

Thermal and Morphological Analysis of TNT and RDX Recovered From Unserviceable Composition B Explosive for Re-Utilization

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Summary: Energetic materials being sensitive in nature require careful handling during manufacture, storage, transportation and field utilization. Special care is required when these materials are declared Unserviceable (US), degraded or deteriorated. Original high explosive seldom initiates under ordinary circumstances unless appropriate explosive train is provided. But US explosive materials possess high risk of inadvertent initiation. The present study is aimed at finding out thermal behavior and possible degradation mechanism of US Composition B (Comp B) explosive containing RDX and Tri-nitrotoluene (TNT), so that viable means for reutilization of these unwanted energetic materials can be sorted out. Solvent based technique has been used for the successful recovery of US Comp B explosive ingredients. Various analytical techniques such as Thermo gravimetric/ Differential Thermal Analysis, Scanning Electron Microscopy, X-Ray Diffraction and Fourier Transform Infra Red have been used for the analysis of five types of explosive samples to provide insight into thermal behaviour and structure of each explosive sample. Finally, analytical results of both recovered TNT and RDX have been compared with original TNT and RDX samples to find out any possible changes in their thermal behaviour. It has been noticed that the purity and other characteristics like melting point, decomposition temperatures of the recovered versions are almost comparable with original TNT and RDX.

Key words: Composition B (Comp B), RDX, Thermal analysis, Kinetic parameters, TNT, Unserviceable (US).

Introduction

Energetic materials find widespread application for military as well as commercial applications. They are being used for multiple purposes ranging from war field weapons to the commercial mining and underwater blasting areas. Explosive materials are casted into military shells by two different methods i.e. melt cast and press cast method [1]. Just like other chemical compositions, energetic materials have specified shelf life after which they become unserviceable (US) for use especially in military operations. Out of various classes of energetic materials, nitramines are ranked at top due to their high energetic properties and that is why technical application of these energetic materials is always useful [2, 3]. Composition B (Comp B) explosive is a mixture of 60% RDX, 40% TNT but in some cases 1% wax is also added as desensitizing agent. Since both RDX and TNT are mostly used as main explosive charge for filling the military munitions, therefore, successful re-utilization of these precious materials after completion of shelf life helps to reduce the wastage of these energetic materials. Since US explosives are always considered dangerous keeping in view abrupt changes in their thermal and kinetic behavior. Therefore immediate disposal through conventional techniques including demolition, incineration, oxidation and biodegradation are carried out. Application of

unwanted explosive materials in the surface mining industry is widespread demand [4]. Similarly the conversion of these energetic materials into various forms of raw materials such as TNT into DAT gives its applicability into plastic industry [5]. Globally, efforts are in hand for the safest disposal of these unwanted explosives but these techniques are still hazardous for human beings. Similarly, degraded particles present in the soil after demolition process produces adverse biological effects on human beings [6-8]. The present research work is aimed at successful recovery of RDX and TNT from US Comp B explosive through solvent based technique. This technique is not only safe but environmentally acceptable because energetic materials are treated with solvent without heating or exposing to external stimuli. After successful recovery of RDX and TNT from US Comp B explosive, the samples were characterized through different instruments. Thermo-gravimetric/ Differential Thermal Analysis (TG/DTA), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infra Red (FTIR) techniques were used for the purpose of thermal and morphological analysis. Special focus has been made on TNT explosive because of its insensitive nature, thermal stability and relative cost-effectiveness [9-11]. For the same purpose, Rec TNT and RDX explosive samples from

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US Comp B has been compared with Original TNT and RDX samples for in-depth analysis. SEM analysis has particularly been done so that morphological changes between Original and US explosive samples could be compared.

Experimental

Material and Methods

US Comp B, Original TNT and Original RDX were purchased from Pakistan Ordnance Factories (POFs) Wah. Chloroform was selected as solvent for recovery of Comp B ingredients (i.e. RDX and TNT). Analytical grade chloroform was then purchased from local market. Solvent based method was used for the successful recovery of RDX and TNT from US Comp B explosive for further investigation and characterization along with Original TNT and RDX.

Recovery of RDX and TNT from US Comp B explosive

Comp B containing 59.5 % RDX / 39.5 % TNT and about 1% paraffin wax is a melt cast explosive mixture. In order to recover RDX and TNT from US Comp B explosive sample through solvent based technique, the solubility of RDX and TNT per 100 g of solvent was studied at temperature range of 20-25°C from Table-1 and Table-2 respectively [12].

Table-1: Solubility of RDX in gram per 100 g of Solvent.

Solvent Type	Solubility at 20-25°C
Water	0.006 (25 °C)
Ethanol	0.11 (20 °C)
Diethyl ether	0.055 (20 °C)
Chloroform	0.008 (20 °C)
Toluene	0.02 (20 °C)
Benzene	0.05 (20 °C)
Dimethyl sulfoxide	41.0 (25 °C)
Acetone	8.2 (25 °C)
Dimethylformamide	37.0 (25 °C)

Table-2: Solubility of TNT in gram per 100 g of Solvent.

Solvent Type	Solubility at 25°C
Water	0.02
Ethanol	1.5
Diethyl ether	3.8
Chloroform	25.0
Toluene	67.0
Benzene	88.0
Dimethyl sulfoxide	128.0
Acetone	132.0
Dimethylformamide	142.0

Table-1 and 2 revealed that Chloroform, being the most important solvent, based on solubility difference, could be used for the recovery of RDX and TNT from US Comp B explosive sample [12]. A

small amount of Chloroform was added to powdered US Comp B explosive sample in a separating funnel. The mixture was completely shaken and then allowed to remain stationary on the clamp stand for a while so that RDX and TNT could be completely recovered from US Comp B in two distinct layers based on solubility difference in the Chloroform. This process was repeated a number of times before finally white crystalline particles of RDX were recovered, collected and dried in the open air environment. Chloroform solvent completely evaporated. Similarly, TNT particles in brownish colour were also collected in crystalline form after heating in oven bath at a temperature just below its melting point of 81 ± 1 °C. In the final phase, distilled water was added to TNT/ wax mixture so that insoluble wax floating on the top-most layer could be easily recovered and collected. Rec TNT and RDX were then analyzed through different techniques to find out their thermal behavior and morphology.

Analytical Techniques

Thermal and morphological analysis of all five samples including US Comp B, Rec RDX, Rec TNT, Original TNT and Original RDX have been carried out. Instruments used were Scanning Electron Microscopy (SEM-6490A JEOL made in Japan), Thermo gravimetric /Differential Thermal Analyzer (TG/DTA- Perkin Elmer Model Pyris Diamond), X-Ray Diffraction (XRD- made by Theta-Theta Toe, Germany) and Fourier Transform Infra Red (FTIR- Model Spectrum 100).

Scanning Electron Microscope

SEM, being one of the most versatile tools in identification of structural information, can be employed in the field of explosive detection and identification. To carry out the present work, scanning electron microscope (SEM) instrument, 6490A JEOL has been used. Variable voltages of 2-20kV and magnifications of 1500, 3000 and 10000 were applied at different angles keeping in view the sensitivity and nature of the samples

Thermo Gravimetric / Differential Thermal Analysis (TG/DTA)

TG/DTA is a very strong tool for thermal and kinetic studies of the sample under controlled temperature program. Perkin Elmer Model Pyris Diamond TG/DTA (Thermo gravimetric/ Differential Thermal Analysis) instrument available at SCME, NUST has been used for the thermal analysis of various samples. Five different samples including US Comp B, Rec RDX, Rec TNT, Original TNT and Original RDX were examined using Perkin Elmer

TG/DTA. This instrument works at a heating rate of $0.001^{\circ}\text{C}/\text{min}$ to $200^{\circ}\text{C}/\text{min}$. In order to calibrate the apparatus, standards were run and then initial setup for actual analysis was made. Nitrogen was used as purging gas for creation of inert atmosphere. All samples were subjected to a heating rate of $10^{\circ}\text{C}/\text{min}$ and temperature range was kept between 25°C to 350°C .

X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis has also been carried out in the present research work due to its wide range of investigation for a particular sample. Various parameters such as crystal structure, atomic arrangement, phase orientation, lattice parameters, grain size and density etc. of any sample can be easily identified.

Fourier Transform Infra Red (FTIR)

This instrument is particularly used to observe band position, shape and peak intensity of various samples so that characteristics of functional groups can be identified. It has a wave number ranging from 10000 cm^{-1} to 100 cm^{-1} . In this technique infra red spectrum of absorption, emission and Raman scattering of a solid, liquid or gas can be obtained.

Results and Discussion

Scanning Electron Microscope Analysis

In Fig. 1, US Comp B explosive sample in powder form was subjected to SEM analysis and investigation. From SEM images it has been revealed that US Comp B has spindle-like structure with multiple cracks and porosity of 160-521 nm size visible on the surface. The sample was examined at variable voltages between 3-5kV because at higher magnification and with increase in voltage, sample behavior showed abrupt changes which proved unsafe for further analysis. The sample has completed its shelf life; therefore various climatic changes may have rendered multiple cracks and porosity in its surface. These cracks adversely affect the sensitivity of this explosive and render it unsafe.

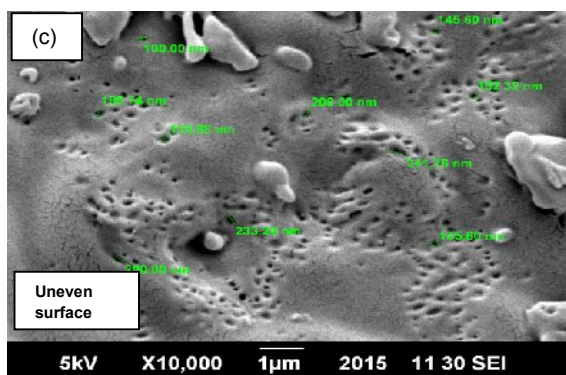
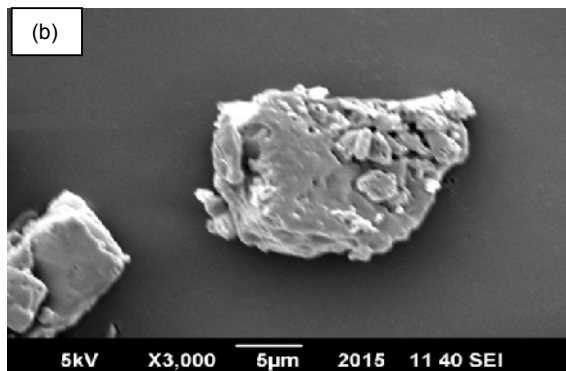
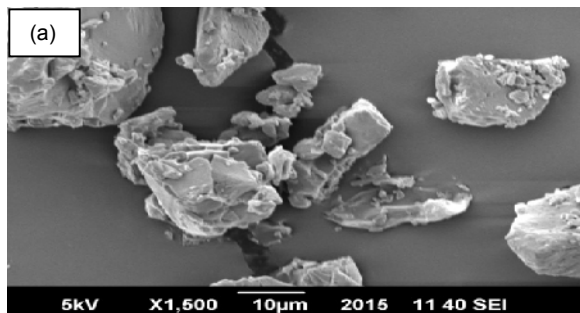


Fig. 1: SEM Images of US Composition B explosive sample at 5kV and Magnifications of (a) 1500; (b) 3000; (c) 10000.

In Fig. 2, a small quantity of Original TNT was investigated for its morphology. It has been noted from the in-depth analysis that Original TNT has an even surface with irregular blocks shape microstructure. Very few pores can be seen in the image which shows that the sample is uniform having integrated particle structure and is defect-free explosive sample unlike Rec TNT sample. Presence of cracks on explosive surface has multiple reasons, some of which may be inappropriate storage conditions and adverse climatic effects. An explosive material is designed to be free from any kind of filling or formulation defects, otherwise it may cause premature ignition of the munitions. Similarly, exudation process can also be a cause of some defects during hot climate. For the explosive materials, both the physical as well as chemical behaviors are most important aspects. These include explosive materials crystalline or non crystalline shape, pore size and its density, ignition temperature etc.

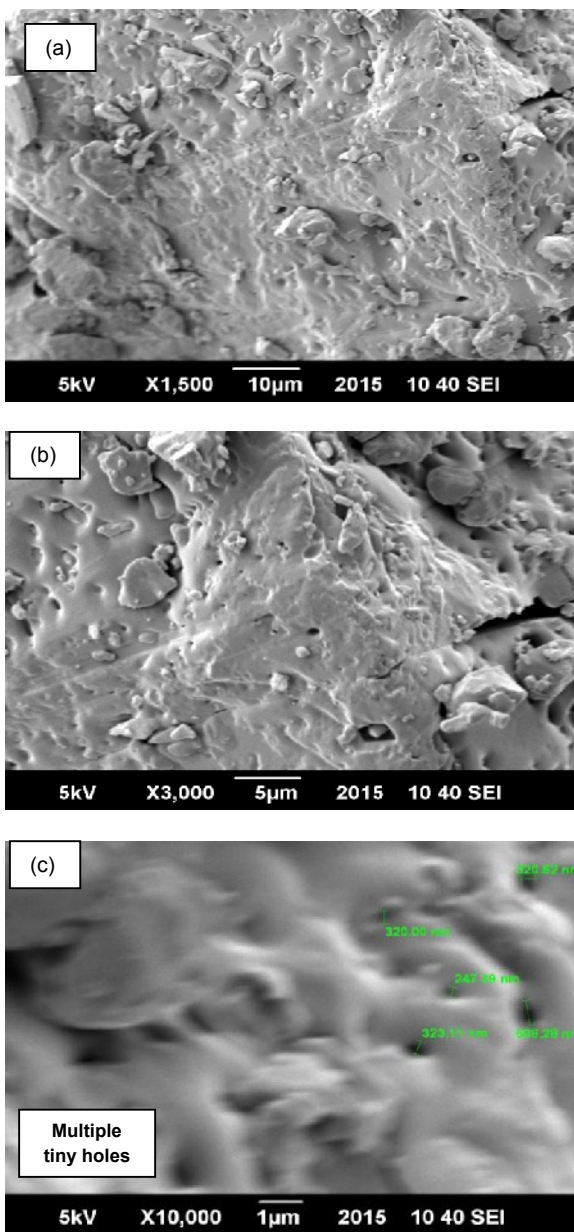


Fig. 2: SEM Images of Recovered TNT explosive sample at 5.0kV and different Magnifications of (a) 1500; (b) 3000; (c) 10000

In Fig. 3, a small quantity of Rec TNT sample was examined through SEM analysis at 5kV and different magnification for its complete picture. Morphological studies reveal that the sample has an irregular shape with no specific orientation. Multiple pores in the size range of 247-608 nm are visible which render this sample unsuitable for field utility as compared to Original TNT sample whose surface is smooth and homogeneous [13]. Since sample was treated with water during separation process,

therefore chances for increase in porosity cannot be ruled out. However, a major reason for large number of pores on the surface is long shelf life.

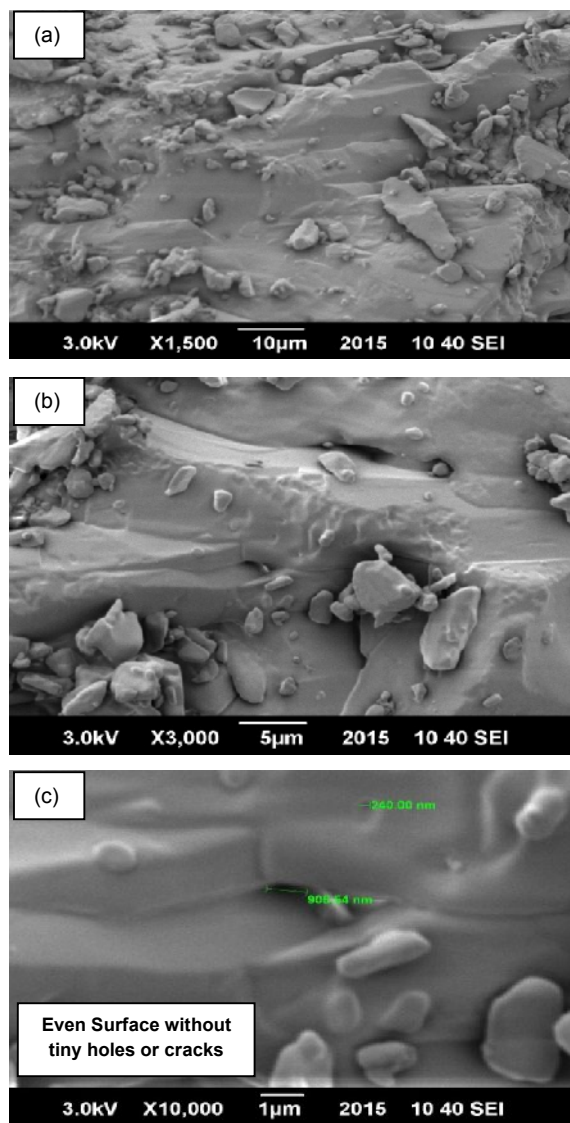


Fig. 3: SEM Images of Original TNT explosive sample at 3.0kV and different Magnifications of (a) 1500; (b) 3000; (c) 10000.

In Fig. 4, SEM analysis of Rec RDX revealed that this particular sample is more dangerous in nature especially once exposed to an high temperature environment. The sample was analyzed at constant voltage of 5kV respectively keeping in view its erratic behavior. Sample has multiple cracks with width sizes of 212- 384 nm and varied lengths. The surface seems to be more compact and flat in shape. Multiple cracks on its surface are quite evident.

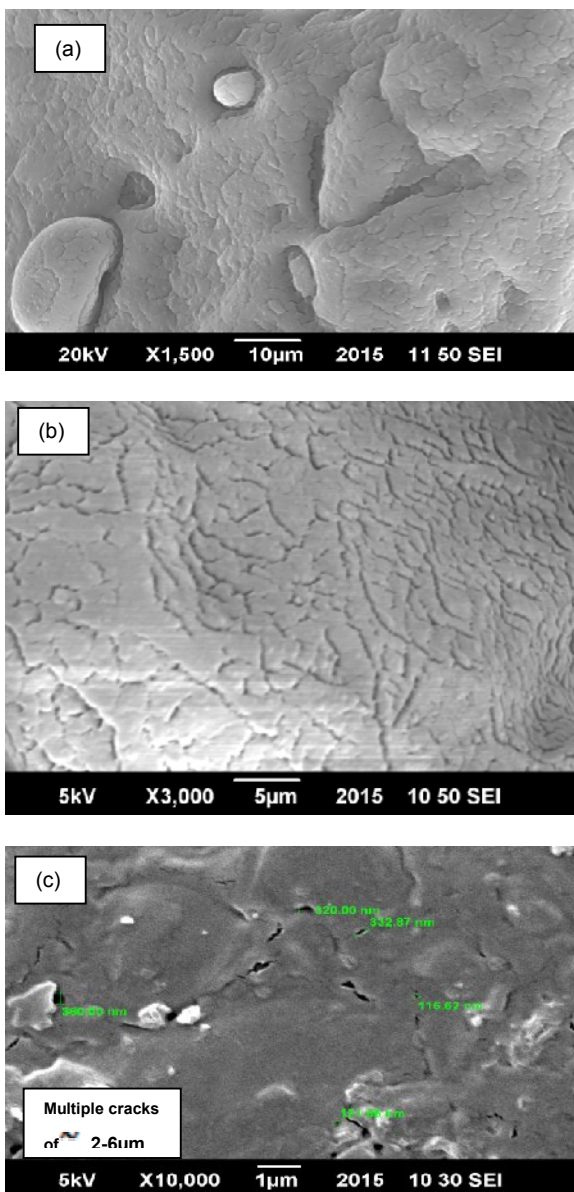


Fig. 4: SEM Images of Recovered RDX explosive sample at 20-5.0kV and different Magnifications of (a) 1500; (b) 3000; (c) 10000

In Fig. 5, SEM analysis of original RDX revealed that this particular sample has spherical shaped morphology with multiple tiny holes spread across the surface. Analysis was carried out at constant voltage of 5kV but at different magnifications of 1500, 3000 and 10000. No much difference has been observed in this particular sample as compared to the Rec RDX Sample. Surface is flat with multiple cracks of 170.88-475.39 nm sizes and varied lengths.

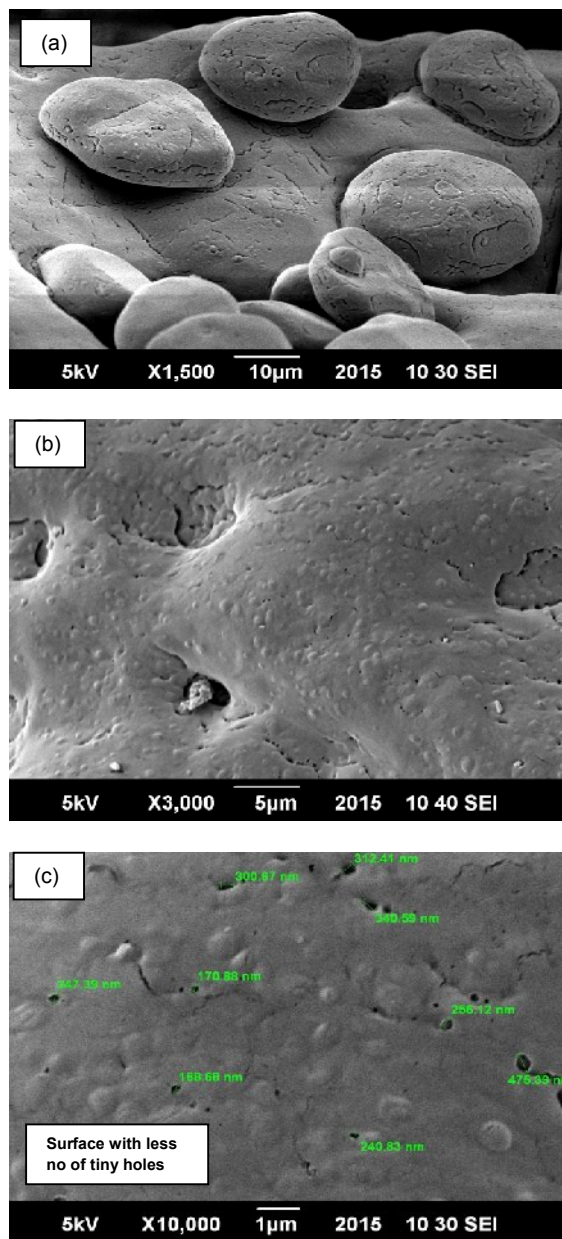


Fig. 5: SEM Images of Original RDX explosive sample at 5kV and different Magnifications of (a) 1500; (b) 3000; (c) 10000.

Thermo Gravimetric / Differential Thermal (TG/DTA) Analysis

TG curves of all five explosive samples including Rec TNT, Original TNT and Original RDX are given in Fig. 6. It has been noted that TG curves for all samples exhibit nearly 100% mass loss in a single step. Onset of mass loss for TNT samples both in Rec and Original samples seems to start near 165°C, whereas for RDX sample, mass loss is observed to start near 180°C. A rapid shift in mass

loss has been identified between 180-245°C due to thermal decomposition of TNT and RDX. Hence the total mass loss for all the samples over controlled temperature range of 165-245°C was found to be nearly 99%.

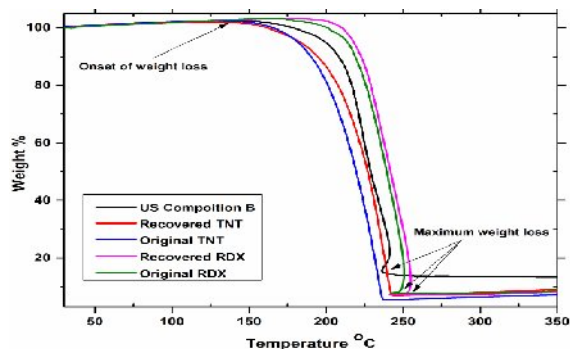


Fig. 6: TG Curves of five different samples.

Fig. 7 shows DTA thermograms for various explosive samples including US Comp B, RDX and TNT. Two different thermal behaviors have been found with endothermic reaction occurring in first stage. Before melting of TNT, there is no significant change in the thermal behavior of TNT and RDX. However, sharp endothermic event can be observed between 81-83°C which corresponds to melting of TNT [14-16]. Similarly, early stage melting of RDX is obtained near 190°C in case of US Comp B and original RDX sample melting near 204°C [17-19] can be deduced from Fig. 7 above. This shift in melting point of RDX is due to presence of more impurities in case of US Comp B sample and slightly less number of impurities for Rec RDX. In the next stage, exothermic peaks are visible for RDX decomposition between 239-250°C, which corresponds to thermal decomposition of RDX. However, for TNT, thermal decomposition between 235- 239°C occurs with endothermic reaction. A few degrees temperature difference for all thermograms in respect of RDX and TNT is probably because of the presence of impurities in Comp B sample and variation of environmental condition during solvent treatment of the samples.

XRD Analysis

XRD results of RDX and TNT shown in Fig. 8 reveal several different distinctive diffraction peaks with varying intensity. It has been observed that both TNT and RDX maintain crystalline structure in all types of state. XRD spectra exhibited these peaks in the range of 10 to 40 (2 theta degree).

The diffraction pattern of RDX can be easily distinguished from TNT. Spectra revealed that TNT exists in monoclinic structure possessing more stability than meta-stable state in both samples under observation. Miller indices have been identified on XRD spectra with number of h, k, l values of (-202), (004), (021), (-315) for TNT and (111), (210), (102) and (132) for RDX crystals. Spectra showed that RDX exists in cubic crystal structure and its peak at h, k, l value of (102) seemed to be more intense and sharp due to high crystalline nature. It has also been noted that both Rec and original RDX exhibits almost similar spectra. Similarly, TNT peak with h, k, l value of (004) gives more intense value due to higher degree of crystalline nature in TNT crystal. Experimental results so obtained are in agreement with literature values for TNT and RDX in original form and thus proves its existence in its actual state even after treatment with solvent.

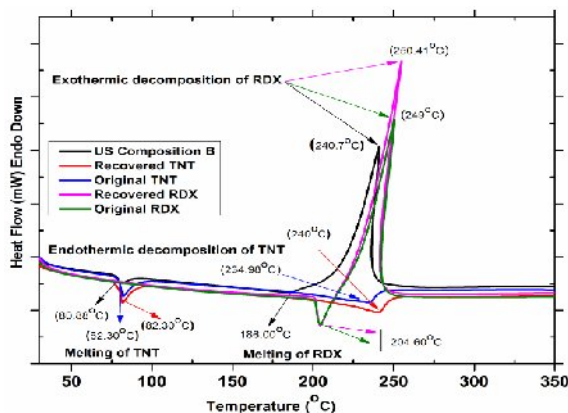


Fig. 7: DTA Curves of US Composition B, RDX and TNT samples.

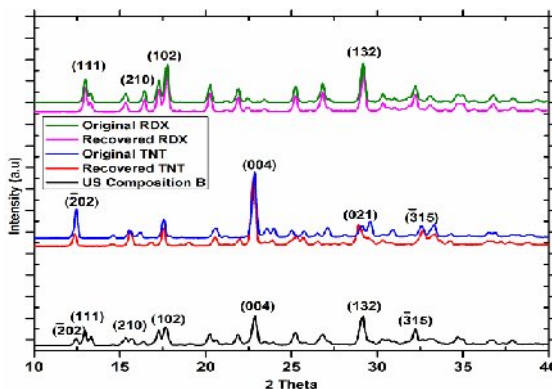


Fig. 8: XRD patterns of five different samples.

Table-3: Experimental vibrational frequencies (cm^{-1}) of RDX and TNT observed in FTIR spectra along with their descriptions

Name of Explosive	Experimental vibrational frequencies (cm^{-1}) of RDX and TNT	Available literature data on vibrational frequencies (cm^{-1}) of Original RDX and TNT	Description of the normal modes of vibration	Peak strength
RDX (Original and Recovered)	3074.76	3075	C-H stretch (symmetric)	Strong
	3074.96			
	1591.79	1593	N-O stretch	Strong
	1591.88			
	1386.32	1390	C-N stretch	Strong
	1386.10			
	1038.51	1040	C-N stretch	Strong
TNT (Original and Recovered)	1038.49	783	N-N-O bend	Strong
	779.48			
	779.51			
	585.07	590	Ring distortion at C atoms	Medium overlap
	585.10			Weak
	3095.98	3097	C-H ring stretch (antisymmetric)	
	3096.00			
TNT (Original and Recovered)	1351.62	1354	C-C ring stretch	Very strong
	1351.72			
	639.41	639	C-C ring bending	Small
	460.87	462	Ring torsion	Very small

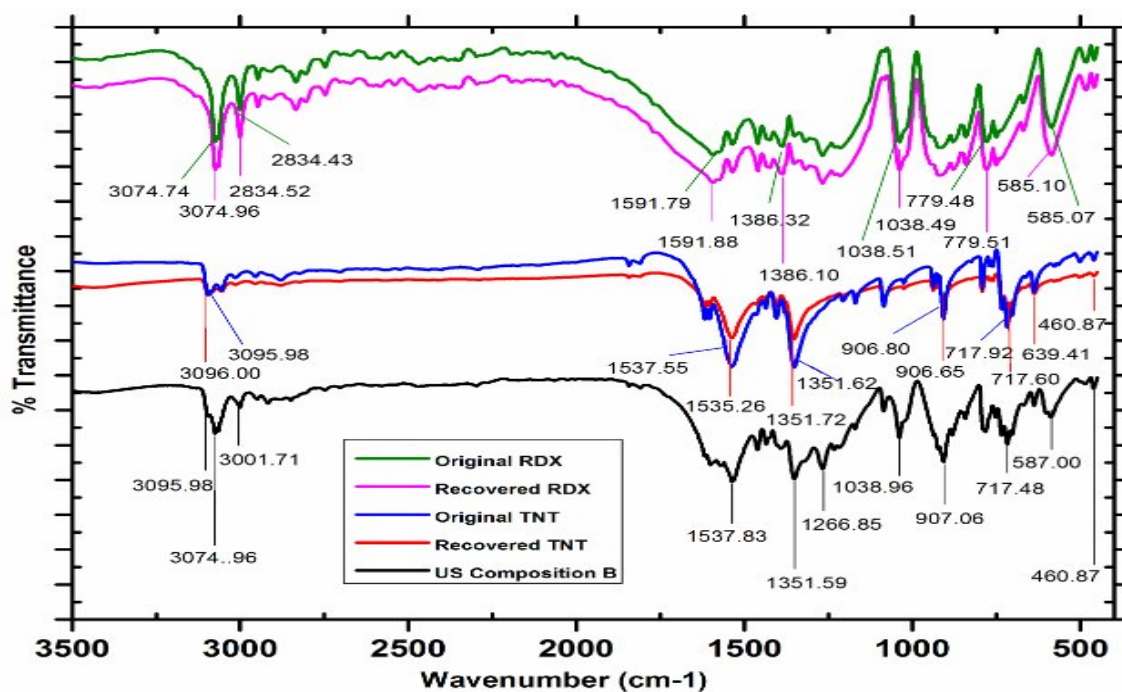


Fig. 9: FTIR Spectra of US Composition B, Recovered TNT, Original TNT, Recovered

FTIR Analysis

All selected explosives sample shown in Fig. 9 were subjected to spectroscopic characterization between 350 cm^{-1} to 3600 cm^{-1} and various absorption lines have been observed in this range. Observed vibrational frequencies of Original and Rec TNT samples are 460.87, 639.41, 717.92, 717.60, 1351.62, 1351.72, 3095.98 and 3096.00. However, for Original and Rec RDX, numerous vibrations of 585.07, 585.10, 779.48, 779.51, 1386.51, 1038.49, 1591.79, 1591.88, 3074.74 and 3074.96 have been identified. Table-3 gives experimental vibrational frequencies of TNT and

RDX observed in FTIR spectra along with available literature data on original explosive [20].

Conclusion

In this study various aspects like thermal behavior, possible degradation, crystalline structure and morphology have been identified for US Comp B, Original TNT, RDX and recycled versions of TNT and RDX. Results from these analytical techniques indicate that the presence of impurities in these energetic materials have ultimately resulted into degradation of these substances and thus rendered them US for further use. However, these US explosive substances can be effectively reutilized in

multiple applications such as for civil, industrial and commercial purposes after the modification. Solvent based technique used in the present research work has resulted into successful recovery of TNT and RDX from US Comp B. The technique is quite safe, cost effective and environmentally friendly process for reutilization of unwanted but most precious commodity i.e. highly energetic materials. It has been noticed that recovered TNT and RDX samples are of good purity and have various characteristics like melting point, decomposition temperatures comparable with original TNT and RDX. Thus these energetic materials, if properly managed can be reutilized in various civil, industrial and commercial applications including plastic industry, polymers, for rock blasting, mining, quarrying etc.

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