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Capillary column gas chromatography/mass spectrometry of explosives

Tsippy Tamiri^a; Shmuel Zitrin^a

^a Division of Criminal Identification, Israel National Police, Jerusalem, Israel

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CAPILLARY COLUMN GAS CHROMATOGRAPHY/
MASS SPECTROMETRY OF EXPLOSIVES

Tsippy Tamiri and Shmuel Zitrin*

Division of Criminal Identification,
Israel National Police,
Jerusalem, Israel

ABSTRACT

Gas chromatography/mass spectrometry (GC/MS) using a 15 m long capillary column has been employed in our laboratory for the analysis of explosives. The technique is suitable for most of the common military explosives. Nitroaromatic compounds like TNT were analysed easily and with high sensitivity and so were the volatile nitrate esters like glycerine trinitrate. Success was also achieved in the analysis of PETN and RDX, which had previously been reported to pose problems under GC conditions. Tetryl was shown to decompose during the analysis but its decomposition product was well defined and could serve as evidence to the presence of tetryl. The method was successfully applied to post-explosion debris from actual cases.

* Author to whom correspondence should be addressed.

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INTRODUCTION

Many of the explosives encountered by the Israel Police laboratories are organic military explosives and therefore are analysed by the usual analytical methods for organic compounds. Analysis is performed both on unexploded explosives and on post-explosion debris. It is post-explosion analysis where special difficulties exist. The important steps before the analysis are collecting the right exhibits from the explosion site and using suitable extraction and purification processes. The samples are then subjected to thin layer chromatographic (TLC) analysis.¹ Although TLC often gives satisfactory results, it is our policy not to base an identification of an organic compound in a forensic laboratory on chromatographic results only.² Usually infrared (IR) spectrometry or mass spectrometry should be used to confirm the TLC results but this is not always feasible in post-explosion analysis. IR is often impractical: not only that the amount of the explosive is too small but it is often accompanied by large amounts of impurities from the debris, which obscure the IR spectrum. We report here the choice of GC/MS as a reliable method by which TLC results from post-explosion cases could be confirmed.

This choice raises the question of the thermal stability of explosives under GC conditions. Nitroaromatic compounds pose no problems in their GC analysis but possible thermal decompositions were reported for some nitrate esters and nitramines.³ The

working conditions described in this paper are suitable for the GC analysis of most common explosives.

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 μ m coating of DB-5. Temperatures were programmed from 70°C to 270°C at 15°C/min. Injector temperature was 180°C. Ion source temperature was 140°C. Scan range was 30-500 or 40-500 mass units. Scan rate was 1 scan/sec. Electron energy was 70 eV both in electron impact (EI) and chemical ionization (CI) modes. Helium was the GC carrier gas and methane was used as the CI reagent gas.

RESULTS AND DISCUSSION

Figure 1 shows the total ion chromatogram of the mixture of 6 common explosives: glycerine trinitrate (NG), 2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), 1,3,5-trinitro - 1,3,5-triazacyclohexane (RDX) and 2,4,6-trinitrophenylmethylnitramine (tetryl). All emerged from the column as well separated sharp chromatographic peaks. The separation was made on a 15 m capillary column (see EXPERIMENTAL). Poorer results were obtained on a 30 m column: PETN and RDX failed sometimes to emerge from the longer column.

FIC DATA: E.P100 #543 SCANS 1 TO 798
 05 04/86 15:02:00 CALI: FC2 #1
 SAMPLE: MIX STD EXP 100 MG
 COMPS.: GCCL: 08-5/15M: 78-278 (15 0 M) INJ. 128
 RANGE: G 1.1137 LABEL: N 9. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3

84992.

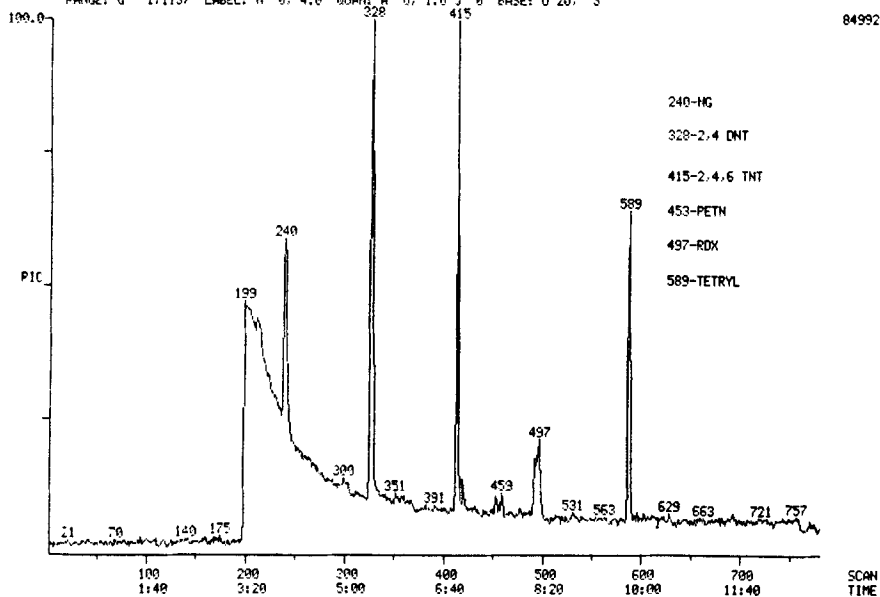


FIGURE 1

Total ion chromatogram of a mixture containing six explosives.

It seems that the use of shorter columns minimizes the thermal decomposition of explosives with greater thermal instability. The loss of resolution caused by the use of the 15 m column is not a major problem and conditions can be found in which a satisfactory separation is achieved on the short column. In most explosive analyses the GC column serves mainly as a selective entrance to the ion source of the mass spectrometer so that mass spectrometry could be applied to post-explosion extracts.

Figure 2 shows the total ion chromatogram of a mixture containing 10 ng of each of the above listed explosives: all but PETN emerged as distinct chromatographic peaks from which complete EI mass spectra could be recorded.

A typical post-explosion total ion chromatogram is shown in the lower part of Figure 3. The peak emerging after 321 seconds belongs to TNT, as was proven by its EI mass spectrum. The upper part of Figure 3 shows the mass chromatogram for the m/z 210 ions, which are the most abundant ions in the EI mass spectrum of TNT. The mass chromatogram is helpful when there is an a priori indication - often based on TLC results - about the identity of the explosive. In this way the chromatographic peak of the explosive is immediately located and its mass spectrum recorded. The advantage of the mass chromatogram mode is demonstrated in another post-explosion extract (Figure 4), where it is evident

CTC DATA: E.F10 #1 SCANS 1 TO 800
 DATE: 84 05 15:23:00 CHLT: FC3 #4
 SAMPLE: NI: STD E*P 10 NG
 COMPS.: GC/EL: DE-5/15M, 70-270 (15 D-M) INJ. 100
 PULSE: G 1.1059 LABEL: N 0, 4.0 DURAN: A 0, 1.0 J 0 BASE: U 20, 3

53988.

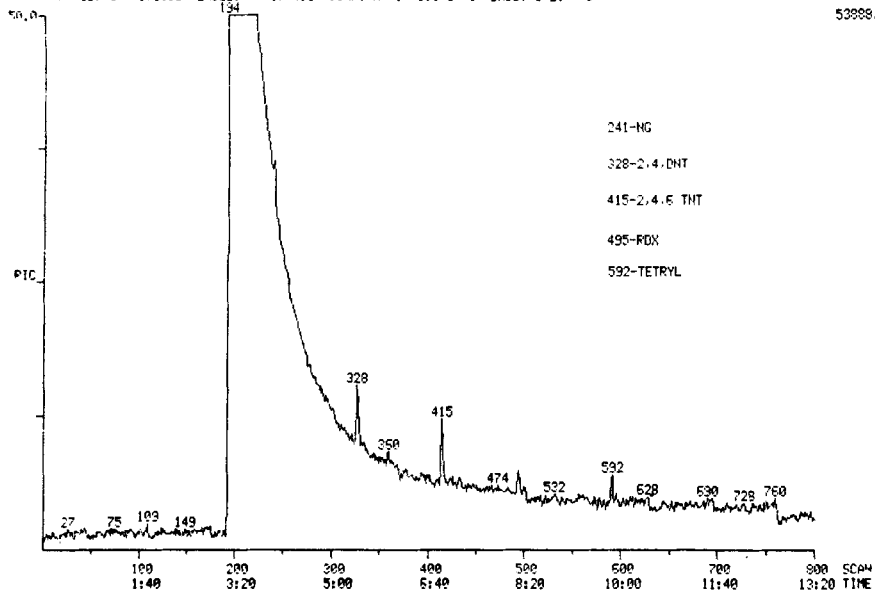


FIGURE 2

Total ion chromatogram of 10 ng of each of the following explosives: NG, 2,4-DNT, TNT, PETN, RDX and tetryl. All but PETN were detected.

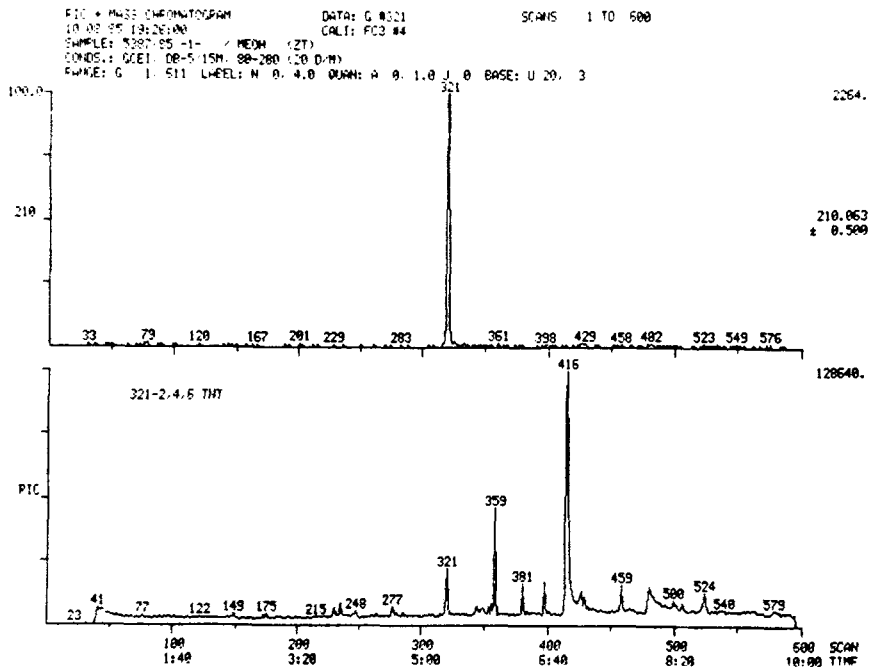


FIGURE 3
 Total ion chromatogram of a post-explosion extract (case 5387/85).
 The peak emerging after 321 seconds was identified as TNT.

FIC - MASS CHROMATOGRAM DATA: 16772 #1 SCANS 1 TO 600
 MS 05 86 11:14:00 CALI: FC3 #4
 SAMPLE: 1677 86 -2- MICH (ZT) SA
 COME: G0EL-DB-S/ISM: 70-279 (15 D-M) INJ. 180
 NAME: G 1:1145 LABEL: H 0. 4.0 QUAN: A 0. 1.0 J 0 BASE: U 20. 3

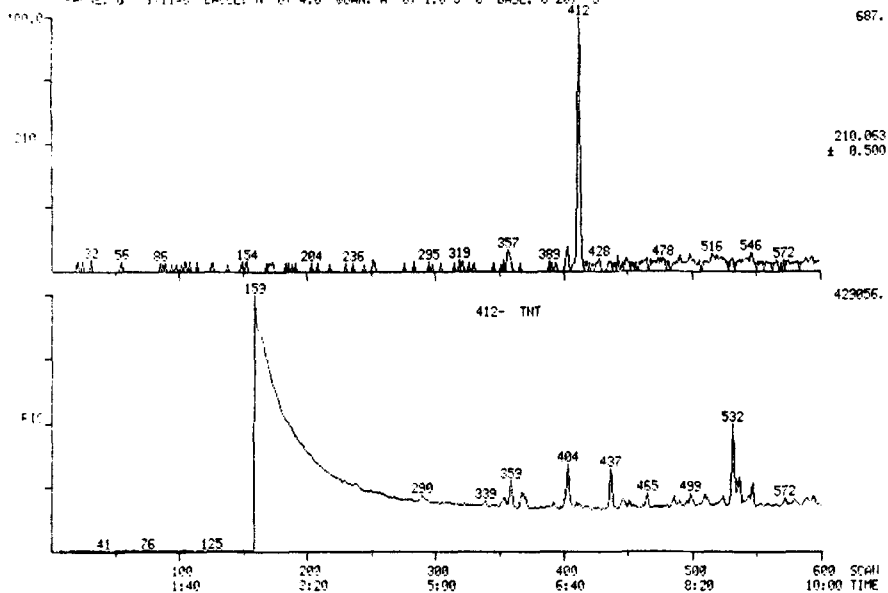


FIGURE 4
 Total ion and mass chromatograms of a post-explosion extract (case 1667/86). The peak emerging after 412 seconds was identified as TNT.

that by looking only at the total ion chromatogram the presence of TNT could be missed. Using the m/z 210 mass chromatogram the peak belonging to TNT was located and its EI mass spectrum recorded (Figure 5). A similar example is taken from a case where a bomb was exploded on the roadside near the city of Nablus. The chromatographic peak of RDX is negligible in the total ion chromatogram (Figure 6; marked with an arrow) but it was located by the m/z 30 and 46 mass chromatograms. Its complete mass spectrum is shown in the upper part of Figure 6.

Many nitrate esters have very similar EI mass spectra. Thus, the EI mass spectra of NG, ethylene glycol dinitrate (EGDN) and PETN contain characteristic ions at m/z 30 (NO^+), 46 (NO_2^+) and 76 (CH_2NO_2^+) but no molecular ions⁴. This causes difficulties in the identification of nitrate esters by EIMS. In order not to base their identification on GC retention times only, we use CIMS for the identification of nitrate esters. CI mass spectra of nitrate esters⁵ contain molecular weight information and the different esters are easily distinguished. It should be noted, however, that GC/CIMS of explosives on our instrument and under our working conditions (See EXPERIMENTAL) is less sensitive than GC/EIMS.

MASS SPECTRUM
 06:05:06 11:14:00 + 6:52
 SAMPLE: 1677/86-2- MEOH (ZT) 5A
 COMOS.: GC/EL, DB-5/15M, 70-270 (15 D/M) INJ, 180
 GC TEMP: 173 DEG. C
 #311 TO #413 SUMMED - #409 TO #409 - #415 TO #415
 DATA: 16772 #412
 CALI: FC3 #4
 BASE M/Z: 210
 RIC: 16272.

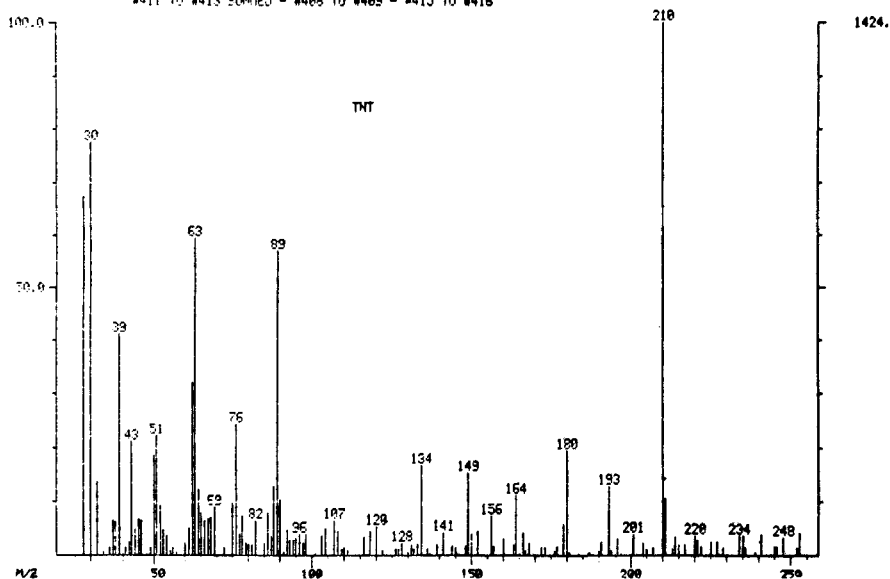


FIGURE 5
 EI mass spectrum of the peak emerging after 412 seconds (Figure 4), corresponding to the EI mass spectrum of TNT.

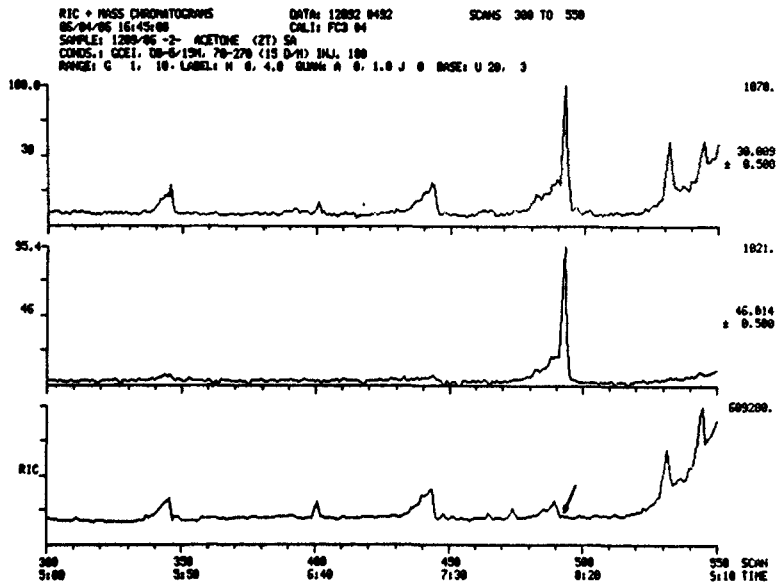
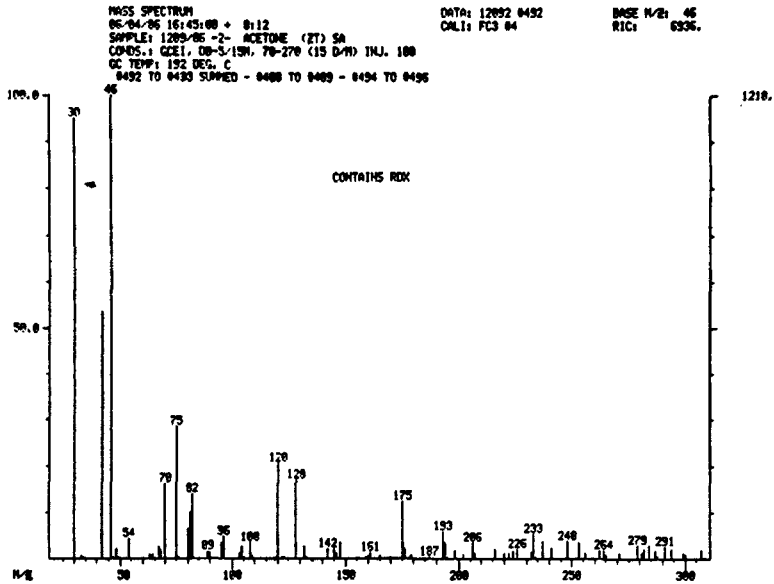
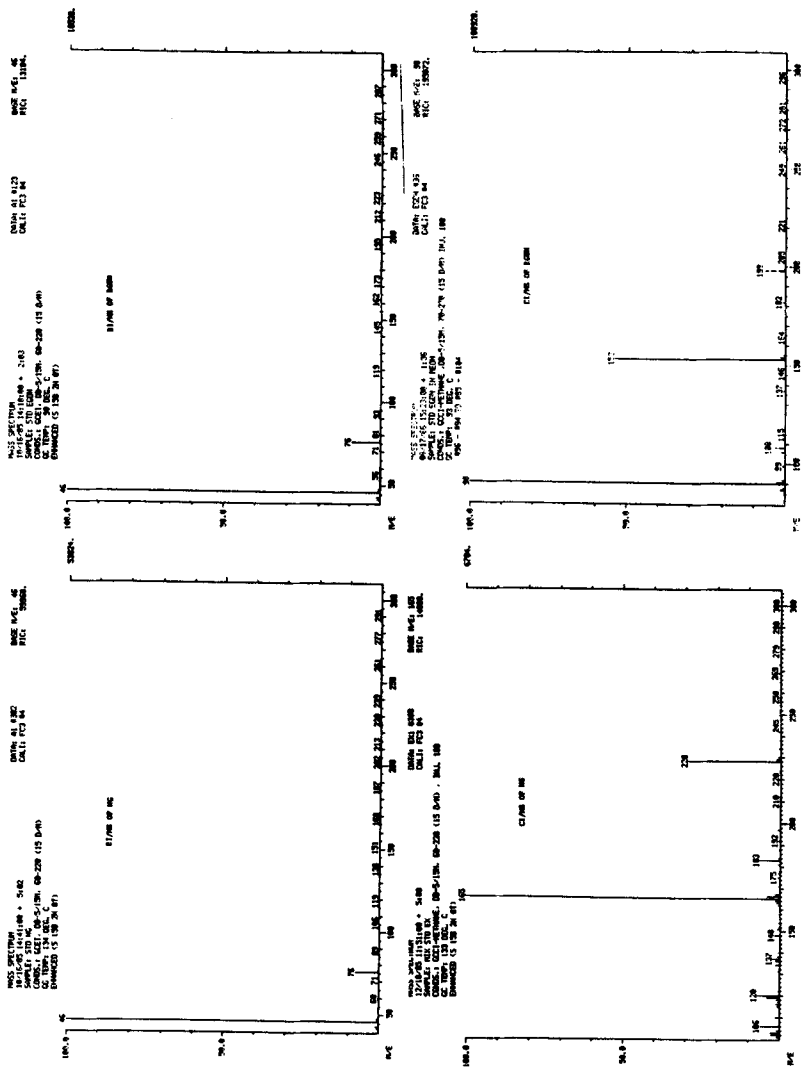


FIGURE 6
 Total ion and mass chromatograms of a post-explosion extract (case 1209/86) and EI mass spectrum of the peak emerging after 492 seconds, identified as RDX.

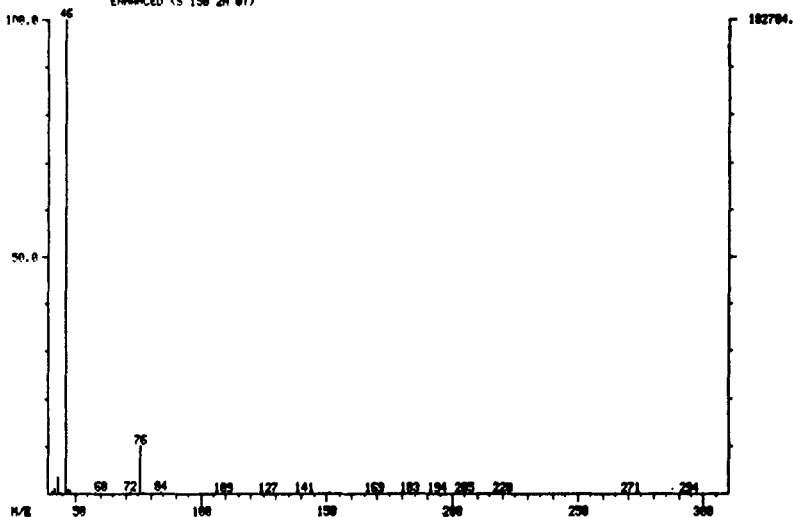
The similarity between the EI mass spectra of NG and EGDN as well as the differences in their CI-methane mass spectra are demonstrated in Figure 7. The major fragment ions in the CI-methane spectra are at m/z 165 and m/z 90 for NG and EGDN, respectively. They result by the loss of nitric acid from the corresponding protonated molecular ions, a well known process in the CIMS of nitrate esters.^{5,6} The use of GC/EIMS and GC/CIMS for post-explosion analysis involving a nitrate ester explosive is demonstrated in Figures 8 and 9, respectively. The extract was taken from the debris left by a bomb which had been exploded near Tel Aviv University. Following the TLC results, the presence of NG was first confirmed by its GC/EIMS data, shown in Figure 8. However, the EI mass spectrum is not unique enough and other nitrate esters cannot be definitely excluded. The GC/CIMS data, shown in Figure 9, give conclusive evidence for the presence of NG.

Another example involving the identification of NG was the post-explosion analysis of an improvised explosive concealed in a litter can near the Government House in the city of Gaza. Figure 10 shows the total ion chromatogram of the extract, using GC/EIMS. NG appeared as a very small chromatographic peak emerging after 297 seconds; again, it was conclusively identified by GC/CIMS. The main chromatographic peak in Figure 10 was identified as ethyl centralite, a common stabilizer in smokeless

FIGURE 7
EI and CI-methane mass spectra of NG and EGDN, using capillary
GC/MS.



MASS SPECTRUM DATA: 765 8274 BASE P/E: 46
 02/07/85 9:51:00 + 4:34 CALI: FC3 84 RIC: 217344
 SAMPLE: 8137/85 -2- MEOM (ZT) SA
 COND.: GC/EL. DB-5/15M, 60-270 (15 D/M) INJ. 100
 GC TEMP: 127 DEG. C
 ENHANCED (S 150 2H 0T)



RIC + MASS CHROMATOGRAM DATA: 765 8274 SCANS 1 TO 700
 02/07/85 9:51:00 CALI: FC3 84
 SAMPLE: 8137/85 -2- MEOM (ZT) SA
 COND.: GC/EL. DB-5/15M, 60-270 (15 D/M) INJ. 100
 RANGE: C 1.754 LABEL: H 0, 4.0 GAIN: A 0, 1.0 J 0 BASE: U 20, 3

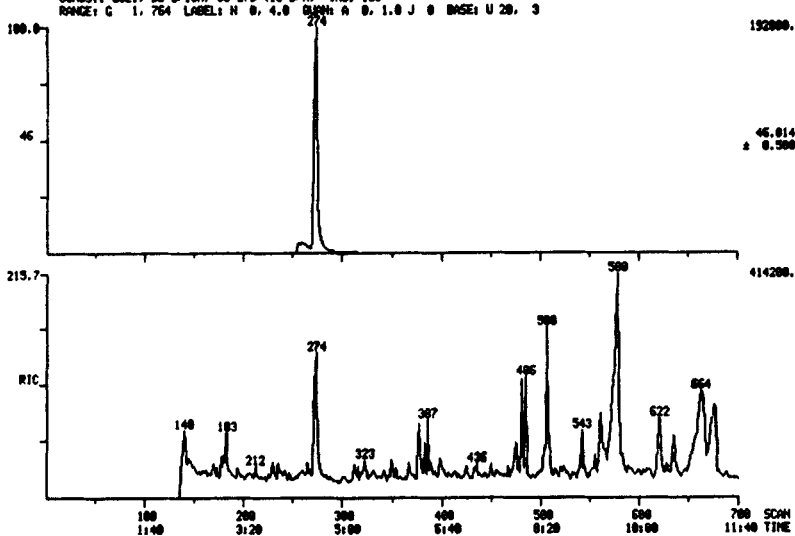
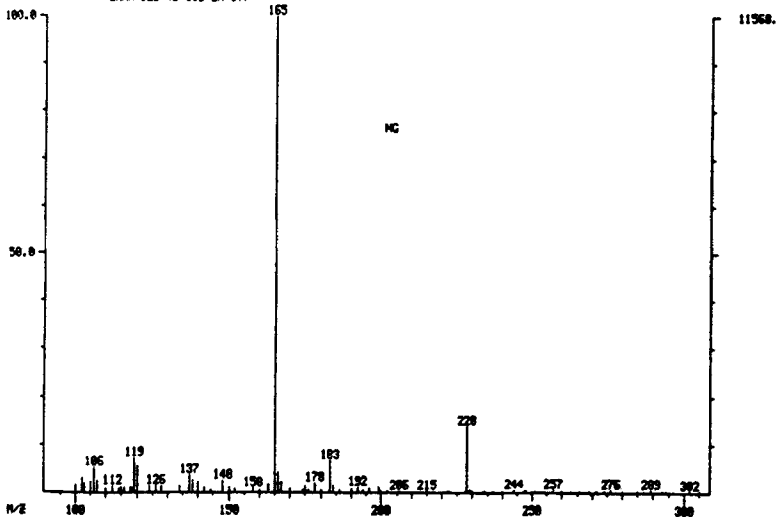


FIGURE 8

Total ion and mass chromatograms of a post-explosion extract (case 8137/85) and EI mass spectrum of the peak emerging after 274 seconds, identified as NG.

MASS SPECTRUM
 02/18/85 11:54:00 + 4:38 DATA: 8137 8278 BASE M/E: 163
 SAMPLE: 8137/85 -2- METH (2T) SA CALI: FC3 04 RIC: 25312
 COND: 1 GC1 - METHANE, 00-5/131, 60-270 (15 D/N) INJ. 100
 GC TEMP: 127 DEG. C
 ENHANCED (5 150 24 0T)



RIC + MASS CHROMATOGRAMS DATA: 8137 8283 SCANS 1 TO 700
 02/18/85 11:54:00 CALI: FC3 04
 SAMPLE: 8137/85 -2- METH (2T) SA
 COND: 1 GC1 - METHANE, 00-5/131, 60-270 (15 D/N) INJ. 100
 RANGE: 1. 13 LABEL: H 0. 4.0 QUANT: 0. 1.0 J 0 BASE: U 20. 3

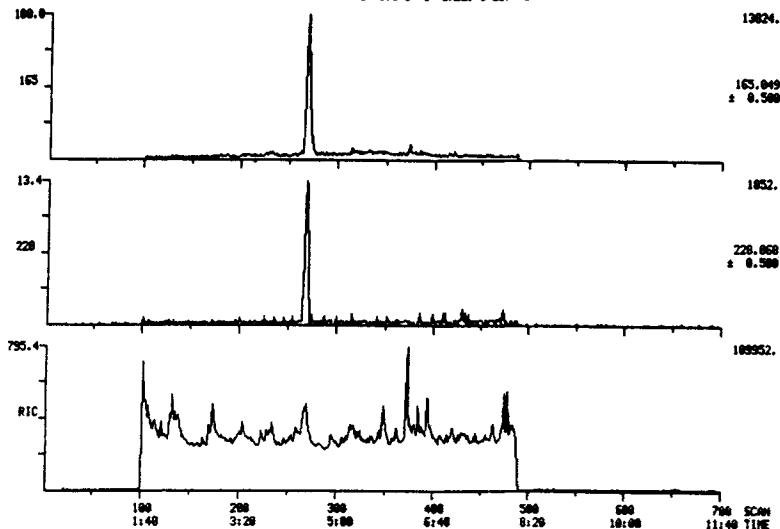


FIGURE 9

Total ion and mass chromatograms (CI-methane) of a post-explosion extract (case 8137/85) and CI-methane mass spectrum of the peak emerging after 270 seconds, identified as NG.

PIC DATA: STD2 #598 SCANS 1 TO 1200
12-08-85 11:35:00 CALL: FC3 #4
SAMPLE: 6527/85-NEOH (2T)
CONDENS.: OCE1, 08-5:15H, 50-220 (150-H) INJ.100
PULSE: G 1.1200 LABEL: N 0, 4.0 DURH: A 0, 1.0 J 0 BASE: U 20, 3

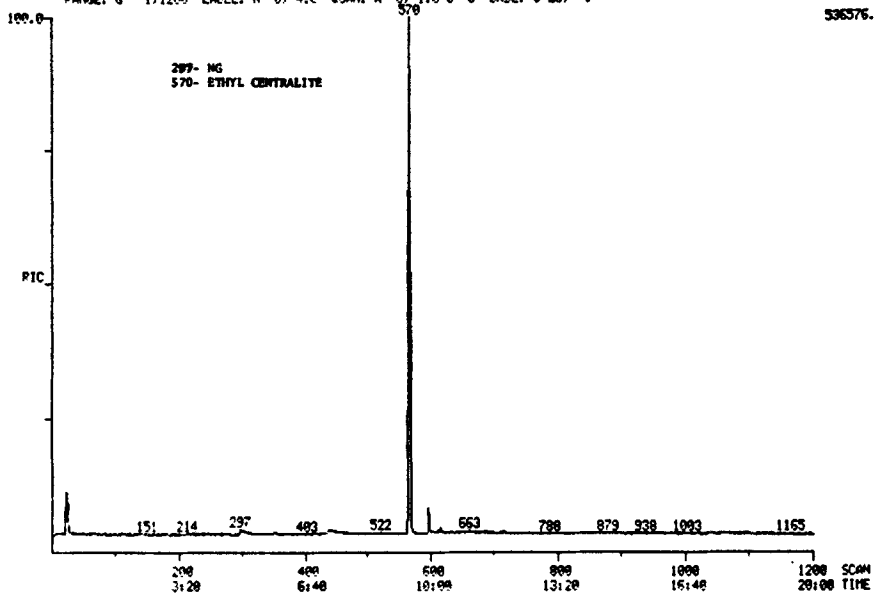


FIGURE 10

Total ion chromatogram of a post-explosion extract (case 6527/86). The peaks emerging after 297 and 570 seconds were identified as NG and ethyl centralite, respectively.

powders. Its presence indicated that the origin of the NG was smokeless powder rather than dynamite.

Smokeless powder is used by terrorists in Israel as the main charge in home-made improvised explosives. It is collected from ammunition and when suitably confined in a pipe it serves as an explosive charge. Compared with the unexploded propellant, the ratio between the amounts of ethyl centralite and NG in Figure 10 seems unusually large, even after allowing for possible thermal decomposition of NG and lower sensitivity in its detection by total ion current. A possible explanation could be that NG decomposes during the explosion (or burning) of smokeless powder while ethyl centralite does not.

It is evident from Figure 2 that the sensitivity of GC/EIMS for PETN is not as high as for the other explosives studied. As stated above, we use GC/CIMS to confirm the presence of nitrate esters and this - under our working conditions - lowers the sensitivity even more. As a result our record in confirming TLC results for PETN by GC/MS has not been satisfactory, although we have had some success.⁷ In several cases where GC/MS failed to confirm TLC results indicating PETN we successfully obtained its mass spectrum by direct probe insertion. In these cases cleaning the post-explosion extract on a chromatographic column is a necessary prerequisite. The CI-methane spectrum of an extract from debris left after a safe in a diamond-polishing factory had been

blown up is shown in Figure 11. The extract was cleaned on a florisil column, concentrated and then introduced directly into the mass spectrometer via the direct probe. PETN was conclusively identified by the resulting CI-methane spectrum. The ions at m/z 317 and m/z 254 correspond to $[M+H]^+$ and $[M+H-HNO_3]^+$, respectively. Two unusual adduct ions are observed at m/z 346 and m/z 362, corresponding to $[M+NO]^+$ and $[M+NO_2]^+$, respectively.⁵⁻⁷

The chromatographic peak attributed to tetryl in Figure 1 gave an EI spectrum (Figure 12) which was different from previously published^{6,8,9} EI mass spectra of tetryl. The spectrum obtained by GC/CIMS also differed from the previously published^{5,6,10} spectra and indicated a possible molecular weight of 242. As the previously reported spectra were obtained by using a direct probe, we assumed that tetryl decomposed during its GC analysis. The EI and CI-methane mass spectra of the product emerging from the column during the GC/MS of tetryl could correspond to N-methylpicramide. We prepared N-methylpicramide by hydrolysing tetryl.¹¹ Its EI and CI mass spectra were similar to those obtained by GC/MS of tetryl, except that the synthesized product contained also some picramide. The hydrolysis of tetryl during the GC analysis could take place at the injector, which was held at relatively high temperatures. The hydrolysis scheme is shown in Figure 13.

MASS SPECTRUM
12/17/85 9:15:00 + 2:03
SAMPLE: 6935/85 1 AFTER COL.
COND.: SPCI-METHANE
GC TEMP: 127 DEG. C
#123 - #87 - #160

DATA: Z1 #123
CALI: FC3 #4

BASE M/E: 254
RIC: 53632.

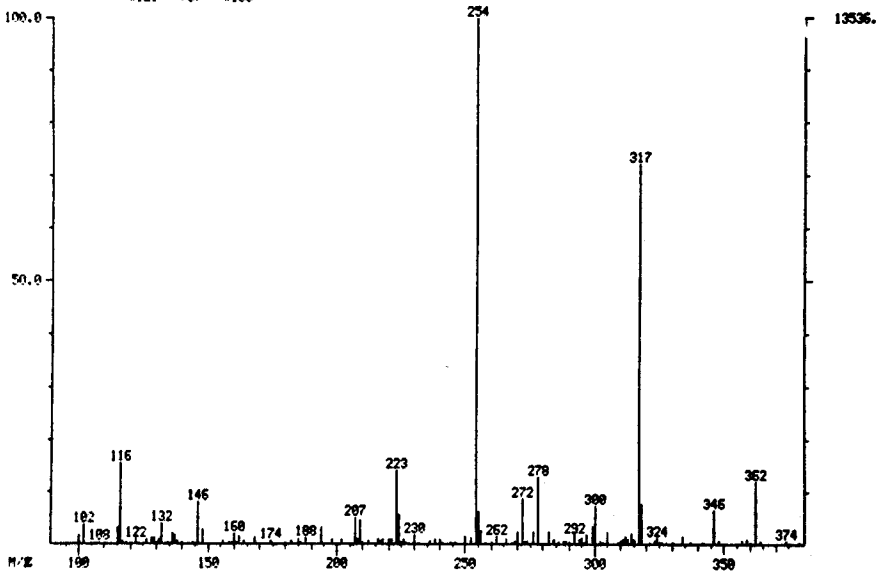


FIGURE 11

CI-methane mass spectrum (using direct probe) of a post-explosion extract (case 6935/85). PETN was identified.

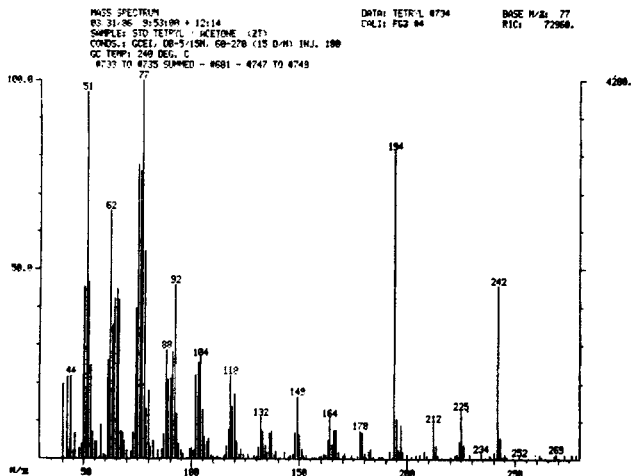


FIGURE 12
 EI mass spectrum of the chromatographic peak emerging in GC/MS of tetryl. It was identified as N-methylpicramide.

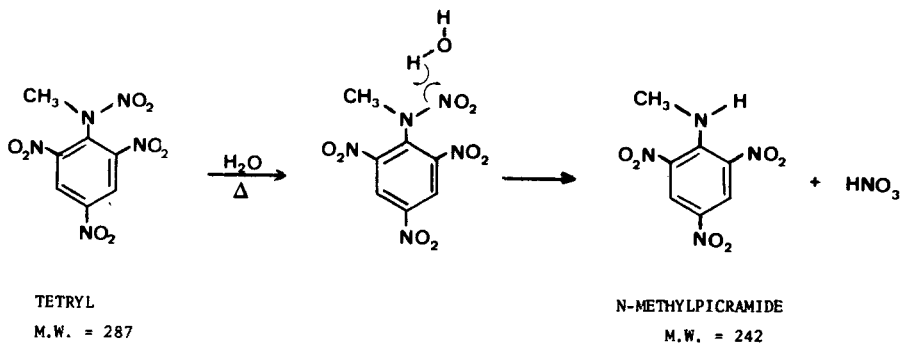


FIGURE 13
 The hydrolysis of tetryl to N-methylpicramide.

RIC DATA: 4512 #594 SCANS 1 TO 1000
 06/19/86 13:48:00 CALL: FC3 #4
 SAMPLE: 451/84 -2- MEDM (ZT) SA
 COND: GCE1, DB-5/15M, 70-270 (15 D/M) INJ. 100
 RANGE: G 1: 685 LABEL: H 0, 4.0 QUAN: A 0, 1.0 J 0 BASE: U 20, 3

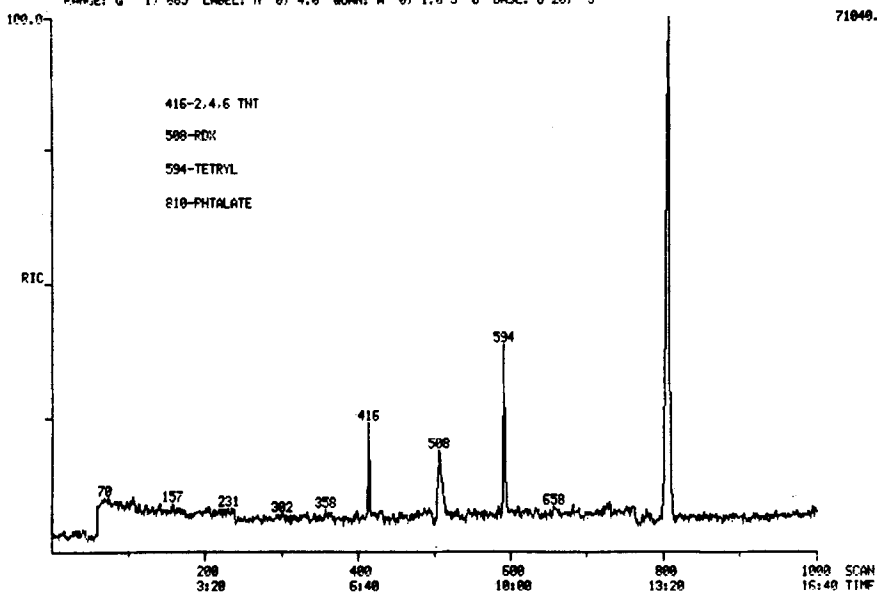


FIGURE 14

Total ion chromatogram of a post-explosion extract (case 451/84). The peak emerging after 594 seconds was identified as N-methylpicramide, indicating the presence of tetryl. The peaks emerging after 416 and 508 seconds were identified as TNT and RDX, respectively.

Thus, the identification of N-methylpicramide by GC/MS, combined with TLC results indicating tetryl could serve as evidence for the presence of tetryl. Figure 14 shows the total ion chromatogram of a post-explosion extract from the residues of a bomb which had been detonated on a roadside in Lebanon. The N-methylpicramide, identified by its EI mass spectrum, indicated the original presence of tetryl. RDX and TNT were also identified in this extract.

CONCLUSIONS

The "real life" examples discussed above prove that although some explosives are thermally labile, GC/MS is an excellent practical method for a reliable post-explosion identification of explosives.

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REFERENCES

1. M.A. Kaplan and S. Zitrin, J. Assoc. off. Anal. Chem. 60, 619 (1977).
2. S. Zitrin, J. Energetic Materials, this issue.

3. J. Yinon and S. Zitrin, "The Analysis of Explosives", Pergamon Press, Oxford, 1981 Chapter 6 p. 86.
4. R.T.M. Fraser and N.C. Paul, J. Chem. Soc. (B), 659 (1968).
5. C.T. Pate and M.H. Mach, Int. J. Mass Spectrom. Ion Phys. 26, 267 (1978).
6. S. Zitrin and J. Yinon, Advances in Mass Spectrom. in Biochem. and Medicine, 1, 369 (1976).
7. A. Basch, Y. Margalit, S. Abramovich-Bar, Y. Bamberger, D. Dafna, T. Tamiri and S. Zitrin, J. Energetic Materials, this issue.
8. F. Volk and H. Schubert, Explosivstoffe, 16, 2 (1968).
9. S. Zitrin and J. Yinon, Advances in Mass Spectrom. 7 , 1457 (1978).
10. S. Zitrin and J. Yinon, Org. Mass Spectrom. 11, 388 (1976).
11. T.L. Davis and C.F.H. Allen, J. Am. Chem. Soc. 36 , 1063 (1924).