preliminary experiments were concerned with obtaining appropriate LC/MS conditions for optimum HMTD detection, using a YMC ProC18 method development column and APCI+ ionisation. The configuration of the HPLC system has been outlined in the experimental section. Initial parameters were chosen for the APCI+ source based upon previous experimental experience of LC/MS detection of explosives.

Using the LC/MS system under the conditions described, a full scan APCI+ chromatogram was obtained for a 5 µl injection of 50 ng μl^{-1} HMTD solution (≡250 ng absolute mass injected). The total ion chromatogram (TIC) yielded a weak and broad, asymmetrical peak, with a maximum at ~23.5 min. The shape of this peak was indicative of column overloading. Examination of the corresponding mass spectrum revealed the strongest peak to possess a mass/charge ratio (*m*/*z*) of 209. Since the relative molecular mass of HMTD is 208, this *m*/*z* peak was assigned to the $[HMTD + H]^+$ ion.

In addition to the *m*/*z* 209 peak, a number of less intense peaks were observed in the mass spectrum. To clarify which of the *m*/*z* peaks resulted from HMTD fragmentation, single ion chromatograms for all of the significant ions were examined. In general, all of the single ion chromatograms exhibited peaks at either ~21.5, or ~23.5 min. Since the *m*/*z* 209 peak had already been assigned to the $[HMTD + H]^+$ ion, all other single ion chromatograms exhibiting a peak at ~23.5 min were assigned to HMTD fragments. Ions resulting from HPLC elution at ~23.5 min were those with *m*/*z* peaks of 62, 90, 106, 179, 207 and 209 in the full scan mass spectrum. All remaining *m*/*z* peaks in the mass spectrum, namely 88, 92, 99, 117 and 134, exhibited single ion chromatograms with a peak at ~21.5 min. Additional LC/MS analyses showed that these ion peaks were present in the acetone solvent used to prepare the HMTD solutions and were assigned to an impurity, not yet identified at the present stage of the method development. As a result, all subsequent experiments involving selected ion monitoring (SIM) used detection of the six assigned 'HMTD' ions to confirm the presence of HMTD.

Since the HMTD prepared for use in this study was not purified following its synthesis, it was necessary to verify that the peak at ~23.5 min did not arise from one of the synthetic starting products. Thus, LC/MS analyses of hexamine (Sigma-Aldrich, UK) and citric acid (Sigma-Aldrich, UK) were acquired. Since the peak at ~23.5 min exhibited a *m*/*z* ion peak of 209 (attributed to $[HMTD + H]^+$) it was unlikely that hexamine (RMM 140.2) or citric acid (RMM 192.1) were responsible. Indeed, the resulting LC/MS analyses did not show any peaks in their respective total ion chromatograms, at ~23.5 min. Additionally, of the peaks that did appear in the TIC, none exhibited *m*/*z* ion peaks corresponding to those attributed to HMTD.

Following acquisition and analysis of the full scan APCI+ chromatogram, a further injection of 5 µl of 50 ng μl^{-1} HMTD solution was analysed in SIM mode, using the eleven 'HMTD' and 'impurity' ion masses. Again, single ion chromatograms were examined for all eleven masses in order to confirm those which resulted from HMTD fragments, and those that resulted from the unknown impurity. The results agreed definitively with those obtained in full scan acquisition mode.

Before proceeding on to experiments using the analytical ProC18 column, SIM analysis was carried out following injection of 1 µl of the 50 ng μl^{-1} HMTD solution (≡50 ng). As expected, the problem of column overloading, observed in the two previous experiments, was significantly reduced. The total-ion chromatogram, collected for the 'HMTD' and 'impurity' ion masses, exhibited baseline resolution between the impurity peak at ~21.5 min and the HMTD peak at ~23.5 min. Monitoring of the six 'HMTD' *m*/*z* ions resulted in an observed signal-to-noise ratio of ~30 for the HMTD peak, illustrating that at this early stage of the method development, HMTD could be detected at quantities corresponding to trace levels.

Finally, a series of experiments were carried out in which the *m*/*z* 209 ion was selectively monitored while the APCI cone voltage was varied between 5 and 15 V. Application of a potential to the cone is used when fragmentation of a compound is required. These experiments showed that the strongest and weakest responses for HMTD were obtained with the cone potential at 5 and 15 V, respectively. Such findings are unsurprising, since a high cone voltage would be expected to result in the loss of the parent ion, especially in an energetically unstable molecule.

B. Method development using a Pro C18 analytical column

Having established a suitable set of HPLC conditions and approximate parameters for the APCI+ source, the method development column was exchanged for a ProC18 analytical column, described in the experimental section. Initially, 1 µl of the 50 ng μl^{-1} HMTD solution was injected and analysed in LC/MS SIM mode, using the eleven selected ion masses. Examination of the single ion chromatogram for *m*/*z* 209 ($[HMTD + H]^+$) showed the retention time for elution of HMTD to be ~15.5 min. Once again, examination of the single ion chromatograms for the five 'impurity' ions showed that an unknown impurity eluted at ~14.3 min.

In order to obtain the appropriate experimental parameters for optimum detection of HMTD, a series of experiments were carried out in which single specific parameters were independently varied, while all others remained constant. For the purpose of this study, experiments were limited to those involving the variables that were most likely to produce a significant change in LC/MS response, such as column oven temperature, APCI probe temperature, source temperature, corona pin voltage, sample cone potential and drying gas flow rate. All other variables were held at the manufacturers default settings. The following discussion briefly describes the outcome of each variation and assumes that any observed change arose as a consequence of the independent variation. In all cases, the

various responses were compared as a function of peak area. All of the experiments were performed in SIM mode, using the eleven ion masses previously mentioned.

1. Variation of column oven temperature

LC/MS analyses of 1 μl of the 50 ng μl^{-1} solution of HMTD (≡50 ng absolute mass injected) were carried out with the column oven temperature set to 10, 20 and 30 °C, respectively. In order to evaluate which oven temperature yielded the best response for HMTD detection, SIM chromatograms for the eleven selected ions were examined for each temperature. At 10 and 30 °C, the responses for both the impurity and HMTD were reduced, especially at 30 °C, in comparison to the responses at 20 °C. Since 20 °C appeared to yield the optimum response, this oven temperature was used throughout the remaining experiments.

2. Variation of the nebuliser temperature, corona pin voltage, source temperature and drying gas flow rate

Experiments were carried out in which the nebuliser temperature, corona pin potential, source temperature and nitrogen drying gas flow rate were varied independently. The nebuliser temperature was varied between 100 and 450 °C, while the corona pin potential was varied between 2.5 and 3.5 kV. The source temperature was varied between 100 and 120 °C, while the flow rate of the drying gas was varied between 300 and 350 l h^{-1}. As for all other experiments the results were compared as a function of HMTD peak area, based upon data acquired for the *m*/*z* 209 ion in SIM mode. All experiments were carried out using 1 μl injections of a 10 ng μl^{-1} acetone solution of HMTD.

Initially, the temperature of the nebuliser was varied between 100 and 450 °C, in increments of 50 °C, in order to obtain an approximate value for the optimum HMTD response. The strongest HMTD response was obtained with a nebuliser temperature of 250 °C. Fine tuning of the nebuliser temperature was then carried out in the region of 250 °C, with the strongest response for HMTD occurring with a nebuliser temperature of 240 °C. Comparison between the most intense (240 °C) and weakest (450 °C) *m*/*z* 209 peaks, illustrated that a 10-fold increase in response was observed at the optimised nebuliser temperature.

Similar experiments were carried out in which the applied corona pin potential was varied between 2.5 and 3.5 kV. The results of these experiments showed that the most intense *m*/*z* 209 peak was obtained at 3.0 kV. However, in comparison to the weakest observed response, the increase was relatively insignificant (~10%). It was found that varying the flow rate of the drying gas between 300 and 350 l h^{-1}, and the source temperature between 100 and 120 °C, resulted in relatively insignificant differences in the areas of the respective *m*/*z* 209 peaks. Consequently, for the remaining experiments the drying gas flow rate and source temperatures were set at 350 l h^{-1} and 110 °C, respectively.

3. Variation of sample cone voltage

Relatively coarse experiments, using the method development ProC18 column, had already illustrated that a cone voltage of 5 V resulted in the most intense chromatographic peak for HMTD, compared with higher potentials. In a series of 'fine tuning' experiments the cone potential was varied in increments of 1 V (around 5 V) to ascertain the dependence of HMTD detection sensitivity upon the sample cone voltage. Again, 1 μl injections of a 10 ng μl^{-1} solution of HMTD were used. The results showed that the strongest HMTD response was obtained at 5 V, although compared to the responses for cone voltages of 3 and 7 V, the increased response was relatively insignificant (~20% peak area).

4. Limit of detection for HMTD

Using the optimised conditions for LC/MS detection of HMTD, experiments were conducted with the aim of obtaining an approximate lower limit for detection (ng) of HMTD (LOD). In order to obtain the lower LOD an approximate method was employed. For forensic identification purposes, an analyte is deemed to have been positively detected if the signal-to-noise ratio of a given chromatographic peak is 3, or more, and the retention time accurately agrees with that of a known reference.[17] Under the current LC/MS conditions, a peak exhibiting a S/N ratio of 3, denoted smallest discernible peak (SDP), corresponded to a peak area of ~40,000 arbitrary units. By directly comparing the peak area for a known quantity, *e.g.* 1 ng, with that for the SDP peak (~40,000 arbitrary units), an approximate theoretical LOD could be calculated. Although this method represented a relatively crude way of obtaining the lower LOD, and assumed that the mass injected is linearly proportional to the corresponding peak area, it was appropriate for the current stage of the method development. In future studies, a more rigorous investigation will be performed, using absolute mass injections to obtain the lower LOD.

Following injection of 0.1 μl of a 10 ng μl^{-1} solution of HMTD (≡1 ng), the single ion chromatogram for *m*/*z* 209 was obtained. Integration of the peak at ~15.5 min yielded an area of ~850,000 arbitrary units. Comparison of this peak with the SDP peak reveals that a mass of 0.05 ng would yield a peak exhibiting a S/N ratio of ~3.

Fig. 2 shows the chromatogram obtained following injection of 0.1 μl of the 10 ng μl^{-1} HMTD solution and subsequent summation of the single ion chromatograms for the 'HMTD' ions with *m*/*z* 62, 90, 106, 179, 207 and 209. In this case, the area of the peak at 15.5 min was ~2.1 × 10^6 arbitrary units. Comparison of this peak with the SDP peak reveals that a mass of 0.02 ng would yield a peak exhibiting a S/N ratio of ~3. Assuming routine injections of 1 μl, this value corresponds to a concentration of 20 pg μl^{-1}. A more useful way of expressing this quantity, with respect to unknown samples, is to express the LOD as a mass per 100 μl, since such volumes are commonly obtained in routine analysis. Expressed in these terms the theoretical LOD for HMTD is ~2 ng per 100 μl. Taking into

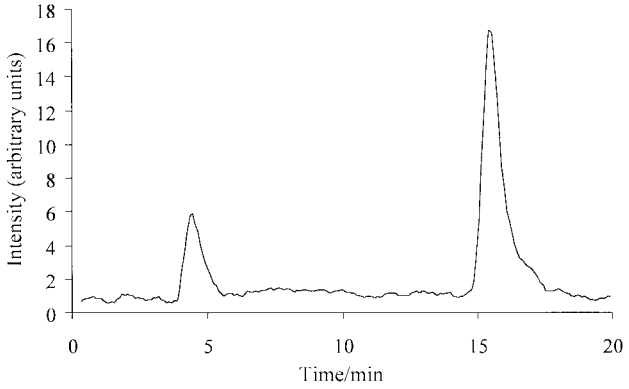

Fig. 2 Composite chromatogram for the *m*/*z* 62, 90, 106, 179, 207 and 209 ions, obtained following injection of 0.1 μl of the 10 ng μl^{-1} HMTD solution. The peak at ~4.5 min arises from the acetone solvent.

account the errors associated with HMTD solution concentrations, this figure is likely to represent an underestimation of the true detection limit.

Although this study represents a relatively rapid investigation into HMTD detection *via* LC/MS, it is clear that LC/MS is an extremely valuable analytical technique for the identification and quantification of trace amounts of the primary explosive. Even at this early stage of the method development it is extremely useful to compare the theoretical limit of LC/MS detection for HMTD with the limits of detection routinely observed for other explosives using GC/TEA and GC/MS. For the latter two techniques, limits of detection are often quoted in the low nanogram per 100 µl and, consequently, it can be seen that the limit of detection for HMTD, using LC/MS, is comparable. Since it would appear that LC/MS is one of the few analytical separation techniques that is capable of reliably identifying HMTD at trace levels, it is essential that further development and refining of the LC/MS method described in this paper is carried out.

Acknowledgements

The authors would like to acknowledge the help and advice of Martyn Sime (Forensic Explosives Laboratory) and Charles White (UK Business Manager, YMC Europe GmbH).

References

1 J. Yinon and S. Zitrin, *Modern Methods and Applications in Analysis of Explosives*, Wiley, Chichester, 1st edn., 1986.
2 P. Brown, *Advances in Chromatography*, Marcel Dekker, New York, 1998
3 J. Yinon, *J. Chromatography A*, 1996, **742**, 205.
4 D. Swern, *Organic Peroxides Volume III*, Wiley, New York, 1st edn., 1972.
5 A. Noponen, *Chem. Eng. News*, 1977, **55**, 5.
6 J. Köhler and R. Meyer, *Explosives*, VCH, 4th edn., 1993.
7 A. Baeyer and V. Villiger, *Chem. Ber.*, 1900, **33**, 2479.
8 C. von Grisewald and H. Siegens, *Chem. Ber.*, 1921, **54**, 490.
9 S. Zitrin, S. Kraus and B. Glattstein, *Proc. 1st Int. Symp. on Analysis and Detection of Explosives*, FBI Academy, Quantico, VA, 1983, 137.
10 D. J. Reuter, E. C. Bender and T. L. Rudolph, *Proc. 1st Int. Symp. on Analysis and Detection of Explosives*, FBI Academy, Quantico, VA, 1983, 149.
11 J. Chládek, *Proc. 4th Int. Symp. on Analysis and Detection of Explosives*, Lab. Fed. Crim. Police, Prague, Czech Rep., 1993, 73.
12 Forensic Explosives Laboratory, Dstl Fort Halstead, unpublished work.
13 W. Gielsdorf, *Fresenius' J. Anal. Chem.*, 1981, **308**, 123.
14 Forensic Explosives Laboratory, Dstl Fort Halstead, DERA/CES/FEL/CR9701 internal report (unpublished work).
15 Forensic Explosives Laboratory, Dstl Fort Halstead, DERA/CES/CS/CR000229 internal report (unpublished work).
16 B. T. Federoff and O. E. Sheffield, *Encyclopaedia of Explosives and Related Items*, Volume 7, 1975.
17 Forensic Explosives Laboratory, Dstl Fort Halstead, Standard Method 110 'GC-TEA analysis of explosives'.