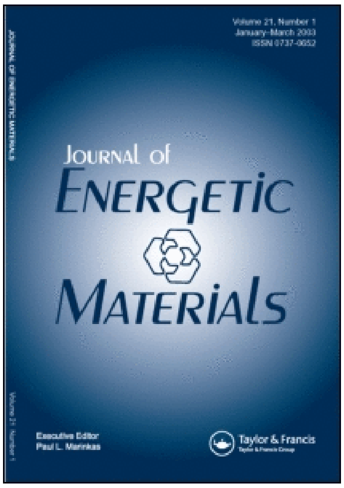

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Analysis of explosives by nuclear magnetic resonance spectrometry

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ANALYSIS OF EXPLOSIVES BY NUCLEAR MAGNETIC RESONANCE SPECTROMETRY

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ABSTRACT

In order to evaluate the applicability of NMR to the analysis of explosives, the method was used to analyse explosives from actual cases. The results were then compared with results from other analytical methods, mainly TLC and GC/MS. For unexploded samples NMR was found to be a simple, fast and reliable method, often allowing the identification of mixtures without pre-separation. Some post-explosion samples were also successfully analysed by NMR. Although sensitivity problems still exist, NMR showed a surprisingly promising prospects for the difficult field of post-explosion analysis.

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INTRODUCTION

Nuclear magnetic resonance (NMR) spectrometry, a major technique in modern analytical organic chemistry, has not yet become a routine method in forensic laboratories. The cost of the instrumentation and the need of qualified operators are probably among the principal reasons. There are also some fields in forensic analysis where the sensitivity of NMR is not sufficient.

^{1}H-NMR and ^{13}C-NMR spectra of common explosives have been recorded[1] but only few reports on the use of NMR in actual police cases involving explosives were published.[2,3] The application of NMR to post-explosion analysis has not been reported.

Some of the earlier works[4,5] on NMR of explosives were carried out on 60 MHz instruments. Modern instruments operate at 200-400 MHz and also utilize computer techniques to increase signal to noise ratio. In this state of art, the present work could be considered a feasibility study for the identification of post-explosion samples by NMR. It also includes identification of samples before explosion.

EXPERIMENTAL

The NMR spectrometer was Bruker WM-250, operating (for protons) at 250 MHz. Chemical shifts were expressed in ppm, relative to tetramethylsilane (TMS). The amount of samples before explosion was 1-5 mg, dissolved in 0.6-1.0 ml acetone-d_6. The number of pulses for these samples was 1.

Post-explosion samples (prepared by extracting the debris with acetone) were dried, dissolved in acetone-d_6 and their spectra recorded. The number of pulses for post-explosion samples was 100-400.

RESULTS AND DISCUSSION

The first step was to record and compile the NMR (protons) spectra of 16 common organic explosives and some of their mixtures.[6] The spectra corresponded to previously published ones.[4,5,7] The nitroaromatic explosives were 2,4- dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3,5-trinitrobenzene, 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitro-m-xylene, 2,4,6-trinitrophenol (picric acid), 2,4,6-trinitroanisole and 2,4,6-trinitro-m-cresol. The chemical shifts of the nitroaromatic ring protons are in the range of 7-9 ppm. Protons of methyl substituents on the nitroaromatic ring resonate at $\delta \sim 2.5 - 3.8$ ppm. The protons of the methoxy group in trinitroanisole resonate at $\delta = 4.19$ ppm.[3]

The nitrate esters recorded were ethylene glycol dinitrate (EGDN), diethylene glycol dinitrate, glycerine trinitrate ("nitroglycerine"; NG), pentaerythritol tetranitrate (PETN) and cellulose nitrate ("nitrocellulose").

The chemical shifts of the methylene protons adjacent to the nitrate group are in the range of 4.2-5.2 ppm. The CH proton in NG resonates at δ= 5.92 ppm. The nitramine explosives recorded were 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro - 1,3,5,7-tetrazacyclooctane (HMX) and 2,4,6-trinitrophenylmethylnitramine (tetryl). The methylene protons in the heterocyclic nitramines resonate at δ= 6.26. It is therefore practically impossible to distinguish between RDX and HMX by their chemical shifts. The aromatic ring protons in tetryl resonate at δ= 9.38 ppm and the protons of the N-CH_3 at δ = 3.78 ppm.

In the next stage the NMR spectra of 13 unexploded samples from actual cases were recorded.[6] The samples were taken from the Israel Police laboratory, where they had been analysed by other methods, mainly thin layer chromatography (TLC).[8] Some samples were analysed again by gas chromatography /mass spectrometry (GC/MS).[9] In general there was a good agreement between results from NMR and TLC. In some old cases 2,4-DNT and 2,6-DNT which accompanied TNT had been missed by the TLC analysts while their presence could be deduced from the NMR results. GC/MS verified their presence.

Figure 1 shows the NMR spectrum of an explosive which belonged to an apprehended terrorist. TNT and tetryl could be easily identified. The NMR spectrum of a more complex mixture which was concealed in a tractor but did not explode is shown in Figure 2. RDX, 2,4-DNT, TNT and nitrocellulose can be observed.

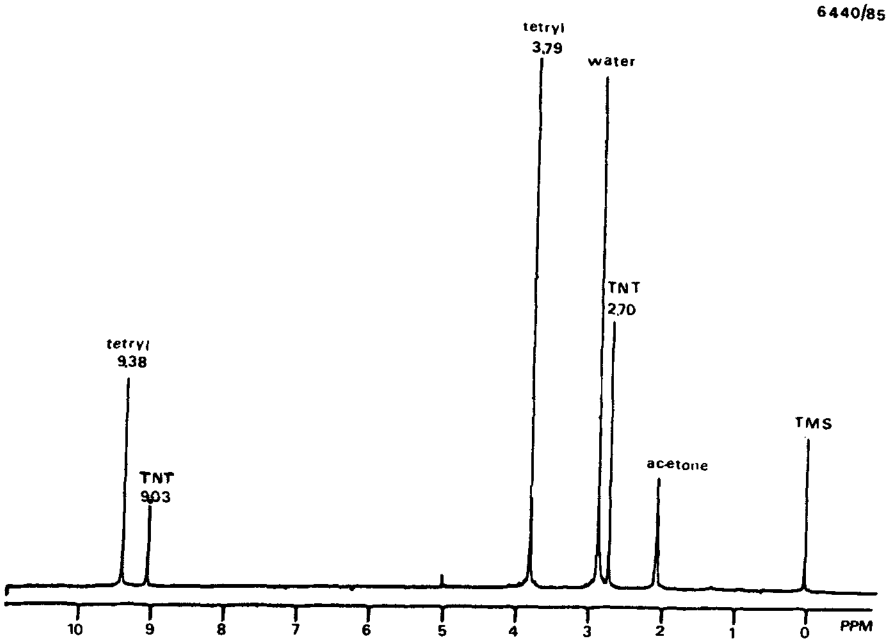

FIGURE 1
NMR spectrum of an explosive mixture (case 6440/85). TNT and tetryl were identified.

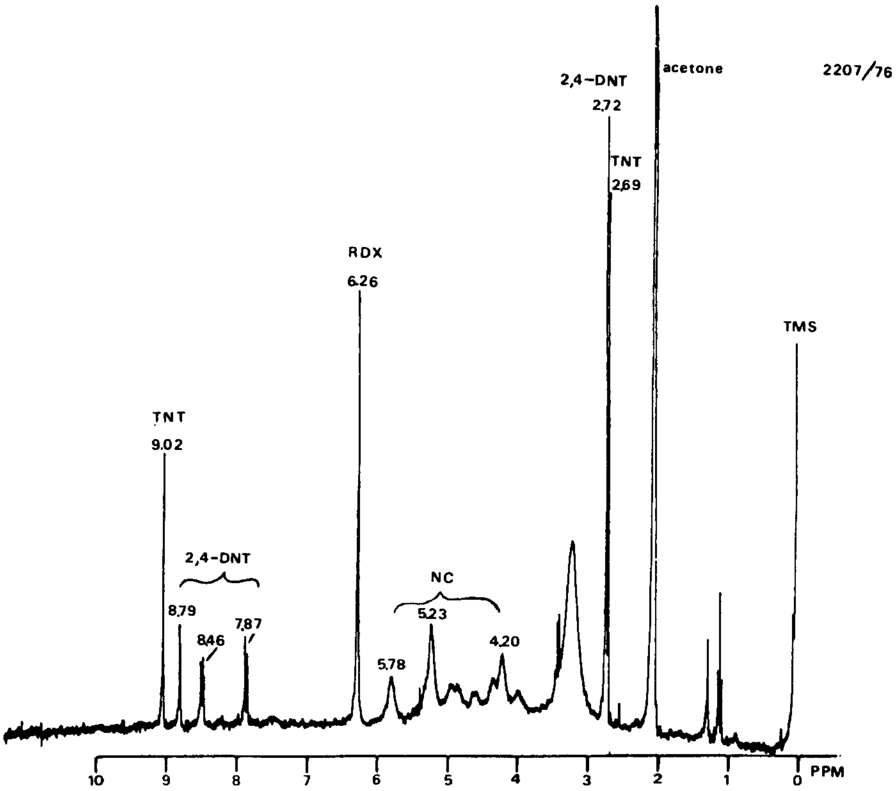

FIGURE 2
NMR spectrum of an explosive mixture (case 2207/76). RDX, 2,4-DNT, TNT and nitrocellulose were identified.

The examples in Figures 1 and 2 demonstrate the applicability of NMR spectrometry to the analysis of explosive mixtures. The method is simple, reliable and requires no pre-separation. Quantitative results can be obtained by integration, taking into account the number of protons in each explosive which are responsible for the integrated peak.

While the successful application of NMR to the analysis of unexploded samples was hardly surprising, we did not expect much success in applying the method to post-explosion samples. These samples usually contain very little of the original explosive, mixed with large amounts of impurities. Other methods, like infrared (IR) spectrometry or direct probe-mass spectrometry often failed to identify explosives in post-explosion samples, even when preceded by cleaning the samples on a chromatographic column.

NMR analysis was carried out[6] on 14 post-explosion samples which had been analysed in the Israel Police laboratory during the years 1983-1985. The samples were extractions of post-explosion debris with acetone. In order to increase signal to noise ratio, the number of scans in the post-explosion analysis was 100-400 vs. 1 scan in normal analysis (see EXPERIMENTAL). Under these working conditions it was estimated that 10 μg was the lowest amount of explosive which could give a meaningful spectrum. Of the 14 samples subjected to NMR analysis, the results of the laboratory were fully or partly confirmed in 8 samples. In the remaining samples the explosives could not be identified by NMR. The results of the laboratory were again based mainly on TLC and in some cases on GC/MS.

Figure 3 is a typical example of a post-explosion sample. The amount of impurities is large enough to obscure the presence of the explosive. Yet the two distinct peaks of PETN (δ=4.89 ppm) and RDX (δ=6.26 ppm) can be observed in the enhanced part of the spectrum. The decision to attribute the peak at δ=6.26 ppm to protons of RDX rather than to protons of HMX (which resonate at the same chemical shift) was based on TLC, by which the two explosives were easily distinguished.[8] In another post-explosion sample, shown in Figure 4, the small peak at δ=6.26 should be attributed to HMX and not to RDX, following the TLC results. The case involved an extract from the debris left after a rocket had been exploded, killing a young boy.

Figure 5 shows the NMR spectrum of a post-explosion extract from a blown up safe. PETN is clearly identified by the peak at δ=4.88 ppm. The small peak at δ=4.76 ppm originates from protons of pentaerythritol trinitrate, which was found to accompany PETN in certain post-explosion analyses.[10]

It is interesting to note that the explosives identified by NMR in post-explosion samples were PETN and RDX (or in one case HMX). In 3 samples where the presence of TNT was indicated by TLC

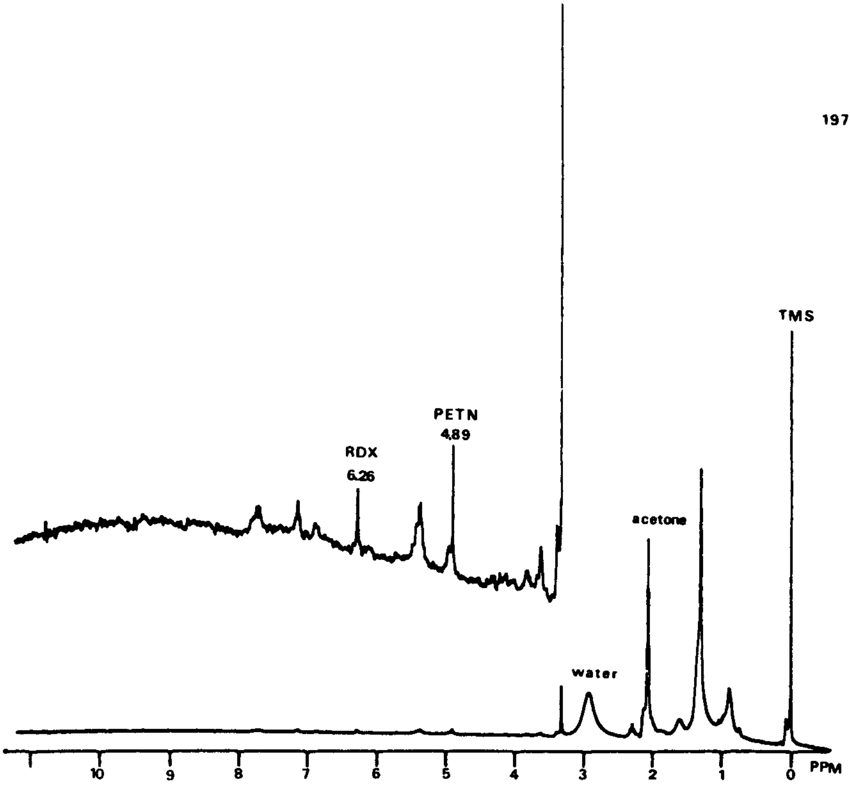

FIGURE 3
NMR spectrum of a post-explosion extract (case 1975/85). PETN and RDX were identified (RDX was distinguished from HMX by TLC).

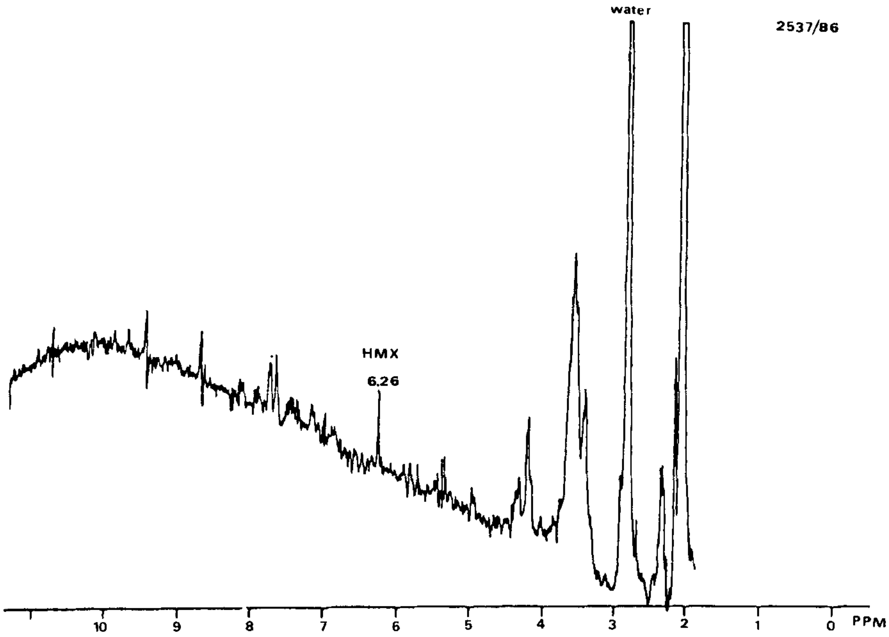

FIGURE 4
NMR spectrum of a post-explosion extract (case 2537/86). HMX was identified (HMX was distinguished from RDX by TLC).

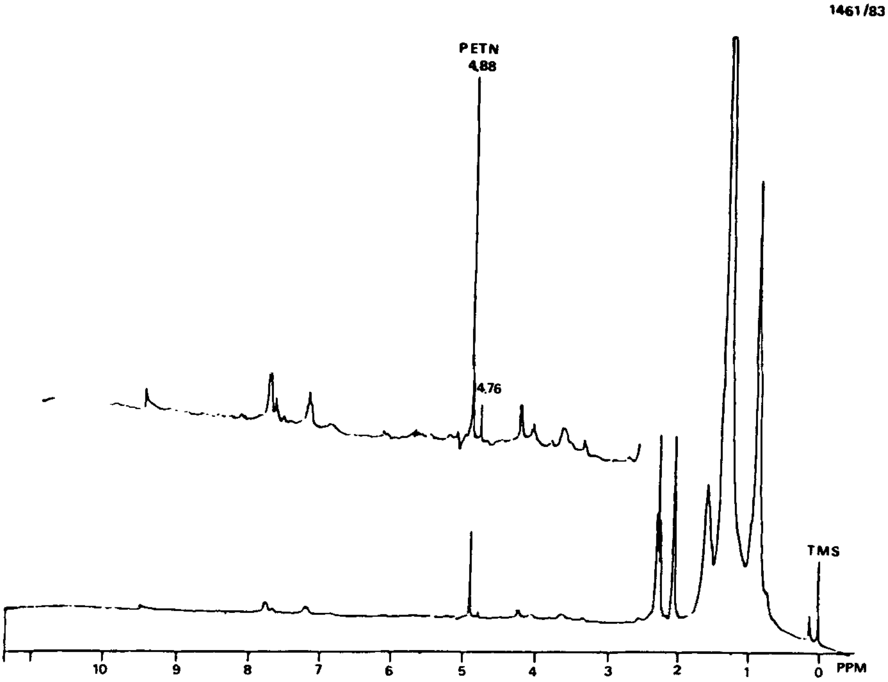

FIGURE 5
NMR spectrum of a post-explosion extract (case 1461/83). PETN and pentaerythritol trinitrate were identified.

and confirmed by GC/MS, NMR failed to detect it. In one of these samples the laboratory identified both TNT and RDX, while the NMR spectrum confirmed only the presence of RDX. In 3 other samples NG and nitrocellulose were found by TLC, indicating the use of double-base smokeless powders. Neither of these results was confirmed by NMR. Although these data are interesting, any attempt to draw conclusions (e.g. about amounts of the original explosives remaining after explosion in different explosives), based on so few examples, is obviously premature.

Figure 6 shows the NMR spectrum of an extract of debris (mainly soil) from a test in which 1 kg of TNT was detonated using a standard military detonator. TNT can be identified by its two peaks, at δ=2.69 ppm and δ=9.02 ppm.

CONCLUSIONS

The advantages of NMR spectrometry have been borne out when the method was applied to the forensic analysis of unexploded samples. Explosive mixtures have been analysed in a simple, rapid and reliable way, without pre-separation or pre-cleaning.

Somewhat unexpectedly, the method showed partial success when applied to post-explosion samples from actual cases. Although there were cases where NMR was not sensitive enough to confirm TLC results and could not match GC/MS, there were other cases in which the explosives residues were clearly identified by the NMR spectra. It seems that although sensitivity problems still exist, NMR should not be ruled out for forensic post-explosion analysis.

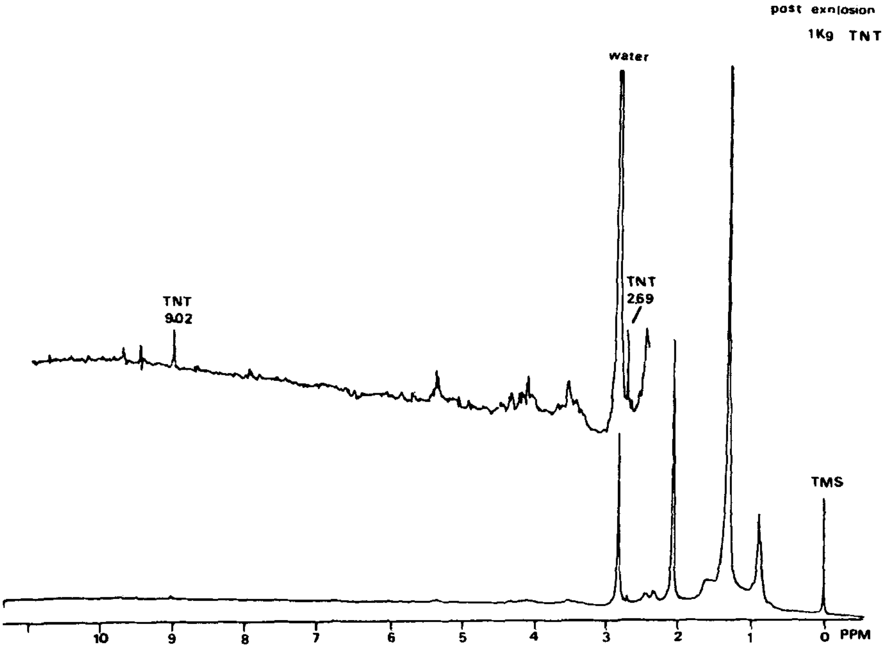

FIGURE 6
NMR spectrum of an extract of the debris (mainly soil) left after a test in which 1 kg TNT was detonated. TNT could be identified.

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