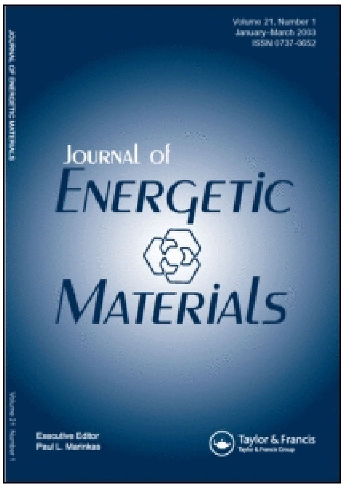

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Decomposition products of petn in post explosion analysis

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DECOMPOSITION PRODUCTS OF PETN
IN POST EXPLOSION ANALYSIS

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ABSTRACT

TLC of post-explosion debris showed that in some cases PETN was accompanied by other compounds which reacted with Griess reagent. The possibility that these compounds could be lower nitrate esters of pentaerythritol (tri- , di- and mononitrate) was examined. Lower nitrate esters were obtained by hydrolysis of PETN and their structures were determined - following separation - by mass spectrometry and NMR. Chromatographic data of these esters matched data of the compounds which accompanied PETN in certain post-explosion cases. The dinitrate and trinitrate esters of pentaerythritol were isolated from post-explosion extracts and their structures confirmed by mass spectrometry and NMR.

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INTRODUCTION

Post-explosion analysis in the Israel Police Laboratory is usually based on the identification of the original explosive rather than its decomposition products.[1] With few exceptions - such as the identification of thiocyanate as an indication to the original presence of black powder[2] - this is the general attitude among forensic explosive analysts. The reason is that many of the decomposition products either escape as gases or are common inorganic salts (e.g. carbonates) from which the type of the original explosive cannot be deduced. In this work we report the appearance of decomposition products which are structurally related to the original explosive - pentaerythritol tetranitrate (PETN). Being unaware of their existence in post-explosion debris could lead to possible errors.

The appearance of decomposition products of glycerine trinitrate in post-explosion extracts was first noticed by Helie-Calmet and Forestier.[3] They found di- and mononitrate esters of glycerine in post-explosion extracts when glycerine trinitrate was involved in the explosion. They prepared the two isomeric glycerine mononitrates and the two isomeric glycerine dinitrates. In all TLC systems tried the R_f of the lower nitrate esters of glycerine corresponded to the R_f of the spots which accompanied glycerine trinitrate in some post-explosion cases. They found similar but less common behaviour in some post-explosion analyses involving PETN.

EXPERIMENTAL

Methods

Thin Layer Chromatography (TLC) . TLC plates were 10 X 20 cm aluminium plates precoated with silica gel 0.2 mm thick (SI F Riedel de Haen). The developing solvent was (unless otherwise stated) trichloroethylene - acetone (4:1). The developed plates were sprayed with 3% KOH in ethanol followed by Griess reagent, which was prepared by mixing equal volumes of two solutions. a) 5.5 g N-1-naphthylethylenediamine in 100 ml nitrite-free H_3PO_4, diluted with water to 1 liter. b) 80 g sulfanilamide in 100 ml nitrite-free H_3PO_4, diluted with water to 1 liter.

Liquid Chromatography (LC) . The LC system included LKB 2152 HPLC controller, 2140 LKB rapid spectral detector and 2150 HPLC pump. Separations were carried out in a reversed phase mode on a 250 X 4 mm (I.D.)column packed with C_{18} Lichrocart (Merck; particles size 7μm). The mobile phase was methanol-water (65:35), operated at a flow rate of 1 ml/min. The solvents were degassed prior to the analysis. UV detection was made at $\lambda =$ 207 nm.

Mass Spectrometry (MS) . Mass spectrometry was carried out in the chemical ionization (CI) mode on a) a DuPont 21490B single focusing magnetic mass spectrometer, using isobutane as reagent gas. b) a Finnigan 4500 quadrupole mass spectrometer, using methane as reagent gas. Samples were introduced directly into the ion source whose temperatures were 200-250°C (in a) and 140°C (in b).

Nuclear Magnetic Resonance (NMR) Spectrometry Proton magnetic resonance spectrometry was carried out on a Bruker WM-250 instrument, using 250 MHz frequency. The solvent was acetone-d_6

Materials

Pentaerythritol tetranitrate (PETN) was isolated from a detonating cord. Its purity was determined by TLC and infrared (IR) spectrometry.

Hydrolysis of PETN was based on a work of Dicarlo et al.[4] 100 ml of dioxane-water (82:18) and 1 ml conc. HCl were added to 1 g PETN and the mixture was refluxed for 6 hours. Dioxane (50 ml) and ethanol (50 ml) were then added and the mixture was concentrated to~20 ml. Solid $Ca(OH)_2$ and dioxane (50 ml) were added, the mixture was evaporated almost to dryness and 50 ml of ethanol were added. Most unreacted PETN, crystallized and was filtered out. The solution was evaporated to dryness and the hydrolysis products were separated on a silica gel chromatographic column. Residual PETN was eluted with CH_2Cl_2; pentaerythritol trinitrate was eluted with CH_2Cl_2 - acetone (96:4) and pentaerythritol dinitrate was eluted with CH_2Cl_2 - acetone (90:10). The purity of the trinitrate and the dinitrate was confirmed by TLC and CIMS. A fraction containing pentaerythritol mononitrate was eluted with CH_2Cl_2 - 2-propanol (90:10) but the pure mononitrate was not isolated.

RESULTS AND DISCUSSION

Figure 1 shows a TLC plate with an acetone-extract from a post-explosion case. The developing solvent was 1,2-dichloroethane - acetonitrile (9:1) and visualization was made by Griess reagent. The highest spot corresponds to PETN. The lower spots could originate from compounds present in the original explosive (e.g. RDX) or from decomposition products of PETN. The difference is especially important because an original mixture of PETN and RDX, known as "Semtex", is widely used by terrorists.

Figure 2 shows a TLC plate of the same extract in a different solvent system: trichloroethylene - acetone (4:1). It is evident that the second highest spot in the post-explosion extract does not correspond to RDX.

Figure 3 shows a TLC plate with an acetone-extract from a post-explosion case involving PETN and the hydrolysis products of PETN. The similarity is obvious.

The hydrolysis products of PETN (1) are pentaerythritol trinitrate (2), pentaerythritol dinitrate (3), pentaerythritol mononitrate (4) and pentaerythritol (5). Their structures are shown in Scheme 1.

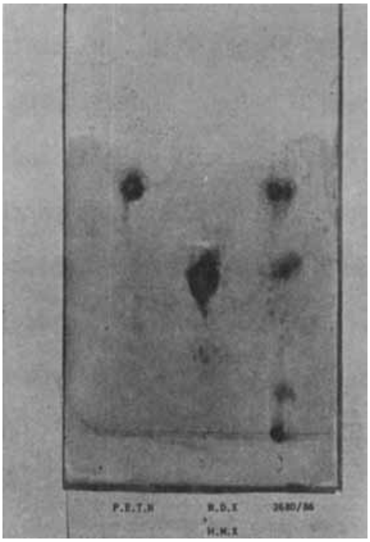


FIGURE 1
Thin layer chromatogram of an acetone-extract from a post-explosion case (developing solvent: 1,2-dichloroethane - acetonitrile 9:1).

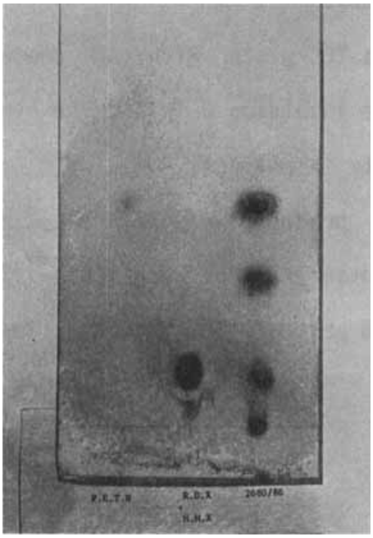


FIGURE 2
Thin layer chromatogram of an acetone-extract from a post-explosion case (developing solvent: trichloroethylene - acetone 4:1).

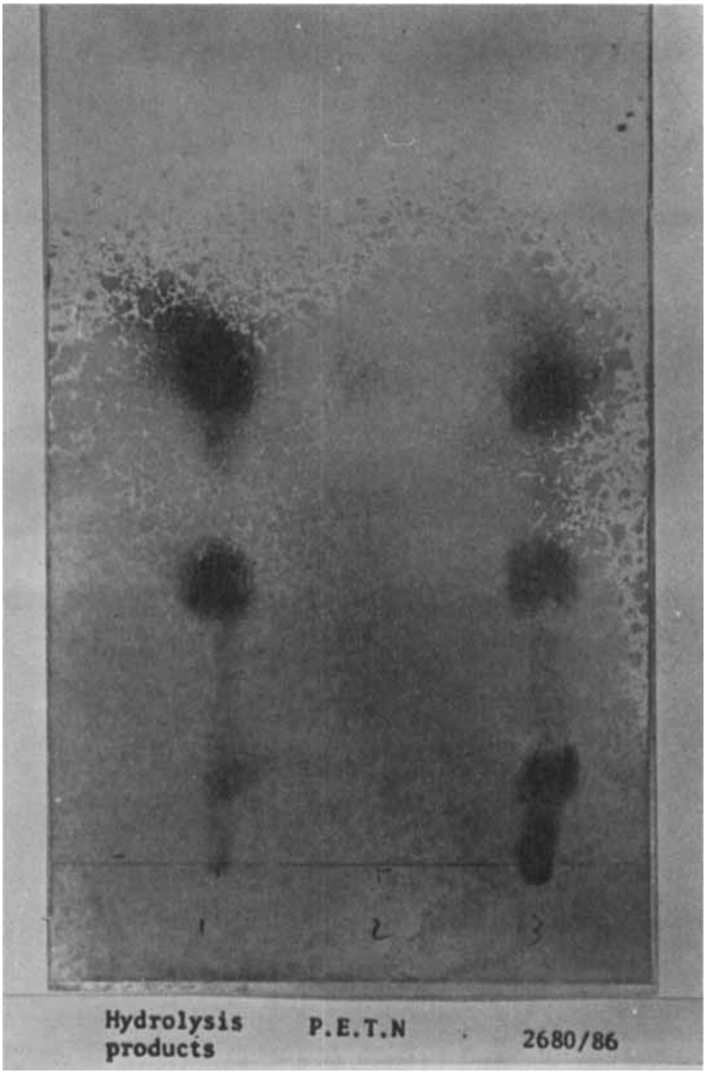
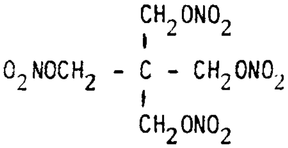
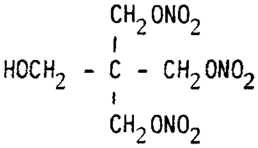


FIGURE 3
Thin layer chromatogram of an acetone-extract from a post-explosion case and of the hydrolysis mixture of PETN (developing solvent: trichloroethylene - acetone 4:1).



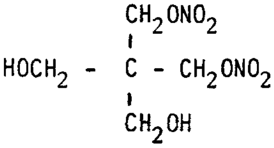
$$\begin{array}{ccccc} & & \mathrm{CH_2ONO_2} & & \\ & & | & & \\ \mathrm{O_2NOCH_2} & - & \mathrm{C} & - & \mathrm{CH_2ONO_2} \\ & & | & & \\ & & \mathrm{CH_2ONO_2} & & \end{array}$$

Pentaerythritol tetranitrate(PETN,1)



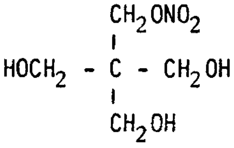
$$\begin{array}{ccccc} & & \mathrm{CH_2ONO_2} & & \\ & & | & & \\ \mathrm{HOCH_2} & - & \mathrm{C} & - & \mathrm{CH_2ONO_2} \\ & & | & & \\ & & \mathrm{CH_2ONO_2} & & \end{array}$$

Pentaerythritol trinitrate(2)



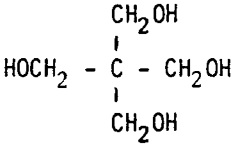
$$\begin{array}{ccccc} & & \mathrm{CH_2ONO_2} & & \\ & & | & & \\ \mathrm{HOCH_2} & - & \mathrm{C} & - & \mathrm{CH_2ONO_2} \\ & & | & & \\ & & \mathrm{CH_2OH} & & \end{array}$$

Pentaerythritol dinitrate (3)



$$\begin{array}{ccccc} & & \mathrm{CH_2ONO_2} & & \\ & & | & & \\ \mathrm{HOCH_2} & - & \mathrm{C} & - & \mathrm{CH_2OH} \\ & & | & & \\ & & \mathrm{CH_2OH} & & \end{array}$$

Pentaerythritol mononitrate (4)



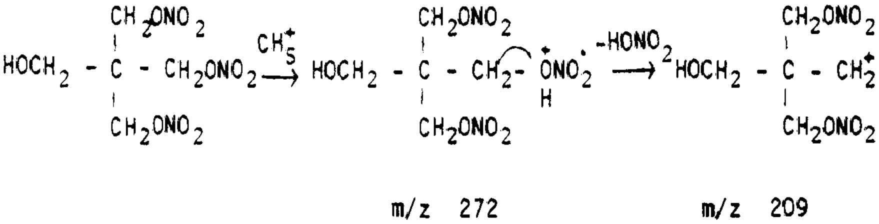
$$\begin{array}{ccccc} & & \mathrm{CH_2OH} & & \\ & & | & & \\ \mathrm{HOCH_2} & - & \mathrm{C} & - & \mathrm{CH_2OH} \\ & & | & & \\ & & \mathrm{CH_2OH} & & \end{array}$$

Pentaerythritol (5)

Scheme 1

The next steps were the isolation and identification of the hydrolysis products of PETN. Only the trinitrate 2 and the dinitrate 3 were isolated from the hydrolysis mixture in a relatively pure form.

The chemical ionization (CI) mass spectra of 2 and 3 were taken, using isobutane and methane as reagent gases. With isobutane, most of the ion current was concentrated in the $[M+H]^+$ ions, at m/z 272 and 227 in the spectra of 2 and 3, respectively. The CI-methane spectra, shown in Figures 4 and 5, include - beside abundant $[M+H]^+$ ions - also some fragment ions. The ions at m/z 209 (Figure 4) and 164 (Figure 5) result by the loss of nitric acid from the corresponding $[M+H]^+$ ions of 2 and 3. The process is known to occur in nitrate esters under CI conditions[5]. The loss of HNO_3 from the protonated molecule of 2 is shown in Scheme 2.



Scheme 2

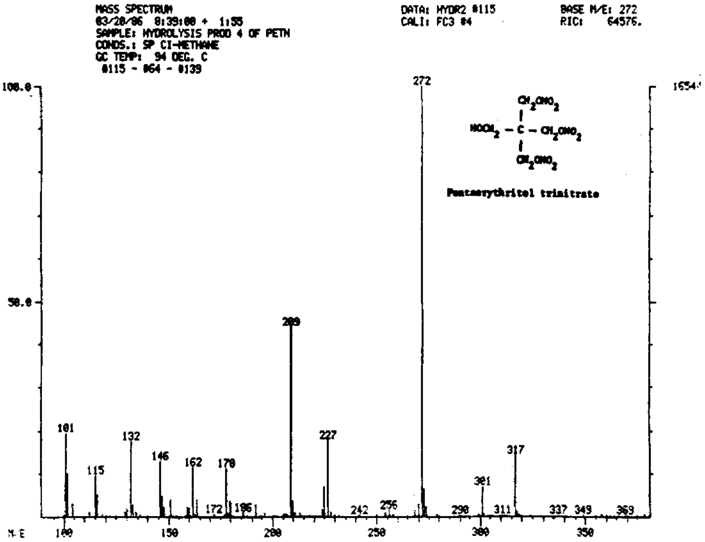


FIGURE 4
CI-methane mass spectrum of pentaerythritol trinitrate (2), isolated from the hydrolysis mixture of PETN.

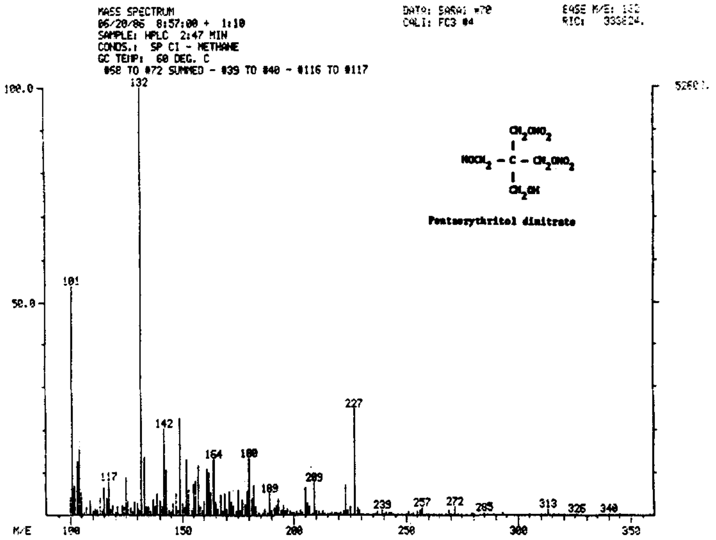


FIGURE 5
CI-methane mass spectrum of pentaerythritol dinitrate (3), isolated from the hydrolysis mixture of PETN.

The CI spectra of the trinitrate <u>2</u> (with both isobutane and methane) include an abundant ion at m/z 227, corresponding to the $[M+H]^+$ ion of the dinitrate <u>3</u> . A loss of 45 m/z units from the $[M+H]^+$ ion of <u>2</u> is highly improbable. The presence of <u>3</u> as an impurity in <u>2</u> was excluded by TLC of the latter. It seems that the trinitrate ester <u>2</u> undergoes hydrolysis in the mass spectrometer to yield the dinitrate <u>3</u> , which is then protonated by the CI reagent gas. Other ions which complicate the mass spectra of these esters correspond to $[M+NO]^+$ and $[M+NO_2]^+$. They were reported earlier[6] in the mass spectra of nitrate esters and were attributed to ion-molecule reactions favoured by high sample concentration and "tight" ion source. The presence of $[M+NO_2]^+$ ion in the spectrum of the trinitrate <u>2</u> (m/z 317 in Figure 4) could lead to the conclusion that PETN was present as an impurity. It was shown by TLC that this was not the case.

The structures of the trinitrate <u>2</u> and the dinitrate <u>3</u> were confirmed by their NMR spectra. The protons adjacent to the nitrate group resonate as singlets at δ= 4.77 ppm and 4.67 ppm in <u>2</u> and <u>3</u> , respectively. By comparison, the protons of PETN resonate at 4.87 ppm. The protons adjacent to the hydroxyl group resonate as doublets at δ= 3.79 ppm and 3.69 ppm in <u>2</u> and <u>3</u>, respectively.

Now that we have proven the formation of <u>2</u> and <u>3</u> during the hydrolysis of PETN, it remained to try and isolate them from actual post-explosion cases.

Figure 6 shows the LC results from an actual post-explosion case involving PETN. The fractions corresponding to the chromatographic peaks B and C were collected and subjected to CIMS and NMR. Their structures fully corresponded to pentaerythritol dinitrate (3) and pentaerythritol trinitrate (2), respectively. Peak D corresponded to PETN while peak A remained unidentified. Figures 7 and 8 show the CI-methane mass spectra of fractions C and B (Figure 6) collected from the LC separation of the post-explosion extract. The similarity to the CI-methane spectra of 2 (Figure 4) and 3 (Figure 5), respectively, is obvious. The NMR spectra of fractions C and B from the LC separation were also identical with the NMR spectra of 2 and 3, respectively.

Figure 9 shows the NMR spectrum of an acetone-extract from a post-explosion case. No separation was made prior to the NMR analysis. The sharp singlets at the relatively low field at δ = 4.88, 4.76 and 4.66 ppm originate from the CH_2ONO_2 protons of PETN (1), pentaerythritol trinitrate (2) and pentaerythritol dinitrate (3), respectively. Taking into account the different number of these protons in 1, 2 and 3, the relative ratio of PETN (1) and its decomposition products 2 and 3 can be estimated from the integration.

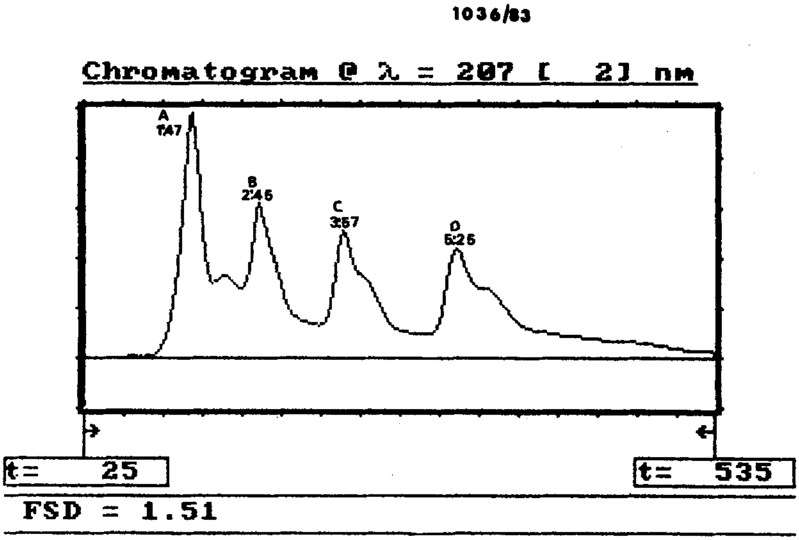


FIGURE 6
Liquid chromatogram of an acetone-extract from a post-explosion case (retention times in minutes are shown under the letters A,B,C,D which mark the peaks).

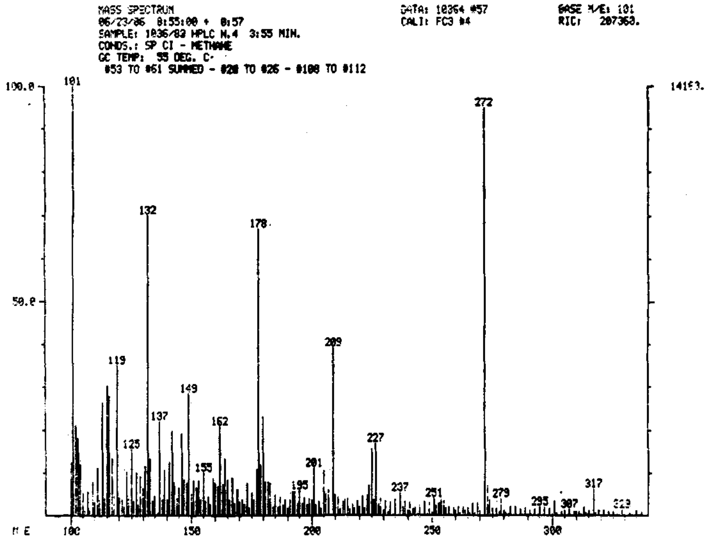
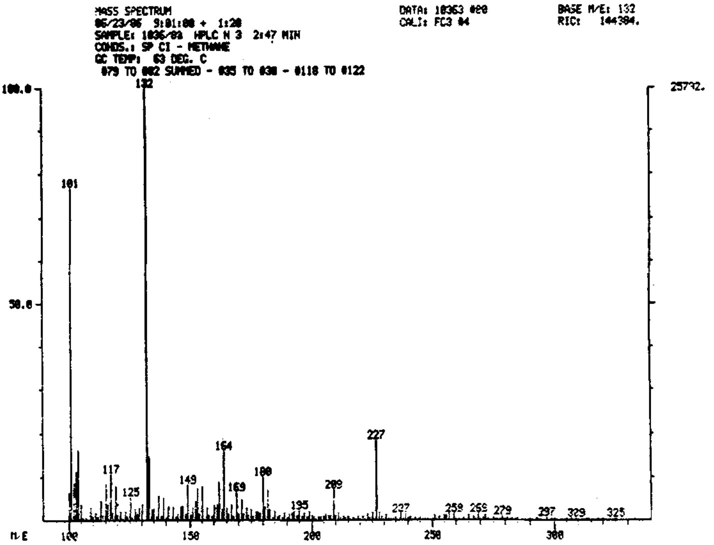


FIGURE 7
CI-methane mass spectrum of pentaerythritol trinitrate (2), isolated by LC (fraction C in Figure 6) from a post-explosion case.



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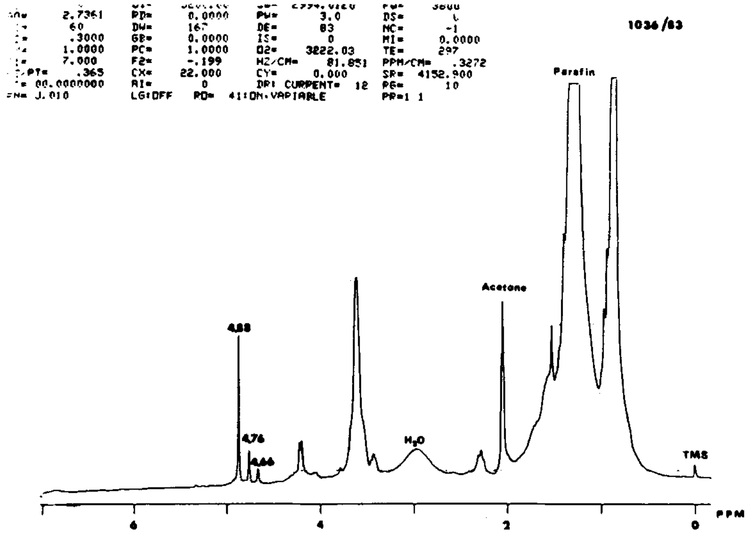
MASS SPECTRUM
06/23/85  9:01:00 + 1:20
SAMPLE: 1036/83  HPLC N 3  2:47 MIN
CONDS.: SP CI - METHANE
GC TEMP: 63 DEG. C
 079 TO 082 SUMMED - 035 TO 038 - 0118 TO 0122
```

```
DATA: 10363 #20
CALI: FC3 #4
```

```
BASE M/E: 132
RIC:   144384.
```

FIGURE 8
CI-methane mass spectrum of pentaerythritol dinitrate ($\underline{3}$), isolated by LC (fraction B in Figure 6) from a post-explosion case.



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     60      DW=    167      DE=      83     NC=     -1
     .3000   GB=    0.0000   IS=      0      MI=    0.0000
    1.0000   PC=    1.0000   O2=   3222.03   TE=    297
    7.000    F2=    -.199    HZ/CM=  81.851  PPM/CM=  .3272
PT=  .365    CX=    22.000   CY=     0.000   SR=  4152.900
 = 00.0000000 AI=    0       DR: CURRENT= 12 RG=     10
FN= J.010    LG:OFF  RD= 41:ON.VARIABLE      PR=1 1
```

FIGURE 9
NMR spectrum of an acetone-extract from a post-explosion case.

CONCLUSIONS

The experimental data discussed above show that lower nitrate esters of pentaerythritol appear in post-explosion debris where PETN was involved in the explosion. We cannot say whether their formation is associated directly with the explosion process or is due to hydrolytic processes occuring in unexploded PETN at the extreme conditions of the explosion.

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