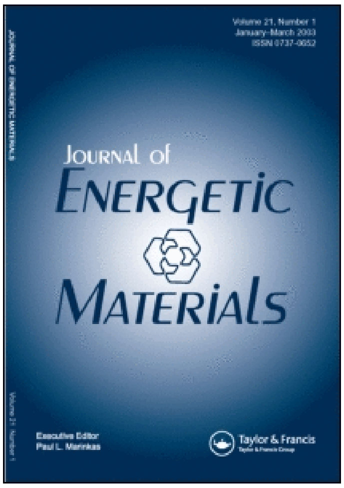

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Characterization and Identification of Explosives and Explosive Residues Using GC-MS, an FTIR Microscope, and HPTLC

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Characterization and identification of explosives and explosive residues collected from different places in India were made using TLC, GC/EI-MS, and GC-FTIR. The explosives used were NG, PETN, TNT, tetryl, RDX, and NH_4NO_3 + fuel oil. Quantitative estimation was made using HPTLC. Mass spectra of the samples using selective ion monitoring (SIM) mode based on the relative intensities of the signals X, X + 1 (intensity of the largest fragment X of the explosive, say, RDX [X = 205] was assumed to be 100%, i.e., X = 100%) show no isotopic substitution. The results were confirmed by FTIR spectra. Some physico-chemical aspects of the explosives are discussed.

Keywords: characterization, explosives, FTIR microscope, GC-MS, HPTLC, identification

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Introduction

Explosives are widely used for military purposes such as war. Other uses are for construction projects such as building roads, dams, and bridges [1,2]. Explosives are also used by the police to maintain law and order.

Recent years have seen a spurt of criminal and terrorist activities all over the world. There has been wanton destruction of private and public properties as well as commercial centers, causing irreparable losses to national and local economies and endangering human lives.

Potentially dangerous explosives like dynamite, assorted military explosives containing nitroglycerine (NG), tetryl, cyclonite (RDX), octogen (HMX), and other homemade low explosives and incendiary devices are now readily available to criminals and terrorists. The indiscriminate and intentional usees of these explosives include taking revenge and for extortion of money, smuggling, political murders, and other terrorist and antisocial activities.

Criminal and terrorist activities (aided by foreign agencies with arms and ammunition smuggled from military sources or others) are on the rise in different parts of India, particularly in the eastern region and neighboring areas, with regular occurrences of explosions in different regions. The explosives and explosive residues collected from the scenes of explosion by different investigating agencies are sent to the Central Forensic Science Laboratory (CFSL) in Kolkata for investigation to identify and estimate the explosives both qualitatively and quantitatively. Identification of detonating mechanisms, guessing the routes taken by explosive trafficking, and apprehending the criminals associated with explosives and explosions are also aimed at.

Various explosive and explosive residues were analyzed qualitatively, and the constituents were estimated quantitatively using TLC, GC-MS, GC-FTIR, and HPTLC. The results of our investigation are reported in this communication.

Experimental

Preliminary microscopic examination and simple analysis showed that a large number of samples contained low explosives made indigenously using commonly available materials such as KNO_3 or $NaNO_3$, $KClO_3$ or $NaClO_3$, S, As_2S_3, C, etc., in varying proportions along with ingredients such as Al powder.

Analysis of the low explosives was presented in an earlier communication [3]. Preliminary investigation and identification were made using thin-layer chromatography (TLC). A number of solvents are suggested by various researchers [1–7]. Some of the solvent systems suggested were trichloroethylene + acetone (4:1), toluene + cychlohexane (7:3), toluene + ethylacetate (9:1), and toluene, acetone, tetrahydrofuran. We found acetone to be an ideal solvent for dissolution of the explosives.

After preliminary investigation, positive identification of explosives and post-explosion residues can be made with analytical methods such as gas chromatography (GC), high-performance liquid chromatography (HPLC), and infrared (IR) and mass spectrometry. However, mass spectrometry GC/MS (using EI and CI modes) is regarded as the most reliable method for the identification of organic compounds and is more suitable than IR spectrometry for post-explosion residue analysis [8]. Yinon [9] prefers LC/MS for explosives that do not elute easily in GC.

However, in the present study, GC/MS (using the EI^+ mode) and Fourier transform infrared (FTIR) techniques were used for confirmatory identification of the explosives and residues, and high-performance thin-layer chromatography (HPTLC) was used for estimation of explosives where required.

The samples were thoroughly rinsed with acetone, which dissolves organic explosives present in the samples, and the acetone extracts were concentrated. Identification of the dissolved samples was made using TLC. The spots were examined under UV light or by spraying a Greiss reagent or diphenylamine. The compounds were identified from the color of the spots and known R_f values of the explosives. The results were further confirmed by GC/FTIR and GC/MS of the isolated samples and comparison of the FTIR and GC/MS of standard samples of explosives.

For the explosive residues, no quantitative estimation was made. However, for unexploded explosives, quantitative estimation was performed using the HPTLC method. The analysis of the samples were made using a Finnigan Trace GC and Trace MS by injecting variable volumes of the experimental solution in acetone with an autosampler using the following parameters: Column-capillary, RTX-5MS, 15 m length, 0.32 mm ID, and 0.25 µm film thickness coating. Oven temperature was programmed between 70 and 250°C with 10°C/min increment. The injector temperature and the interface temperature was 220°C. The system was run at a constant flow mode of 1.2 ml/min. Helium was the carrier gas. MS parameters were mode EI^+, source temperature 140°C, energy 70 ev, source current 150 mA, lens1 = 5 V, lens 2 = 110 V, and mass range scanned 30–400 amu.

GC/FTIR

For the measurement of the IR spectrum using GC, a Perkin Elmer Claurus GC, Spectrum GX FTIR having a mercury cadmium telluride (MCT) detector working at a 77 K liquid nitrogen temperature was used. GC parameters were Column-capillary, RTX-5MS, 15 m length, 0.32 mm ID, and 0.25 µm film thickness coating. Oven temperature was programmed between 70 and 250°C with 10°C/min increments. The injector temperature and the transfer line (light tube) temperature were 200°C. The system was run at a constant pressure mode of 12 psi. Helium was the carrier gas.

FTIR Auto Image Microscope

For the measurement of the IR spectrum at solid state, a Perkin Elmer Spectrum GX-FTIR with an auto-image microscope having an MCT detector working at a 77 K liquid nitrogen temperature was used. The sample solution in acetone was spotted on blank KBr pellets with a microliter syringe. The spot was dried by passing hot air over it. The pellet was placed under the microscope and focused to measure the spectrum between 4000 and 700 cm^{-1} using transmission mode.

GC/MS and FTIR studies of the experimental solution were compared against the standards of the respective compounds.

Table 1
Area vs. weight of TNT in standard sample

Sample no.	Volume (μl)	Weight (μg)	Area
1	3	0.6816	60.3
2	6	1.3632	119.5
3	9	2.0448	183.4
4	12	2.7264	236.7
5	15	3.4080	303.2
6	18	4.0896	357.2
7	21	4.7712	416.7
8	24	5.4528	476.9
9	27	6.1344	532.6

Quantitative Estimation Using HPTLC

Quantitative estimation of explosives was made using an HPTLC of the Desaga HPTLC system with a CD 60 densitometer. E. Merck's precoated TLC plates of 20 cm × 20 cm × 0.25 mm dimensions with 80–100 mesh size were used. The standard solution such as TNT, tetryl, etc., of the explosives and the experimental solutions were spotted by the autosampler at several positions on different plates keeping a 15 mm margin at the bottom and 20 mm each at the right and left sides. Each spot was given by a 3 μl/cycle with a break of 5 sec between two cycles. Standard TNT, tetryl, etc., were

Table 2
Area vs. weight of forensic sample

Sample no.	Volume (μl)	Weight (μg)	Area	% of TNT
1	3	0.7524	55.18	82.9
2	6	1.5048	109.6	83.1
3	9	2.2572	169.2	83.6

Note: Average % of TNT = 83.2.

Table 3

Location, sample type, type of explosives used, and ingredients of seized sample

Sample no.	Location	Sample type	Type of explosive used and %	Other ingredients detected
1	NE	Deactivated hand grenade	TNT, 97.3	–
2	NE	Hand grenade exploded	TNT	–
3	NE	Hand grenade exploded	TNT	–
4	NE	Yellow semisolid	TNT, 83.2	Grease
5	NE	Hand grenade exploded	TNT	–
6	Sealdah Rly station	Black-colored solid	RDX, 87.6	Carbon
7	Sealdah Rly station	Black and cream–colored solid	RDX, 81.05	Carbon
8	Sealdah Rly station	Soil and stone pieces	RDX	–

9	Monipur	Electric detonator	PETN, 93.6	KNO_3, C, S
10	Monipur	Country made detonator without wire and fuse fitings	PETN, 88.2	–
11	Monipur	Post-explosion residues	Tetryl	–
12	Monipur	Yellow oily solid	Tetryl, 87.6	Grease
13	WB	Paper-covered dynamite stick	NG, 56.3	NH_4NO_3 and wood dust
14	WB	Plastic-covered ‘‘Telgex’’ brand	NG, 49.7	NH_4NO_3 and wood dust
15	WB	Plastic-covered ‘‘Sun’’ brand	NG, 51.3	NH_4NO_3 and wood dust
16	WB	Oily gray-colored semisolid materials	NH_4NO_3, fuel oil	Insoluble particle (sand) 3.4%
17	WB	Oily gray-colored semisolid materials	NH_4NO_3, fuel oil	Alluminium powder 0.82%

spotted at nine positions having volumes 3, 6, 9, 12, 15, 18, 21, 24, and 27 µls. The experimental sample was spotted at three positions having volumes 3, 6, and 9 µls on the same plate.

The plates were developed in a Camag developing chamber saturated with a benzene-acetone (95:5) solvent system. The developed plates were scanned with a densitometer using a 254 nm light beam of 8 mm length and 1 mm width. Adjustments of length and width were made depending on the sample used to cover fully the spot areas during the scanning of the spots. Tables 1 and 2 show the area of the spots of standard TNT at different concentrations and those of the individual spots of the experimental samples from which the concentrations of the individual samples were determined. The procedure is the same for all samples. The concentration of the experimental solution was obtained quantitatively from comparison of the area of the spots of the experimental solution with the generated calibration curves of the standard solution of the explosives.

The inorganic impurities were determined using the conventional methods, and the determination of impurities in dynamite were made following the method described by Scott [10]. The location, sample type, their uses, and other ingredients present with the explosives and quantitative values of the explosives are presented in Table 3.

Results

Preliminary experiments using a TLC showed that the samples contained nitroglycerine (NG), pentaerythritoltetranitrate (PETN), trinitrotoluene (TNT), tetryl, cyclonite (RDX), and NH_4NO_3. Impurities included C, wood dust, sand, aluminium powder, K^+, NO_3, S, grease, and fuel oil. The presence of the explosives was confirmed with GC/MS and GC/FTIR.

The characteristic features and m/z values of the compounds were extensively studied by various researchers [2,4,8,11–16]. m/z values of peaks of different explosives using EI^+MS and the reasons attributed are briefly given in Table 4.

Table 4
m/z Values of peaks of explosives

Sample no.	Explosives	m/z values
1	NG	46 (base peak due to NO_2^+), 30 (NO^+), 76 ($CH_2ONO_2^+$)
2	PETN	46 (base peak due to NO_2^+), 76 ($CH_2ONO_2^+$), 30 absent, Molecular ion absent
3	TNT	30 (NO^+, predominents), 46($NO_2{}^+$), 89 $(M\text{-}3NO_2)^+$ (due to loss of $3NO_2^-$ group, $227 - 3 \times 46$), 210 (base peak due to loss of an OH^- radical), ortho effect is pronounced ortho to 2,4,6-TNT due to the presence of two NO_2 groups in the methyl group so that the molecular ion at 227 is hardly observed. Other fragments are 193 ($M\text{-}2OH^-$), 180 ($M\text{-}OH\text{-}NO^+$), 164 $(M\text{-}OH\text{-}NO_2)^+$.
4	Tetryl	241 (base peak using direct sample insertion probe due to $(M\text{-}NO_2)^+$ ion, absent in GC-MS but contains 242 (abundant due to hydrolytic decomposition of tetryl). Other peaks: 224 $(M\text{-}NO_2\text{-}OH)^+$, 210 $(M\text{-}NO_2\text{-}OH\text{-}N)^+$, 194 $(M\text{-}NO\text{-}OH\text{-}N)^+$, 46 ($NO_2^+$), 30 ($NO^+$), 75 $(CHONO_2)^+$,
5	RDX	Molecular ions are not observed. 46 (NO_2^+), 30 (NO^+) most abundant. 120 $(CH_2N_2O_4)^+$. From elemental composition the ion is found to correspond to $CH_2N(NO_2)_2^+$, 148 $[CH_2N(NO_2)_2]^+$, 128 (not properly assigned).

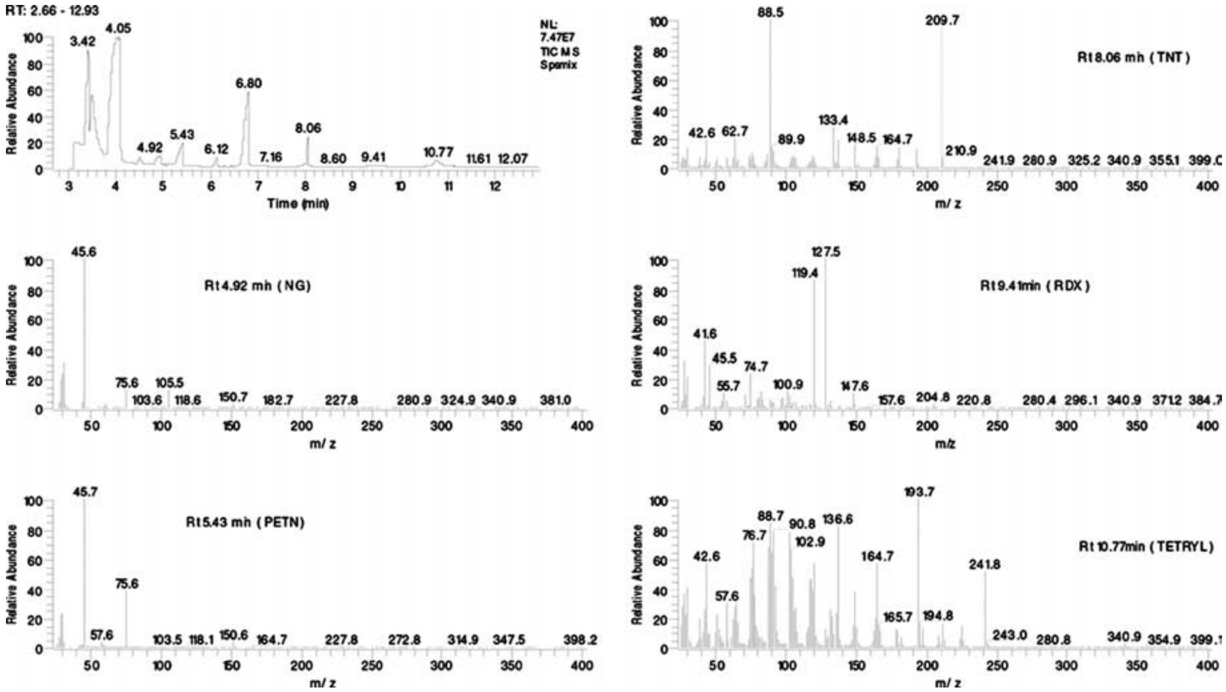


Figure 1. Mass spectra of the standard explosive samples with total ion chromatogram.

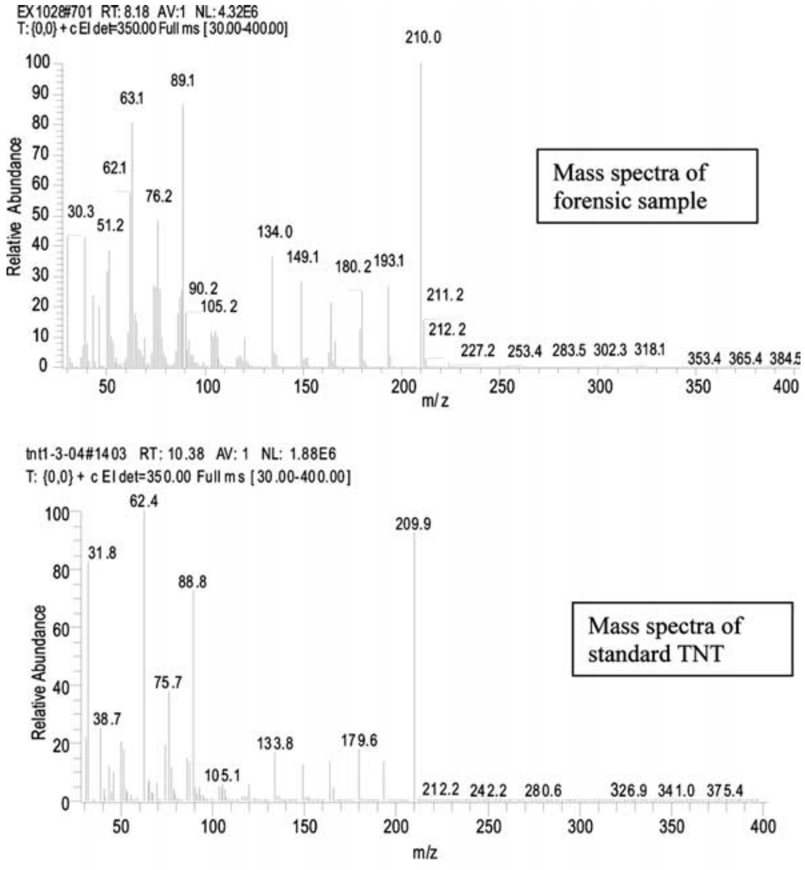


Figure 2. Comparison of mass spectrum of the forensic samples with standard TNT.

All the characteristic features are obtainable in the explosive residues and explosives given in Table 3. A typical EI^+MS of standard samples is presented in Figure 1. A comparative figure (Figure 2) of the standard sample and the experimental sample is also presented for verification. Comparison of the R_t values and the ionization peaks confirms the chemical identity of the forensic samples.

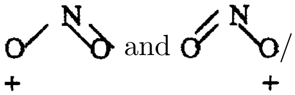
Table 5
IR peaks of groups with and without isotopic substitutions and ratio of peak areas showing natural abundance of elements in explosives

Sample no.	$\overline{\nu}$ of C^{12}–H^2 observed (calculated value) cm^{-1}	Ratio of peak area of H^1/H^2	$\overline{\nu}$ of $N^{15}{=}O^{16}$ observed (calculated value) cm^{-1}	Ratio of peak area of N^{14}/N^{15}	$\overline{\nu}$ of $N^{14}{=}O^{18}$ observed (calculated value) cm^{-1}	Ratio of peak area of O^{16}/O^{18}
TNT	**Std TNT**	**743/0.54**		**1507/16.8**		**1507/3**
1	2173 (2169)	761/0.58	1511 (1513)	1135/13.5	1496 (1500)	1135/2.78
2	2173	758/0.57	1511	1745/19.3	1498	1745/4.28
3	2172	802/0.61	1512	112/1.34	1500	112/0.27
4	2173	618/0.50	1511	842/10.14	1498	842/2.13
5	2173	614/0.50	1509	723/8.0	1498	723/1.70
RDX	**Std RDX**	**289/0.27**		**2106/23.8**		**2106/5.1**
6	2206 (2202)	314/0.29	1557(1562)	1958/22.1	1548 (1549)	1958/4.9

7	2206	266/0.26	1560	2726/32	1548	2726/6.44
8	2206	341/0.30	1561	2823/33	1548	2823/7.10
PETN	**Std PETN**	**320/0.44**		**248/3.4**		**248/0.70**
9	2137 (2139)	1194/1.7	1611 (1614)	2694/40.12	1598 (1600)	2694/8.63
10	2138	1754/1.85	1612	223/3.01	1599	223/0.72
Tetryl	**Std Tetryl**	**353/0.30**		**4203/60.20**		**4203/12.40**
11	2112 (2114)	303/0.30	1508 (1509)	1714/24.3	1495 (1496)	1714/5.6
12	2112	249/0.21	1509	3200/48.36	1495	3200/10.3
NG	**Std NG**	**557/0.43**		**2111/22.70**		**2111/5.10**
13	2139 (2139)	548/0.40	1618 (1619)	2316/24.7	1605 (1605)	2316/5.45
14	2139	732/0.61	1618	2432/27.19	1605	2432/5.33
15	2139	914/0.70	1617	2230/23.8	1605	2230/5.32
ANF						
16			–			
17			–			

IR Spectra

The identification of the compounds were further confirmed via FTIR measurements (see [17–21]). The O atoms of the NO_2 group can be regarded as equivalent due to resonance:



The NO_2 group shows three degrees of vibrational freedom and has three difference frequencies, namely, asymmetric frequency in the region 1530–1560 cm^{-1} (strong), symmetric frequency in the region 1210–1360 cm^{-1} (strong), and bending frequency or scissoring in the region 840–930 cm^{-1} (relatively weak).

The characteristic vibration frequencies of the explosives are presented in Table 5. All the values agree with the values given in the literature. FTIR spectra of TNT, RDX, PETN, and tetryl are presented in Figure 3. A comparative study of the FTIR spectra of explosive residue (TNT), standard TNT, standard tetryl, and a seized explosive sample are also presented in Figure 4 for verification and chemical identification of forensic samples.

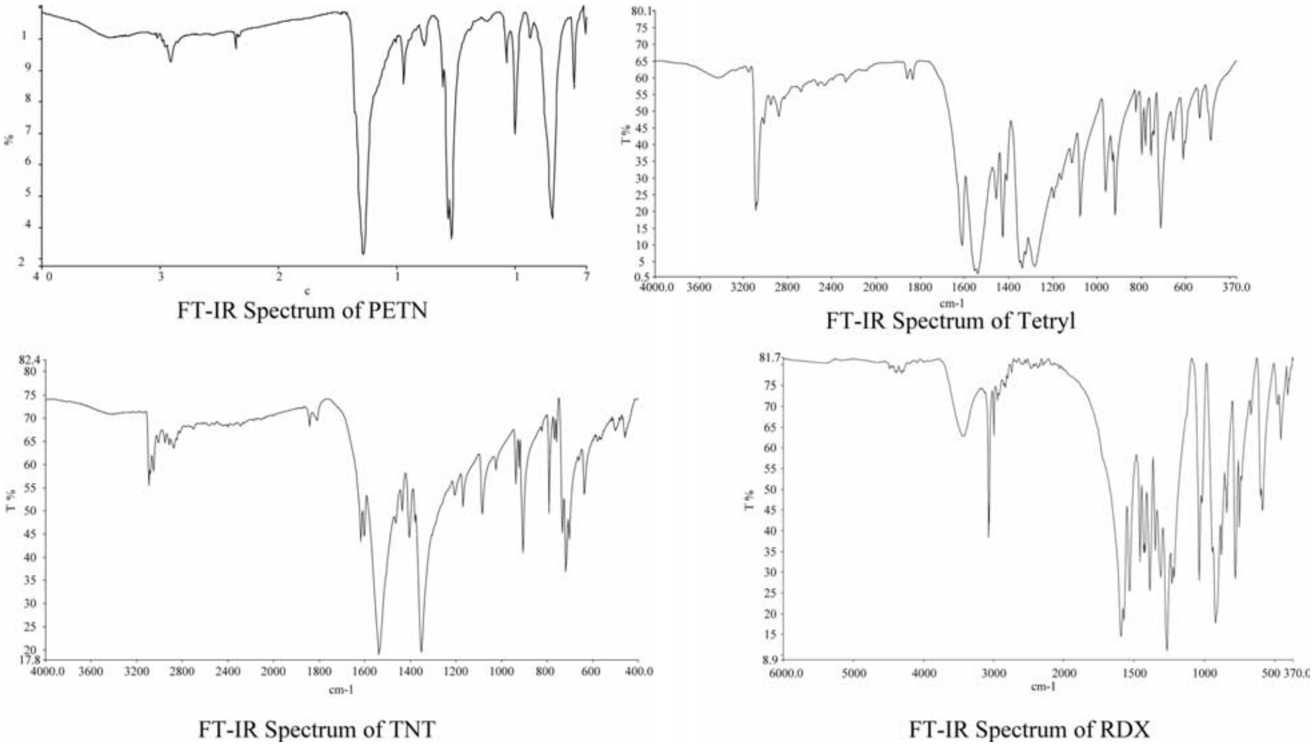
Discussion

Except for NH_4NO_3 all the compounds (NG, PETN, TNT, tetryl, RDX) identified are high explosives, that is, they contain both fuel (C, H) and oxidizer (O) in sufficient amounts to have high sensitivity but require no sensitizer to make them explode. The compounds have high exothermic reaction rates with sudden buildup of sufficient pressure to obtain high detonation velocity [2]. See Table 6.

The explosive compounds are divided into the following classes in order of stability:

1. Nitroaromatics having (Ar)C-NO_2 bonds (TNT, tetryl)
2. Nitrate esters having O-NO_2 bonds (NG, PETN)
3. Nitramines having N-NO_2 bonds (RDX, HMX)

The strength of the bonds is of the order Ar C-N $>$ O-N $>$ N-N.



FT-IR Spectrum of PETN

FT-IR Spectrum of Tetryl

FT-IR Spectrum of TNT

FT-IR Spectrum of RDX

Figure 3. FTIR spectra of the standard explosives.

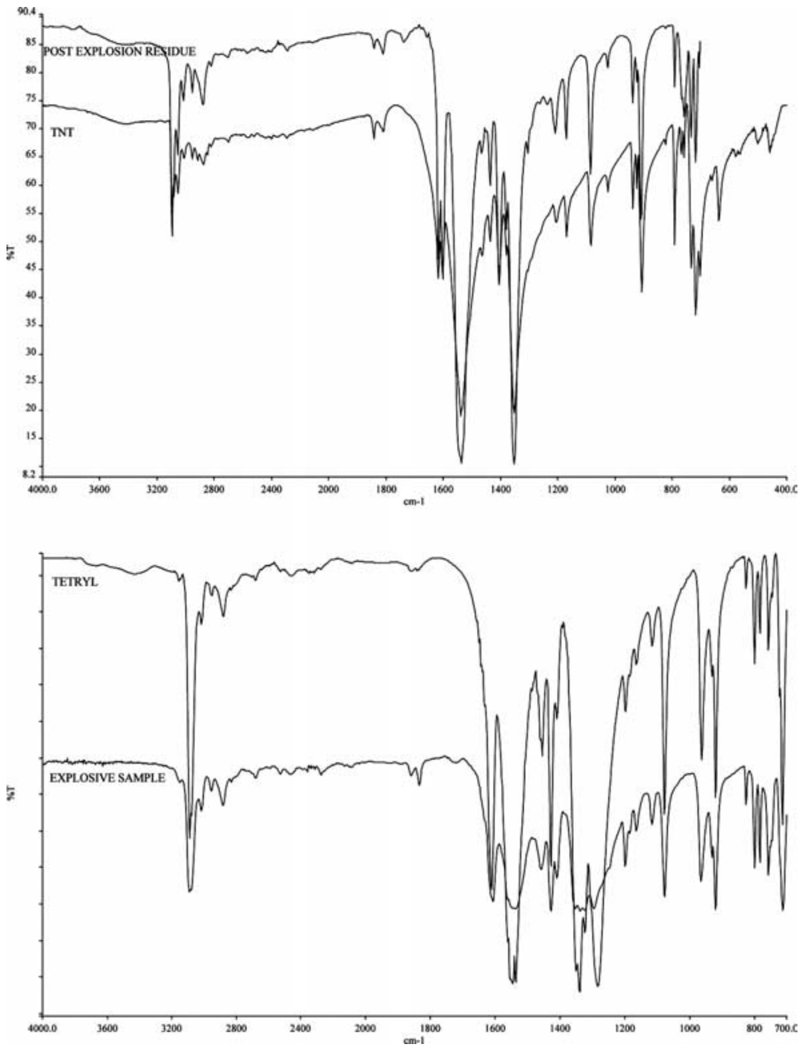


Figure 4. Matching of the FTIR spectra of standard explosives with forensic sample.

All the compounds are of low thermodynamic stability. However, the aromatic compounds TNT and tetryl (less stable) are stabilized due to resonance. Under the conditions of an

Table 6
Detonation parameters of explosives [2]

Sample no.	Explosive	Density (g/cm^3)	Detonation velocity (m/s)	Detonation pressure (Gpa)
1	TNT	1.64	6930	21
2	PETN	1.67	8000	30
3	RDX	1.77	8700	33.8
4	Tetryl	1.71	7850	–

explosion, N-atoms of RDX or HMX have to be converted to free N_2, leading to greater thrusts in RDX or HMX.

In the case of NG and PETN, the decomposition is associated with the rupture of $CH_2{-}CH_2$ bonds and formation $(CH_2{-}O{-}NO_2)_3$ or C $(CH_2{-}O{-}NO_2)_4$, which decomposes to give $CH_2{-}O{-}NO_2$ (m/z 76), NO_2 (m/z 46), NO (m/z 30), and other products including N_2. However, in PETN, NO is absent. The total volume of gases is relatively low. In TNT and tetryl, the rupture of NO_2 groups occurs and is followed by the rupture of aromatic rings. Thus we get NO_2^+ (m/z 46), NO^+ (m/z 30), and $(M\text{-}3NO_2)^+$ m/z 89 for TNT. However, interaction of a CH_3 group with two ortho NO_2 groups results in $(M\text{-}OH)^+$ m/z 210 (base peak) and other decomposition products. The decomposition of tetryl takes place in a different way with NO_2^+ (m/z 46), NO^+ (m/z 30),$(CHONO_2)^+$ m/z 75, etc.

However, rupture of RDX gives $(CH_2{-}N{-}NO_2)_3^+$ (not observed) to be converted into $(CH_2{-}N{-}NO_2)_2$ (m/z 148) ultimately converted to $CH_2N(NO_2)_2^+$ (m/z 120) with the loss of one CH_2N group. But this has been attributed to unusual migration of second NO_2 groups to CH_2N [22]. The unassigned peaks ($m/z = 128$) are likely due to liberation of $-NO_2$, $-NO$, and H_2O from $(CH_2N{-}NO_2)_3^+$, that is, due to $CH_2NNO_2{-}CH_2$ $N.CHN^+$.

However, NO_2^+ (46), NO^+ (30) are present in large amounts arising from the rupture of the NO_2^+ group from the molecules. There are other peaks with unassigned species. The possibilities or tentative species may be with m/z values (a) 98-$C_2H_2N_4O^+$, (b) 83-$C_2HN_3O^+$ or $C_3N_3H_5^+$, (c) 81-$C_2HN_4^+$ or $C_3H_3N_3^+$, (d) 75-$CHNO_3^+$, (e) 71-CHN_3O^+, (f) 56-$(CH_2)_2N_2$, (g) 42-$(CH_2)_2N$ or CH_2N_2.

The physical and chemical evidence for the identification of unexploded explosives and explosive residues is important as evidence in the court of law. However, the process of explosive detection and the identification of explosives, the country of origin, and the distribution network of explosives are important for forensic purposes and to provide evidence to a court of justice.

The tagging program [1,2] has been introduced for the detection of explosives and their country of origin. The investigation showed no color-coded chips, etc., known as *taggants*.

To establish the origin and distribution of forensic samples, evidence is usually collected from the isotopic abundance of the naturally occurring isotopes of H, C, O, N, etc., in illicit drug samples such as heroin. Two chemically identical substances may have different stable isotopic composition depending on the history or origin of the substances, for example, the biosynthetic pathway of production of the original compound (e.g., morphine).

Because H, C, N, and O are the basic components and major elements in both natural and manufactured compounds of forensic interest, it is desirable to determine the natural abundance of isotopes of the elements in compounds from different sources and countries. Comparison of the natural abundance of the isotopes of C, O, etc., between the standard compounds and experimental samples may give an idea of the source.

Among the various methods of determining sample differentiation based on isotope composition, isotope ratio mass spectrometry (IRMS) is useful [23,24]. Sample differentiations are based on intramolecular isotope composition variations at a natural abundance level in the samples of interest.

^{13}C NMR spectra are another useful tool for identification and estimation of ^{13}C in the samples. The use of ^{13}C was made by Becasier [25] for comparison and origin of heroin consignments. However, in view of the lack of these instruments, other simple methods using GC/MS and FTIR were utilized in the present investigations.

A simple approach to identify the possibility of any isotopic substitution in the sample is to use MS and determine the signals X, $X+1$, $X+2$, etc. ($X = 210$ for TNT, $X = 205$ for RDX, etc.) using the selective ion monitoring mode (SIM). The relative intensities of $X+1$, etc., were calculated assuming the intensities of the first peak to be 100% (i.e., $X = 100\%$). Comparison of the results between the standard samples and forensic samples marked 1, 2, 3, etc., are given in Table 7 with the theoretical factors calculated ruling out the possibility of isotopic substitutions.

These results were further confirmed by using FTIR spectra, and FTIR may be utilized to determine the natural abundances of isotopes. All explosives contain C, N, O, and H, and an isotopic substitution of any atom will change the known natural abundance of the isotope of the atom and the isotopic ratio of the system. The determination of the natural abundance of the atoms will provide suitable evidence for possible isotopic substitution.

The natural abundance of any element in explosives can be calculated. Because of very low natural abundances for the isotopes of H, N, and O, the absorption for the different groups containing these isotopes is usually insignificant. Still it is possible to have an idea of isotopic substitution of different atoms using IR spectra. The frequency for the different groups or bonds were determined from the spectra, and the frequency $\overline{\nu}$ in cm^{-1} of the groups due to isotopic substitutions of atoms was calculated using the relations

$$\overline{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}.$$

Here k is the force constant of the bond and is independent of isotopic substitution, and μ is the reduced mass. The calculated frequencies $\overline{\nu}$ of the groups or bonds with isotopic substitution agree with the experimental values. The calculated frequencies and experimentally observed frequencies (absorption peaks)

Table 7
Intensities of signals of explosives using SIM

Sample no.	m/z of the ion considered for isotope calculation	Natural abundances			
		TNT			
	210	210 natural abundance = 100	211 natural abundance = 9.135	212 natural abundance = 1.374	213 natural abundance = 0.100
1		100	9.031	1.364	0.103
2		100	8.926	1.367	0.110
3		100	8.865	1.285	0.100
4		100	9.108	1.391	0.106
5		100	9.010	1.290	0.101

			RDX		
	205	205 natural abundance = 100	206 natural abundance = 5.795	207 natural abundance = 1.149	208 natural abundance = 0.060
6		100	5.627	1.144	0.054
7		100	5.315	1.151	0.041
8		100	5.420		
			PETN		
	76	76 natural abundance = 100	77 natural abundance = 1.623	78 natural abundance = 0.607	79 natural abundance = 0.009
9		100	1.587	0.600	0.007
10		100	1.639	0.602	0.008
			Tetryl		
	241	241 natural abundance = 100	242 natural abundance = 9.512	243 natural abundance = 1.613	244 natural abundance = 0.125
11		100	9.420	1.604	0.123
12		100	9.566	1.583	0.108

(*Continued*)

Table 7
Continued

Sample no.	m/z of the ion considered for isotope calculation	Natural abundances			
		NG			
	76	76 natural abundance = 100	77 natural abundance = 1.623	78 natural abundance = 0.607	79 natural abundance = 0.009
13		100	1.640	0.613	0.011
14		100	1.783	0.617	0.010
15		100	1.662	0.602	0.008
		ANFO			
16		–			
17		–			

such as C−N for the different groups were compared with the standard compounds. The observed peaks (experimental and calculated values in parentheses) are given in Table 5. From the ratio of areas of the absorption curves of the groups with or without isotopic abundance, it is clear that there is no isotopic labeling in the compounds under consideration.

The bold values in Table 5 are for the standard compounds, and the values for the forensic samples are marked 1, 2, 3, etc. The simple method can be utilized to determine the natural abundances of isotope in the standard samples from different sources or countries of origin. Compilation of the natural abundance values of isotopes may be of great help in the identification of the source of the forensic samples.

In addition to the explosive characteristics and isotope labeling, some other important aspects are worth mentioning. It is known that $\overline{\nu} = 1/2\pi c\sqrt{k/\mu}$, where k is the force constant and μ is the reduced mass or $k = 4\pi^2\overline{\nu}^2 c\ \mu\ \mathrm{Nm}^{-1}$, μ is the same for asymmetric, symmetric, and bending modes of the $-NO_2$ group. It is apparent that the strength of the force constants are of the order $k_{\mathrm{asym}} > k_{\mathrm{sym}} > k_{\mathrm{bending}}$, that is, decomposition is associated with the bending modes.

The time period of vibration is on the order of 10^{-12} sec and is associated with asymmetric, symmetric, and bending modes of vibration. The concentrations of the compound is proportional to its area under the peak (Table 5).

The time period of the existence of NO_2 in the different modes of vibration should also be proportional to their areas under the peaks constituting the modes. The percentage residence times of different modes of NO_2 are given in Table 8.

The frequency of vibration is on the order of 10^{-12} sec, and $\overline{\nu}$ due to bending should be of the order of 10^{-13} sec, that is, frequency of decomposition of an NO_2 group should be of the order of kT/h. It is apparent that the existence, that is, residence of the NO_2 group in the bending mode is greater in RDX, indicating easy rupture of the NO_2 group in RDX compared to others.

The accurate determination of the frequencies of the bonds can give the mode of decompositions of the different bonds. The

Table 8
Percentage residence times of different NO_2 modes

Explosives	T_{asym}:T_{sym}:T_{bending} (actual area)	In terms of % residence time T_{asym}:T_{sym}:T_{bending}
TNT	5601:5165:1297	46.43:42.82:10.75
Tetryl	5927:5187:1851	45.72:40.00:14.28
RDX	3623:2350:2310	43.74:28.37:27.89
NG	6550:6510:4547	37.20:36.97:25.82
PETN	16408:9869:6180	50.55:30.41:19.04

EI MS and CI MS together with FTIR can give a clear picture regarding the decomposition of the explosives.

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