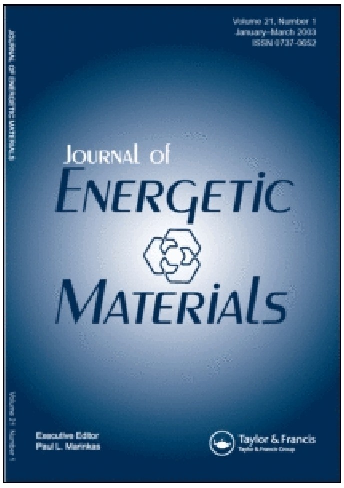

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Post explosion analysis of explosives by mass spectrometric methods

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POST EXPLOSION ANALYSIS OF EXPLOSIVES BY MASS SPECTROMETRIC METHODS

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ABSTRACT

The analysis of trace amounts of explosives from post-explosion debris - one of the most difficult problems in forensic chemistry-is still carried out in many laboratories by chromatographic methods only. In recent years several new methods have been applied to the analysis of explosives. These include mass spectrometric methods (GC/MS, LC/MS and MS/MS) and NMR methods. The possible application of these methods to post-explosion analysis is discussed and various aspects of the techniques are reviewed and compared. The choice of capillary column GC/MS as a routine method in the Israel Police laboratory is explained and examples from actual cases are given.

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INTRODUCTION

Many forensic laboratories base their post-explosion analysis on chromatographic methods only, particularly thin layer chromatography (TLC)[1] and more recently liquid chromatography (LC)[1]. The special implications of a positive identification in forensic analysis led our laboratory to a self-imposed criterion: identification of an organic compound should not rely only on chromatographic methods, even when several combinations of these methods are employed. This criterion is strictly adhered to in the analysis of drugs. If a syringe is suspected to contain traces of heroin, TLC, gas chromatography (GC) or LC are not considered sufficient for positive identification. A mass spectral identification is necessary to confirm the chromatographic results and without it the expert would not give a positive result.

Unfortunately, this criterion cannot always be imposed in the analysis of explosives. There is obviously no problem with unexloded material, where the amount of the sample enables the use of spectrometric methods to confirm the chromatographic results. Infrared (IR) spectrometry, mass spectrometry (MS) and nuclear magnetic resonance (NMR)spectrometry can easily be employed. The problems encountered in applying these methods to post-explosion analysis are described in this paper and the successful use of GC/MS to confirm TLC results from post-explosion exhibits is described.

EXPERIMENTAL

GC/MS was carried out on a Finnigan 4500 quadrupole mass spectrometer. The GC column was a J & W fused silica capillary column, 15 m X 0.25 mm (I.D.) with 0.25 μm coating of DB-5. Temperatures were programmed from 70°C to 270°C at 15°C/min. Injector temperature was 180°C. Electron energy was 70eV in both electron impact (EI) and chemical ionization (CI) modes. Helium was the GC carrier gas and methane was the CI reagent gas. More details are reported elsewhere.[3]

NMR spectrometry was carried out on a Bruker WM-250 instrument, using 250 MHz frequency. More details are reported elsewhere.[4]

RESULTS AND DISCUSSION

The reason that many forensic laboratories use only chromatographic methods in their post-explosion analysis is probably because the application of spectrometric methods (IR, MS, NMR) to samples taken from the explosion site has often been found impractical. Although exhibits from the post-explosion debris are first extracted with acetone and the extract is cleaned (when necessary) on a chromatographic column, large amounts of impurities often remain. This, combined with the fact that only small amounts of the original explosives are present in the extract, excludes IR from being successful in most cases.

Experiments in the use of NMR for post-explosion analysis gave some unexpected results. A priori it was assumed that when applied to post-explosion residues the method would suffer from similar disadvantages as IR: relatively high detection limits and interference from impurities. A study designed to test the applicability of NMR to post-explosion analysis showed that the method was successful in several post-explosion cases[4]. The proton NMR spectra of certain explosives like RDX and PETN are characterized by one singlet at a relatively low field. Therefore interference from protons of usual organic contaminants is minimal. Figure 1 is an example of the analysis of a post-explosion extract by NMR[4], without any separation prior to the NMR analysis. The protons of RDX and PETN, which resonate as singlets at $\delta = 4.89$ ppm and $\delta = 6.26$ ppm, respectively, are clearly observed. The example in Figure 1 proves that NMR could be very valuable in some post-explosion analyses. However, there were cases where spots of nitrate esters and nitramines were detected by Griess reagent on a TLC plate but when the samples were subjected to NMR no explosives were detected. The reason could be the "sensitivity gap" of 1-2 orders of magnitude between the methods ($\sim 10\,\mu g$ for most explosives in NMR[4] vs. 1-0.1 μg in TLC[5]).

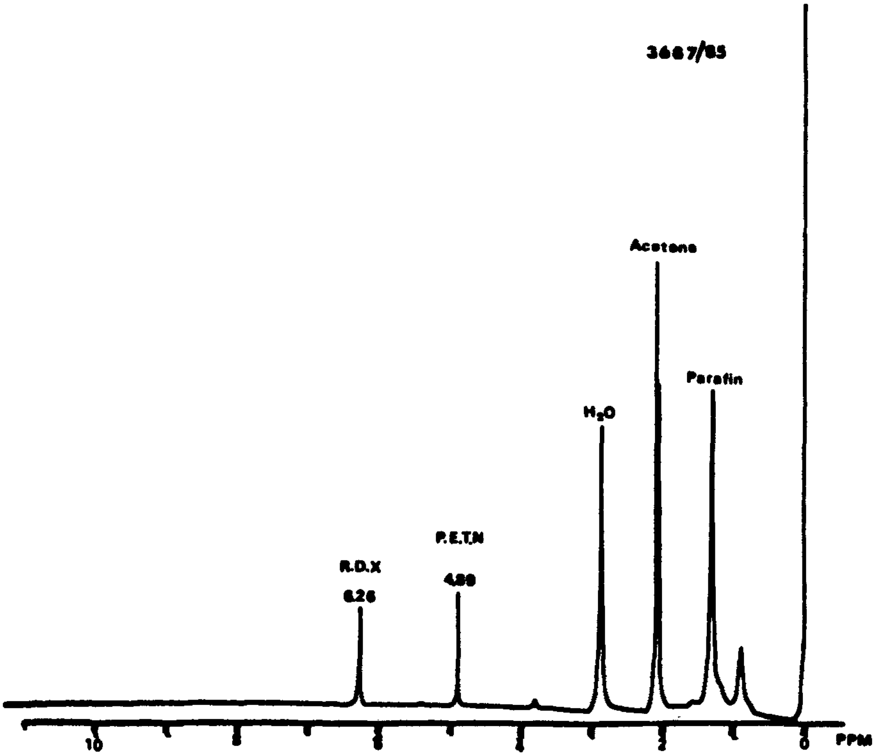

FIGURE 1
NMR spectrum (protons) of a post-explosion extract (case 3687/85). PETN and RDX were identified.

Mass spectrometry is probably the best method available for the analysis of sub-microgram amounts of organic compounds, being a sensitive and a reliable method. Direct introduction of post-explosion samples into the mass spectrometer is in many cases impractical. Even after cleaning the extract on a chromatographic column the ions originating from impurities often give rise to a complicated spectrum from which the explosive cannot be identified. There are, however, some characteristic ions like NO^+ and NO_2^+ in the mass spectra of nitrate esters and nitramines which have analytical value even among the many other unrelated ions. Also, the MS analysis usually follows TLC, so there is an indication about the type of explosive. It is then easier to find significant ions related to the suspected explosive. Although this constitutes an improvement over the "TLC only" situation existing in many forensic laboratories, it does not meet our criteria for positive identification.

When a "gentle" ionization method like CI is employed a relatively simple spectrum is produced. It usually contains fewer ions than the corresponding EI spectrum and often includes molecular weight information. These features make CIMS more suitable for a direct MS analysis of post-explosion samples. Figure 2 shows the CI (methane) mass spectrum of a post-explosion

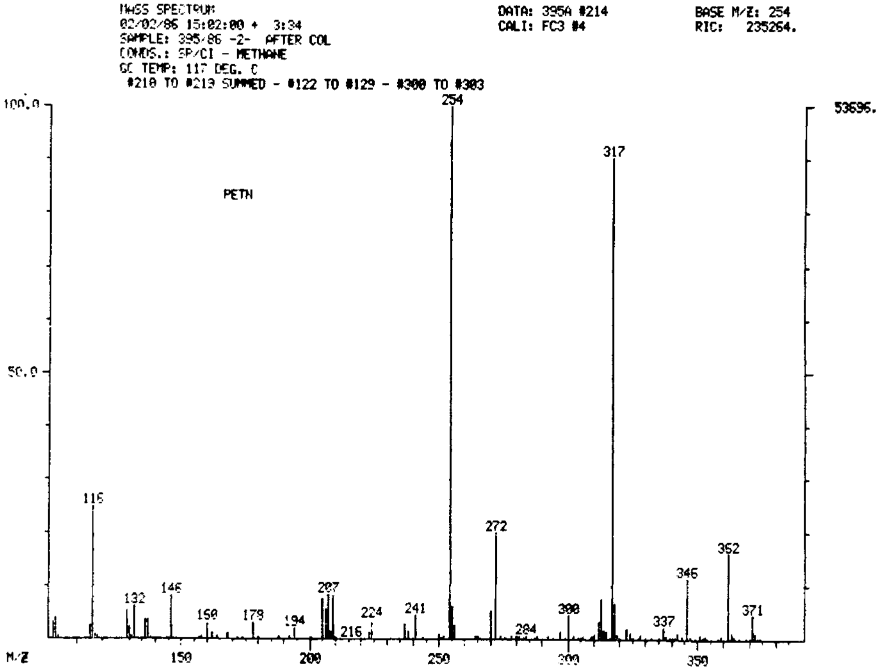

FIGURE 2
CI - methane mass spectrum (using direct probe) of a post-explosion extract (case 395/86). PETN was identified.

extract from the debris of a blown up safe. The sample was introduced to the ion source of the mass spectrometer through the direct probe inlet, after being cleaned on a florisil column. PETN was identified by its $[M+H]^+$ ions at m/z 317 and by some fragment ions, mainly $[M+H-HNO_3]^+$. The mass spectrum shown in Figure 2 seems to be sufficient for positive identification of PETN, especially when an EI mass spectrum is also recorded and the typical low mass ions at m/z 30, 46 and 76 (NO^+, NO_2^+ and $CH_2ONO_2^+$, respectively) are observed. Nevertheless, the method is not general. Some explosives give CI spectra containing only $[M+H]^+$ ions which although indicating molecular weights cannot serve as a basis for positive identification. Moreover, many post-explosion samples will not give interpretable mass spectra even under CI conditions.

The obvious solution seems to use a separation method like LC or GC "on line" with the mass spectrometer. Some explosives are known to be thermally labile under GC conditions. Possible decompositions of RDX[6], PETN[5] and tetryl[3] were reported. Other, like HMX or cellulose nitrate ("nitrocellulose") are too involatile for GC analysis. It seems that LC/MS is the more suitable method for post-explosion analysis, especially with the introduction of the "thermospray" technique[7,8]. There is, The good results obtained with unexploded explosives are hardly surprising. Much more impressive are the results obtained by GC/MS in actual post-explosion samples[3].

Figure 3 shows the total ion and the m/z 46 mass chromatograms from an extract of the debris of a blown up safe. The peak emerging after 587 seconds, located clearly by the m/z 46 mass chromatogram could be attributed to RDX by its EI mass spectrum (Figure 4). The residues from an explosive charge which had been detonated inside a litter can were subjected to GC/EIMS and GC/CIMS. We use GC/CIMS especially when nitrate esters are involved[3]. The total ion and mass chromatograms in the GC/EIMS and GC/CIMS analyses are shown in Figure 5 and 6, respectively. The resulting EI and CI mass spectra gave a positive identification of NG. Other examples for the successful use of capillary column GC/MS in post-explosion analysis is described elsewhere[3].

In recent years tandem mass spectrometry (MS/MS) was tried on several types of compounds[9], including explosives[10]. The equipment is too expensive and too sophisticated for most forensic laboratories so it is not surprising that no reports on analysing post-explosion samples from actual cases have been published. Yet the method seems potentially suitable for

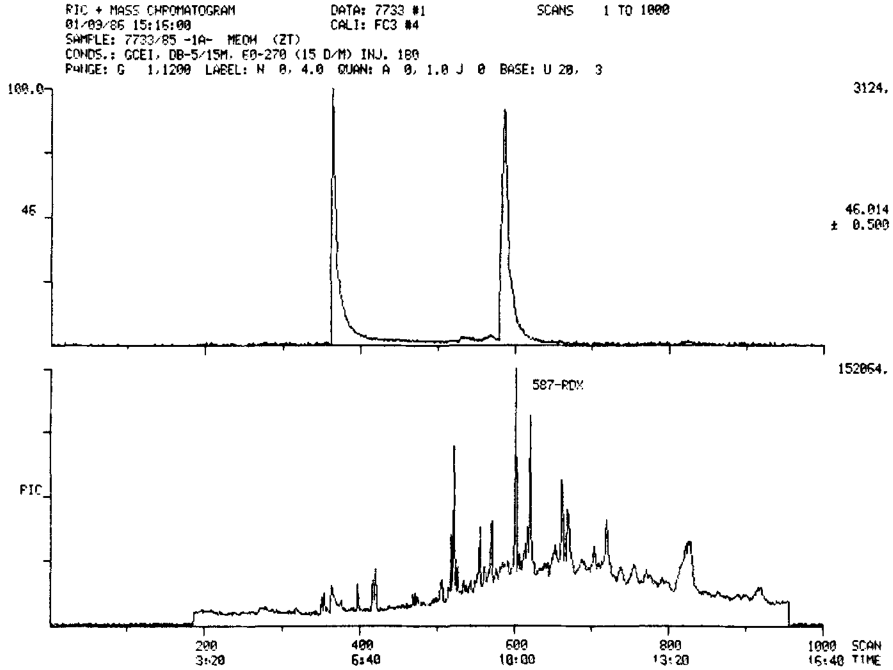

FIGURE 3
Total ion and mass chromatograms of a post-explosion extract (case 7733/85). The peak emerging after 587 seconds was identified as RDX (see Figure 4).

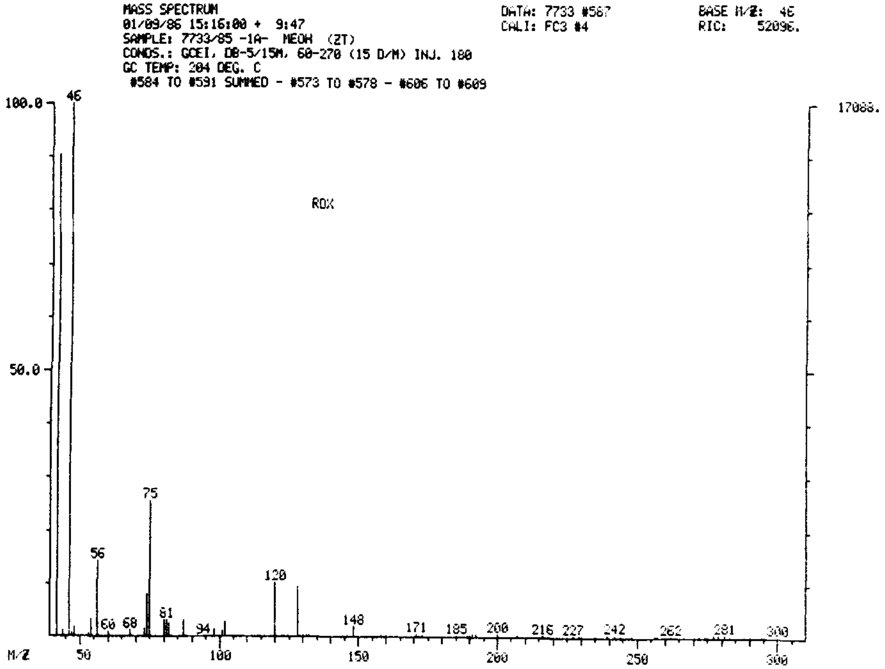

FIGURE 4
EI mass spectrum of the peak emerging after 587 seconds in Figure 3 (case 7733/85). RDX was identified.

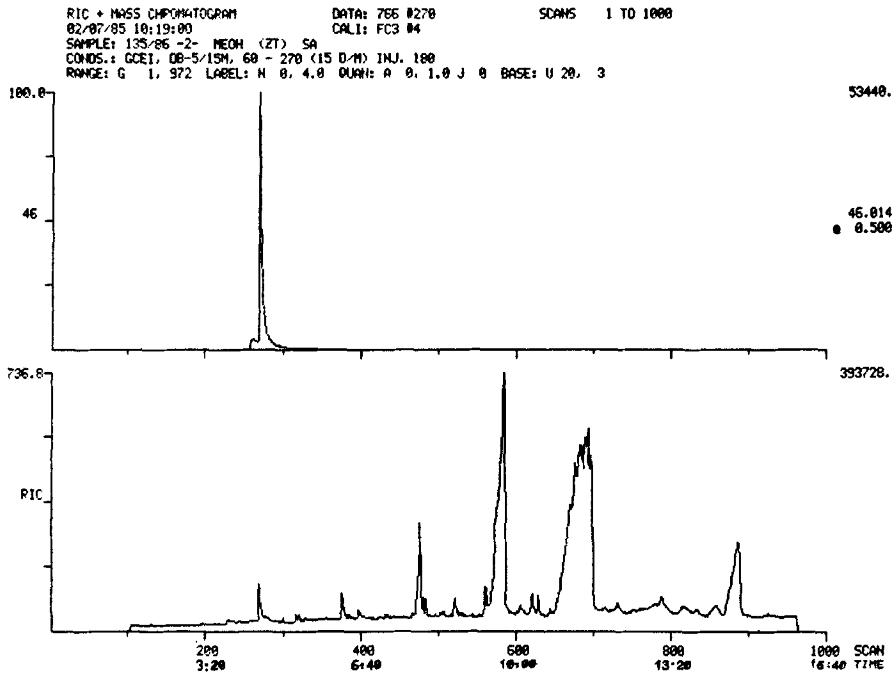

FIGURE 5
Total ion and mass chromatograms of a post-explosion extract (case 135/86). The peak emerging after 270 seconds was identified as NG.

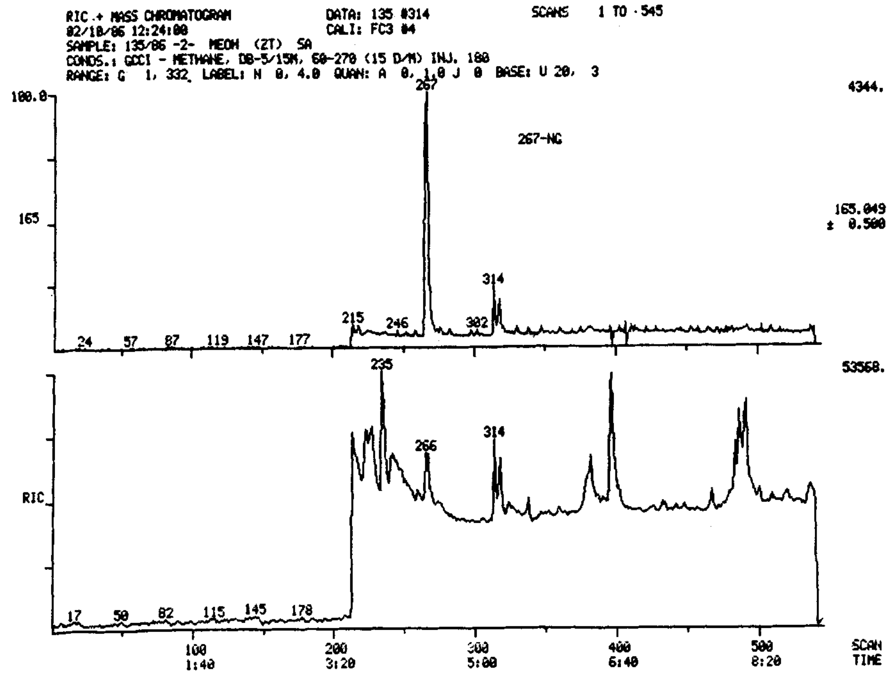

FIGURE 6
Total ion and mass chromatograms (CI-methane) of a post-explosion extract (case 135/86). The peak emerging after 267 seconds was identified as NG.

however, a major practical limitation related to the operation of LC/MS in a forensic, service-oriented laboratory. Most mass spectrometers in multi-function forensic laboratories operate in the GC/MS mode, analysing inflammable liquids, drugs and pesticides. It is not practical - although it may be so in the future - to alternate between GC/MS and LC/MS on an instrument which has much workload.

As this is the case in our laboratory we have chosen GC/MS as the method for positive identification in post-explosion analysis. The same column (see EXPERIMENTAL) is used for drugs, pesticides and explosives. We started our experiments in GC/MS of explosives with a 30 m capillary column.

Nitroaromatic compounds like TNT posed no problem but some nitrate esters (e.g. PETN) or nitramines (e.g. RDX) showed decreased sensitivity and possible decompositions. To minimize thermal decomposition we shifted to a 15 m column. Also, the injector was kept at a relatively low temperature (180°C). Under these conditions we succeeded to analyse 10 ng of most common explosives[3], including TNT, glycerine trinitrate (NG), ethylene glycol dinitrate (EGDN) and RDX. PETN was also analysed but with lower sensitivity. Tetryl decomposed thermally but the product - identified as N-methylpicramide[3] - emerged as a single chromatographic peak from which the original presence of tetryl could be deduced.

post-explosion analysis. From the ions separated by the first mass spectrometer, which come from both the impurities and the explosive, only pre-selected ions (according to the "suspected" explosive) will go into the collisionally activated decomposition (CAD) chamber. The ions formed by CAD will be separated by the second mass spectrometer and the resulting CAD spectra will characterize the explosive. Such procedure could save tedious cleaning of the post-explosion extract. But, as stated before, the method has yet to be tested in actual cases.

CONCLUSIONS

For years forensic laboratories have based their post-explosion analysis only on chromatographic methods, mainly TLC. Although papers about other analytical methods like MS or NMR for the analysis of explosives have appeared, the incorporation of these methods into routine work did not materialize. In the Israel Police Laboratory organic extractions from every post-explosion case are now subjected - following TLC screening - to GC/MS. The examples shown in this paper and elsewhere[3] show demonstrate that GC/MS is a successful method for post-explosion cases involving organic explosives, so the days of "TLC only" should be over.

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