Science of the Total Environment 842 (2022) 156864

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Analysis of samples of high explosives extracted from explosive remnants of war

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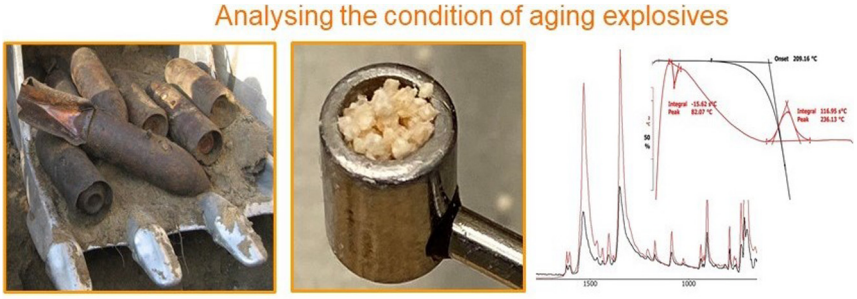
HIGHLIGHTS

- Huge amounts of explosive remnants of war remain in nature.
- The performance and impact sensitivity of WW2 munitions has been studied.
- Analysed high explosives (TNT and PETN) were extracted from live ordnance.
- Explosives were found to be in good condition with no detected decrease in sensitivity.

GRAPHICAL ABSTRACT



High explosives extracted from WW2 munitions analysed and tested for impact sensitivity

ARTICLE INFO

Editor: Yolanda Picó

Keywords:
Unexploded ordnance
Explosive remnants of war
Fourier transform infrared spectroscopy
Impact sensitivity
Thermal analysis

ABSTRACT

Millions of tonnes of dumped ammunition and explosive remnants of war remain in nature both on land and at sea. It is well known that the ordnance could represent a definite explosive risk if disturbed, and that some of the constituents in the ammunition could be harmful to humans and the environment. Nevertheless, a tacit assumption by decision makers is that, if left alone, the ammunition will slowly become harmless over time. Explosive remnants of war, however, represent not only an environmental risk but also a security and safety risk, as members of the public could come into contact with them, and fear is growing that ageing munitions could explode and/or be misused. In recent years, several concerns have been raised regarding the presence of dumped ammunition and explosive remnants of war, the potential dangers they represent, and the fact that the deterioration rate of the explosives could be significantly lower than previously assumed. In the present work, thermal and impact sensitivity studies of high explosives extracted from explosive remnants of war were performed, to determine whether or not the explosives have deteriorated to such a degree that a noteworthy decrease in performance and/or impact sensitivity can be recorded. The thermal behaviour of the explosives was studied using thermogravimetry analysis, and the impact sensitivity was determined using a fallhammer machine and the Bruceton test procedure. The thermal and impact sensitivity results obtained in the analysis indicated no deterioration of high explosives in the examined explosive remnants of war that would denote any significant reduction in performance and/or impact sensitivity.

1. Introduction

In the aftermath of war and armed conflict, millions of tonnes of explosive remnants of war (ERW) and unexploded ordnance have been dumped in landfills, lakes and seas (Kampmeier et al., 2020; OSPAR Commission, 2009). It was believed that the ammunition and explosives would deteriorate and slowly become harmless over time. Although the dumpsites are

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http://dx.doi.org/10.1016/j.scitotenv.2022.156864
Received 4 April 2022; Received in revised form 17 June 2022; Accepted 17 June 2022
Available online 22 June 2022

acknowledged by the authorities, their real extent and their effect on environmental and societal safety are mostly unknown (Kampmeier et al., 2020). As a result, there has been an assumption that, if left alone, the ammunition will generally not represent any significant risk. Consequently, explosives and ammunition in dumping sites, shipwrecks and ammunition-contaminated land are often ignored (e.g., Alexander, 2019; Long, 2005), and in many cases no effort is made to either survey the sites or clear the ammunition. The munitions do, however, represent a steadily increasing concern regarding both safety and security. Although the societal risk related to ERW has been described as more hypothetical, it is now increasingly clear that simply neglecting the problem is no longer a viable solution, as continuous deterioration of the munitions can lead to an increased risk to societal safety (Craig and Taylor, 2011; NATO, 2010; OSPAR Commission, 2009). Studies show that the leaking and bioaccumulation of toxic constituents from corrosive munitions poses a threat to the ecosystem and that several of the chemicals used in ammunition are highly poisonous and have been proven to contaminate living organisms, as well as the surrounding soil and groundwater (ATSDR, 1995; Koske et al., 2019; Koske et al., 2020; Schuster et al., 2021; Yinon, 1990). Some munitions' constituents may also enter the food chain and directly affect human health upon the consumption of contaminated food (Maser and Strehse, 2021).

The most prominent risk, however, is naturally that of an unplanned explosion. Such an explosion could occur as the result of an intended act of terrorism or crime, utilizing the explosive effect of high explosive munitions or harvested explosives from such, or accidentally as a result of the intentional or unintentional disturbance of the ordnance (e.g., construction work, moving, rendering safe or disposing of ammunition). An increasing number of spontaneous detonations have also been reported in ageing munitions, possibly resulting from deteriorating technical or chemical properties (Ford et al., 2005; Nordaas, 2019), and research indicates that ageing explosive ordnance can become increasingly sensitive to external stress (Albright, 2012; Hamer, 2004; Long, 2005; Pfeiffer, 2012).

There are, however, only a very limited number of studies that analyse the properties of high explosives (HE) retrieved from ageing ERW, but those that do exist suggest that the explosives are in very good condition (e.g., Nawała et al., 2020). The main aspect of this work is to analyse explosives retrieved from a representative number of samples of actual ageing ERW, with particular attention paid to the impact sensitivity of these explosives. Whilst the most sensitive part of HE ordnance generally is the primary explosives, this particular study will focus exclusively on a limited selection of secondary explosives: Trinitrotoluene (TNT) and Pentaerythritol Tetranitrate (PETN), as shown in Fig. 1. This selection was made because these particular types of explosives were widely used throughout World War II (WW2) and can be expected to be encountered wherever WW2 munitions are located. Additionally, there is a much higher frequency of secondary explosives being encountered, partly due to the fact that they represent a much bigger mass in comparison with the incorporated primary explosives but also because much of the discarded ordnance was dumped separately from its initiating sources, in which the primary explosives are located (Bełdowski et al., 2019). Although primary explosives are considerably more sensitive to external stress than secondary explosives and can easily detonate by the action of a relatively weak mechanical shock, heat, spark and/or friction, they are often also easily desensitized by the presence of humidity. Additionally, if the initiating source (e.g., the fuze) is fitted to the ordnance, the main explosive charge is normally protected from the explosive impact of the primary explosives by the means of mechanical safety devices, thus preventing a detonation transfer to the main charge. Although secondary explosives cannot be initiated as easily as primary explosives, and are usually therefore initiated by means of a detonator containing primary explosives, they can in practice also be initiated under the influence of other forms of external energy (thermal, mechanical, etc.) (Suceska, 1995). As all interaction with ERW that introduces sufficient external energy to the explosives can theoretically initiate a chemical reaction resulting in a detonation, it is therefore of vital importance to establish the relevant thresholds.

Consequently, this study focuses on the chemical properties of the most common of explosives originating from WW2 ERW, TNT and PETN, and whether or not the ageing of the explosives has led to any significant changes in respect to thermal properties and impact sensitivity.

2. Materials and methods

2.1. Sample characteristics

TNT is by far the most important explosive for the blasting charges of all weapons (Meyer et al., 2005). It is normally charged by casting or pressing and can be applied pure or mixed with other substances such as ammonium nitrate (e.g., Amatols), aluminium powder (e.g., Trional), RDX (e.g., Cyclonite) and combinations (e.g., Torpex). It is considered one of the least impact- and friction-sensitive of all common explosives, and cast charges of TNT are insensitive to blasting caps and require a booster charge (e.g., PETN) for safe initiation. This, combined with a fairly high explosive power and good chemical and thermal stability, has meant that TNT has been the most widely used military explosive since before World War I (WWI) up to the present time (Kaye and Herman, 1980).

PETN, on the other hand, is a much more sensitive explosive and is considered one of the most powerful and brisant explosives known (Kaye, 1978). It is a very stable explosive but, as it is much more sensitive than TNT, requires very little priming charge. PETN is often used in high-capacity blasting charges and detonation cords and, if phlegmatized, may be used to produce boosters and fillings for smaller-calibre projectiles (Meyer et al., 2005). It can be applied pure or mixed with other substances such as TNT (e.g., Pentolite) or RDX (e.g., Semtex).

Both TNT and PETN are considered virtually insoluble in water (Meyer et al., 2005). This property affects their long-term persistence in the aquatic environment; therefore, dependent on a number of factors, the explosive

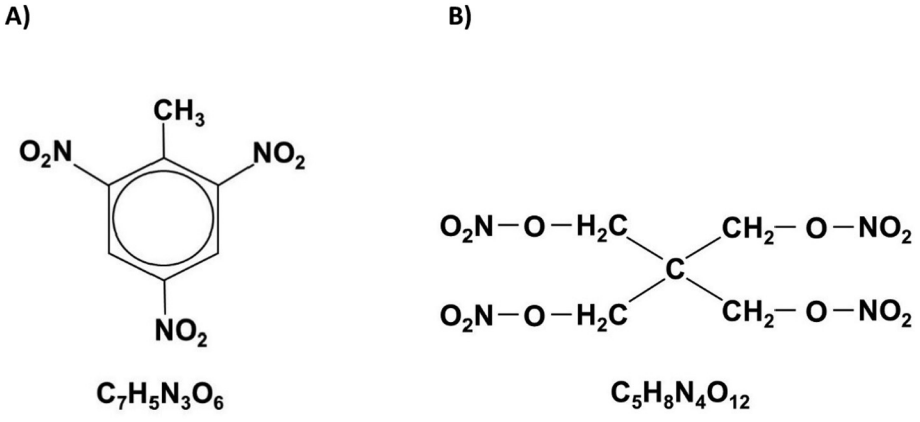


Fig. 1. Chemical formulas of the high explosives extracted from explosive remnants of war in this study; A) TNT and B) PETN.

filler present in munitions could take centuries to dissolve (Craig and Taylor, 2011).

2.2. Sampling location and methodology

To ensure reliable data, all samples have been extracted from live ordnance originating from WW2. Relevant objects were ERW in Norway containing high explosives. Consequently, all explosive objects utilized for the extraction of their high explosives are ERW that have been localized and/or reported to the relevant governmental agencies. All samples of high explosives have been extracted from the relevant objects and analysed within the last three years (i.e., 2020–2022). The author carried out the physical extraction of the high explosives from the ordnance. In situations where it was deemed too unsafe or impracticable to move the explosive objects, the extraction was performed at the location where the object was first discovered. The majority of objects that had to be dismantled in the field were located in areas of heavy fighting during WW2. For the most part, this concentrates around circumpolar Norway, more particularly in Troms and Finnmark county in the northernmost part of Norway. Any required disassembly of the objects in order to access the high explosives was normally carried out with the use of explosives (e.g., shaped charges, etc.), as shown in Fig. 2, and/or with the use of a lightweight, portable and specially customized metal band saw.

Samples that were deemed safe to move and to transport were normally dismantled/disassembled in specialized explosives workshops, belonging to defence agencies under the Norwegian Ministry of Defence, and under the directions and regulations of the Norwegian Armed Forces. Any required disassembly of the objects was normally done mechanically (i.e., reversed engineering), as shown in Fig. 3, with the use of remote-controlled tooling (e.g., lathe, band saw, drill, etc.) or manual dismantling where applicable.

After any required disassembly of the explosive object, an initial sample of the high explosives was retrieved at the point of entry. The explosives were visually examined, and any surface changes in homogeneity (i.e., variations in colour, texture, consistency, etc.) were recorded. Wherever possible, samples were extracted at the central core of the explosives, from any contact surfaces (i.e., where the explosives come into contact with the ammunition body or metal parts), at the entry point, and wherever any fluctuations in homogeneity were observed.

In total, samples of high explosives were extracted from over 60 individual ERW and subjected to analysis and testing. Of these, 50 samples identified as TNT and PETN were included in this study. Analysed samples consisting of other high explosives (e.g., Tetryl, RDX, etc.) or compositions of different explosive substances (e.g., Amatol, Donarit, Pentolite, etc.) are not included in the study, at this time. The preliminary results of the analyses of the explosives omitted from this study indicate, however, that further research should be conducted, as some of the analysed samples demonstrate an impact sensitivity that conflicts with expected values (i.e., a significantly increased impact sensitivity). Of the 50 samples included in this study, 25 were located on land and 25 submerged in water. Twenty-six of the samples were found to be intact, with no exposure of the explosives to the elements, three samples were found to be partially open (i.e., water intrusion to the explosives), and 21 were open (i.e., full exposure of the explosives to the elements). All 50 samples included in this study were extracted at the central core of the explosives. Extracted samples not included in this study (i.e., other than central core) will be subject to further, future analysis.

Fig. 2. German 10.5-cm HE projectile cut with flexible linear-shaped charge.

Fig. 3. German 20-mm HE projectile mechanically disassembled.

2.3. Storage and preparation of samples

Once extracted, the high explosive samples were immediately placed in airtight containers (i.e., 50-ml sterile polypropylene screw-cap tube) and stored in approved ammunition storage facilities. Apart from humidity control (at about $\leq$50 %), the samples were stored in normal atmospheric conditions, in continuation of the normal temperature fluctuations that would appear in nature, albeit with less violent variations, as the samples were stored under cover, protected from direct sunlight.

Preceding the impact sensitivity analysis, the samples were prepared in accordance with the requirements of NATO STANAG 4489 - Explosives, Impact Sensitivity Tests (NATO, 1999) and the United Nations Manual of Tests and Criteria - Classification Procedures, Test Methods and Criteria Relating to Explosives, Test 3 (a) (ii) (United Nations, 2019): Powdered substances are sieved and only a fraction with a particle size of 0.5 to 1.0 mm is used for testing. Pressed or cast substances are crushed and then sieved. The fraction passing a 1000-μm sieve and retained on a 500-μm sieve is used for the test. Rubbery or composite materials are cut into slices of 3-mm thickness and approximately 4-mm length and width (NATO, 1999), or a cylindrical tube of 40-mm^3 capacity (3.7 mm diameter $\times$ 3.7 mm) is inserted into the substance, and, after levelling off the surplus, the sample is removed from the tube by means of a wooden rod (United Nations, 2019).

As several of the objects from which the samples were extracted were damaged (e.g., partially destroyed, corroded, disassembled, etc.), some of the explosives were saturated with water. In preparation of further

analyses, explosives positively identified as TNT or PETN (See Section 3.1) were placed in a humidity-controlled environment to reduce the relevant humidity (RH) in the sample to about 20 % RH.

2.4. Description of analysis equipment and methodology

2.4.1. FT-IR spectrometer analysis

Fourier transform infrared spectroscopy (FT-IR) uses a mathematical process (Fourier transform) to translate the raw data into the actual spectrum. The FT-IR method can be used to obtain the infrared spectrum of transmission or absorption of a sample of explosives. FT-IR identifies the presence of organic and inorganic compounds in the sample, and the specific molecular groups prevailing in the sample will be determined through spectrum data in the automated spectroscopy software (Shameer and Nishath, 2019).

In this study, FT-IR has been used to characterize samples of high explosives retrieved from ERW. A Thermo Scientific TruDefender FT and a Smiths Detection HazMatID 360 apparatus were used for this analysis, and the tests were performed in accordance with the requirements described in the applicable test procedures. The technique involves placing a sample on top of a diamond crystal embedded in a stainless steel disk, whilst an infrared beam is passed up from the spectrometer through the crystal, reflected internally in the crystal and back towards the detector, which is housed within the spectrometer (HazMatID 360). The device collects the molecular fingerprint of the sample, compares it against an onboard chemical library and then provides an identification of the substance or mixture of substances, as well as presenting the sample infrared absorption frequency in the spectrum range 600–4000 cm^{-1}, compared with the relevant library hit(s). Explosive samples positively identified by FT-IR as either TNT or PETN were included in this study and selected for further analysis. An example of the analysed samples is shown in Fig. 4.

2.4.2. Thermal analysis

Thermogravimetric analysis (TGA) is an analytical technique used to determine a material's thermal stability and its fraction of volatile components, by monitoring the weight change that occurs as a sample is heated, cooled or held at constant temperature (Rajisha et al., 2011). The record is a thermogravimetric or TG curve. Single Differential Thermal Analysis (SDTA) is a procedure for recording the difference in temperature between a substance and a reference material, against either time or temperature, as the two specimens are subjected to identical temperature regimes in an environment heated at a controlled rate. The record is the single differential thermal or SDTA curve; the temperature difference is usually plotted on the ordinate, with endothermic reactions downwards, and time or temperature on the abscissa, increasing from left to right (Kaye and Herman, 1980). The analyses were carried out on the high explosive samples, in order to identify characteristic temperatures, which are exhibited whilst heating the sample at a constant rate, with the aim of characterizing the materials with regard to their composition.

A Mettler Toledo TGA/SDTA851e apparatus was used to investigate the thermal properties of the samples. Preceding the analysis, the samples were crushed and then sieved where applicable. After calibration of the apparatus (i.e., weigh-in of empty pan), a weighed sample (≈3 mg) with particle size <500 μm was placed in a 100-μl aluminium pan and positioned in the sample holder of the instrument. All measurements were performed at a single heating rate of 10 K/min, and the data were recorded as mW versus temperature/time from 40 °C to 400 °C. An inert atmosphere was maintained by using a nitrogen gas purge at a rate of 50 mL/min throughout the experiment.

2.4.3. Impact sensitivity analysis

For the impact sensitivity determination, several types of impact testing apparatus, known also as Fallhammer Apparatus, are used. These apparatuses operate on the same principle: a sample of the tested explosive is subjected to the action of falling weights of different sizes, and the parameter to be determined is the height of fall at which a sufficient amount of impact energy is transmitted to the sample for it to decompose or explode (Meyer et al., 2005). The main difference between the various apparatuses is related to their design and the manner in which the sample is subjected to the drop weight impact via different types of plungers (Suceska, 1995). The fallhammer method was modified by the German Bundesanstalt für Materialprüfung (BAM), in order to obtain more reproducible data (Meyer et al., 2005), and this apparatus (the BAM Impact Machine or the BAM Impact Apparatus) is considered to give reasonably reproducible results (Suceska, 1995).

The BAM Impact Apparatus, OZM BFH 12, was used for this analysis, and the tests were performed in accordance with the requirements of the test procedure described in NATO STANAG 4489 - Explosives, Impact Sensitivity, Annex C; BAM Impact Machine (NATO, 1999). The BAM Impact Machine, which is presented in Fig. 5 A, consists of two coaxially arranged steel cylinders with polished surfaces and rounded edges, held in place by a cylindrical steel guide ring with an inner diameter of 10 mm. The impact device is prepared by partially pushing one of the cylinders into a guide ring and positioning it on the intermediate anvil fitted with a locating ring, as shown in Fig. 5 B. Using a measuring spoon, 40 mm^3 of the prepared (e.g., crushed and sieved to particle size 500 μm to 1000 μm) high explosive samples are placed inside the open impact device, making sure that a central heap is formed. The impact device is then closed with a second steel cylinder, by carefully pressing it into the guide ring until it touches the sample. For the impact sensitivity testing, different drop weights, with a mass of 0.25 to 10 kg, are available. The body of each drop weight has two guide grooves, in which it moves between the guide rails. It is equipped with a suspension spigot, which arrests the weight in the release mechanism, and is further provided with a cylindrical striker, a height marker,

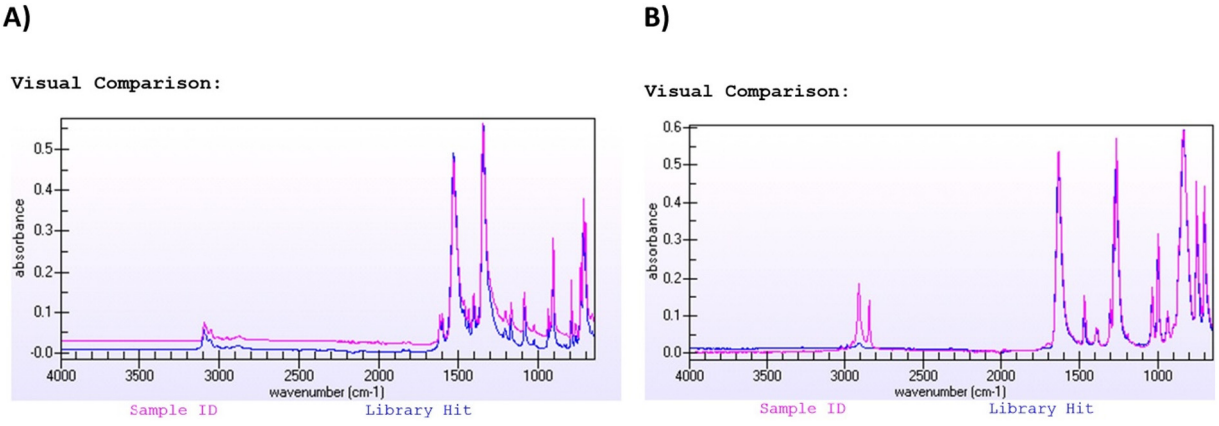


Fig. 4. FT-IR spectra of A) TNT extracted from an intact German 1-Kilogram Sprengbüchse 24 and B) PETN extracted from a partially destroyed German anti-tank mine (booster charge).

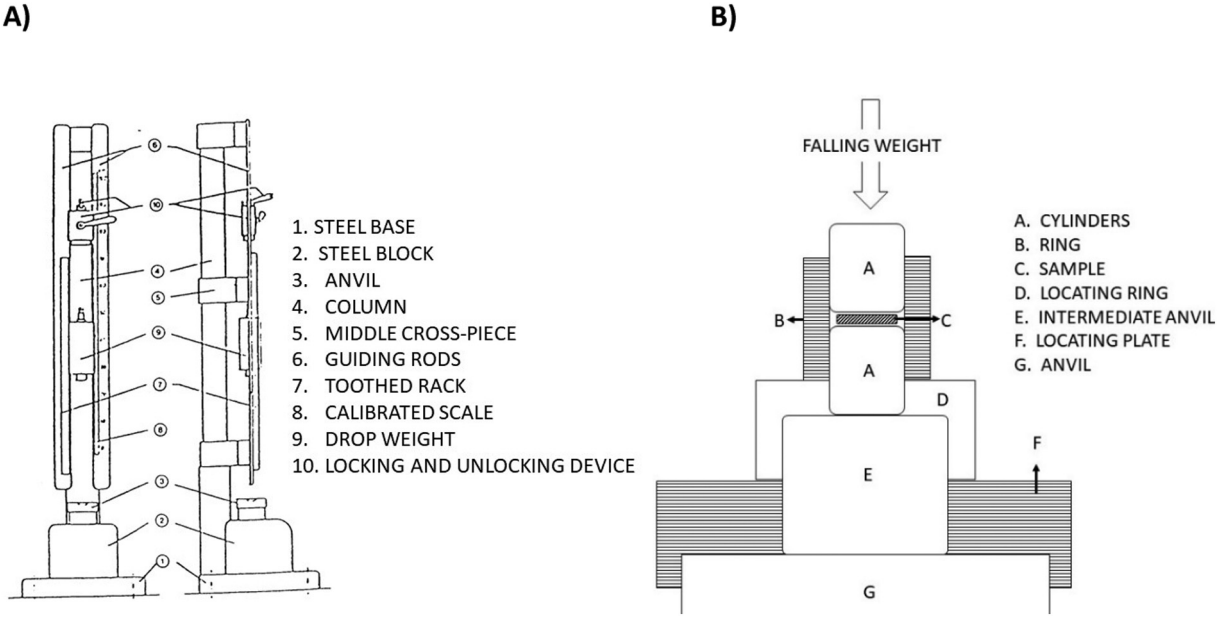


Fig. 5. A) The BAM Impact Machine (NATO, 1999) and B) The fallhammer confinement device (NATO, 1999).

and the rebound catch for stopping the weight after rebounding from the anvil.

When the desired drop weight has been secured in the release mechanism, the weight is then positioned to the desired height. Upon activating the release mechanism, the drop weight is unlocked, consequently impacting the upper roller of the impact device.

Depending on the characteristics of the tested explosive substance, the drop weight mass and the drop height (i.e., impact energy), the initiation of the sample may or may not occur when the weight is dropped. In judging the results, a distinction is made between no reaction, decomposition and explosion, in the sample. Explosion and decomposition can be recognized by several factors, including sound, gas, flame, smoke or by inspection of the impact device for sooty deposits after the upper cylinder has been removed. If none of these effects are noticed, initiation failure (no reaction) is registered. Of the three possible types of reaction, decomposition and explosion are considered positive reactions when testing, according to STANAG test procedures.

The test can be conducted and the test results reported in a number of different ways, including percentage of initiations, relative impact sensitivity with respect to the impact sensitivity of a referent explosive, or as an impact sensitivity curve for a given explosive, i.e., the relation between the percentage of initiations and the drop height of the weight having constant mass. On the basis of the results obtained in the latter, the impact sensitivity can be expressed as the drop height at which 50 % initiations occurred (H_{50}), the minimum drop height at which 100 % initiations occurred (H_{100}) and the maximum drop height at which lack of initiation is observed (H_0). Also, the test results can be expressed by the impact energy (E_1) at which a certain percentage of initiations occurred (Suceska, 1995). According to NATO STANAG 4489, a Bruceton up-and-down procedure shall be applied for the determination of the impact sensitivity of the explosive sample.

In these tests, the impact sensitivity was determined as follows: Beginning at an established starting level, a number of runs was performed to determine the exact drop height which causes 50 % positive reactions of the samples. Every new test was conducted with a new impact device and a new sample. The tests were performed in ambient temperatures (22.5 °C + 2.5 °C). As the scope of the test method is within the range of −30 °C to +80 °C, no particular environmental modification was required. The number of positive reactions and the number of negative reactions during the tests were recorded as either positive (x) or negative (o). In addition to audio-visual observation, a decomposition gas detector (MultiRAE model PGM6208) was used to classify the reactions. The mean (M) and its standard deviation (S) was calculated, and the 50 % drop height (H_{50}) was determined using the formulation $H_{50} = 10^{M} \pm \sigma$, where σ is standard deviation 50 % drop height ($\sigma = 10^{S}$).

The tests were completed when H_{50} was determined and the test results were considered valid (i.e., $0.5 \leq S/D \leq 2.0$). The final results were recorded as both the drop height in centimetres, which caused 50 % positive reactions of the sample explosives, and its calculated impact energy in Joules. A drop weight with a mass of 5 kg was used for testing the impact sensitivity of TNT and a weight of 2 kg for PETN.

2.5. Quality control

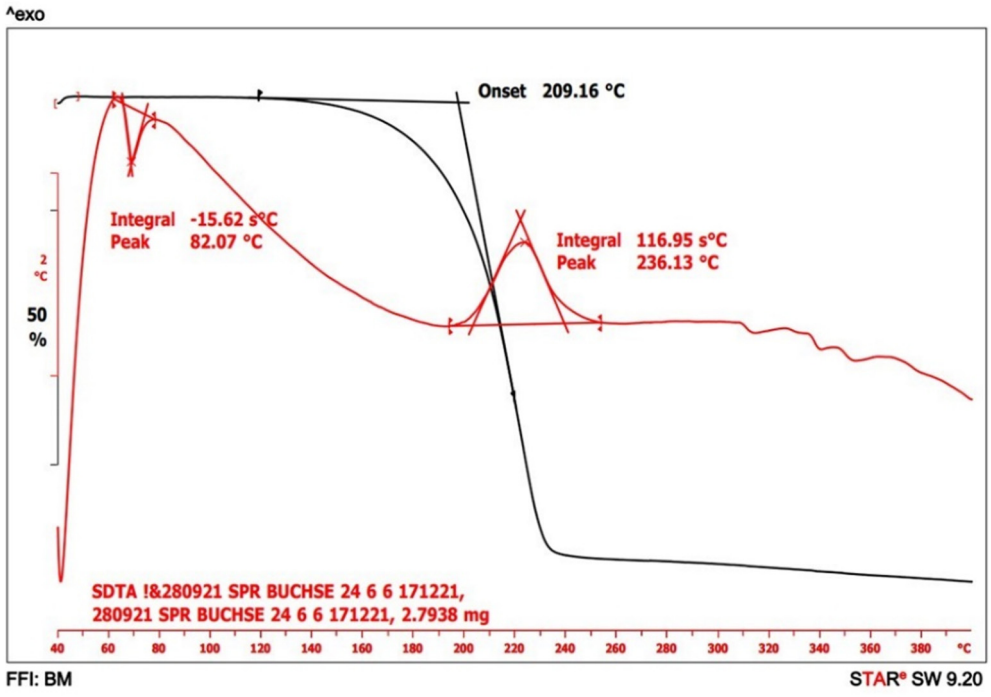
All analysis was undertaken at the Norwegian Defence Research Establishment laboratory. To ensure reliable and comparable datasets, implemented internal Quality Control (QC) procedures, based on ISO standard no. 17025 *General requirements for the competence of testing and calibration laboratories* (International Organization for Standardization, 2017), were observed. Additionally, analyses of bench-mark samples were performed, using recently produced relevant standard explosive samples. These control materials were treated throughout in exactly the same manner as the test materials and subjected to the same analyses (i.e., FT-IR, thermogravimetric analysis and impact sensitivity analysis). The QC TNT sample used in the analyses was “Trinitrotoluene (TNT) Type 1, Flake” with a 0.44 % content of Hexanitrostilbene (HNS), produced by Zaklady Chemiczne “NITRO-CHEM” S.A. in Bydgoszcz, Poland, released for sale following Certification of Compliance / Analysis on 8th September 2017. The QC PETN sample used in the analyses was “PETN Wax NSP452” grains with 7.7 % content of wax, produced by EURENCO Bofors in Karlskoga, Sweden, released for sale following Certification of Compliance / Analysis on 29th November 2018.

3. Results and discussion

3.1. Thermal analysis (TGA/SDTA)

The thermograms for TNT, presented in Fig. 6 A, show a single, gradual weight loss with an average onset temperature at 209 °C. The corresponding SDTA curves typically show an endothermic peak, with its maxima ranging from 81.1 °C to 83.9 °C. This is consistent with the melting point

A)



B)

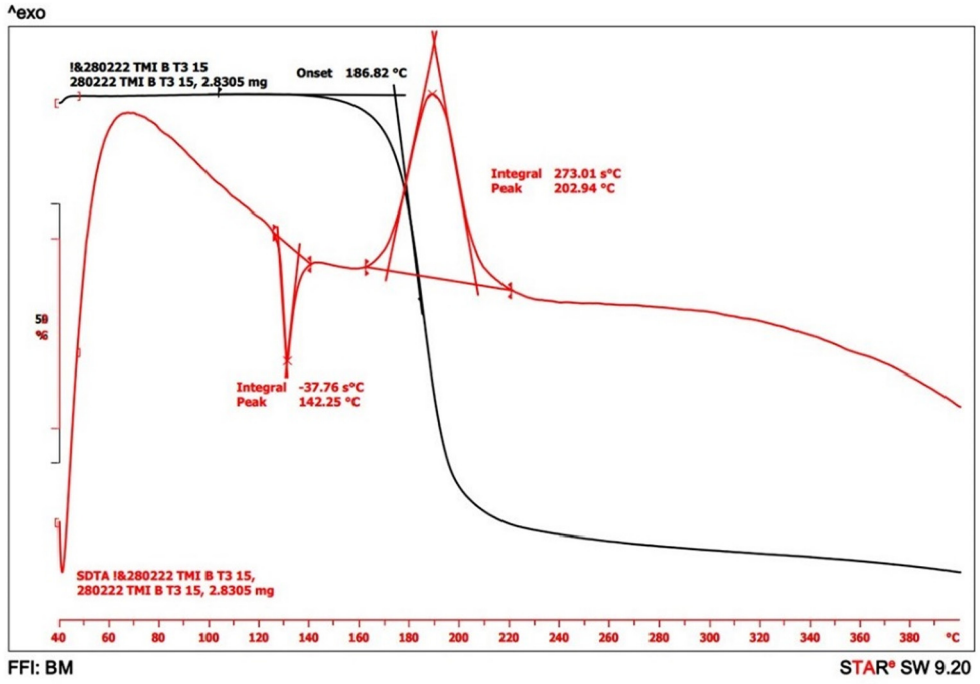


Fig. 6. Examples of TGA (black) and SDTA (red) curves for the thermal decomposition of A) TNT extracted from an intact German 1-Kilogram Sprengbüchse 24 and B) PETN extracted from a partially destroyed German anti-tank mine (booster charge), in N_2 atmosphere at a constant heating rate of 10 °C/min.

of TNT (about 81.0 ± 0.5 °C) (Kaye and Herman, 1980; Tharaldsen, 1950), as the exact melting point of the composite will be dependent on the average heat capacity of its individual elements (e.g., metals, binders, phlegmatizers, other energetic material or compositions thereof, etc.). This heat effect is not accompanied by mass loss. Next, an exothermic peak is observed with maxima at 232.6 °C to 274.9 °C, indicating the decomposition of the TNT, correlating with a decomposition temperature of 250 °C (Meyer et al., 2005).

In the cases of PETN, presented in Fig. 6 B, the thermograms show a single, gradual weight loss with an average onset temperature at 186 °C. The corresponding SDTA curves typically show a sharp endothermic peak, with its maxima ranging from 141.5 °C to 143.1 °C, consistent with the melting point of pure PETN (141.3 °C) (Meyer et al., 2005). This heat effect is not accompanied by mass loss. Next, an exothermic peak is observed with maxima at 194.9 °C to 206.48 °C, indicating the decomposition of the PETN, correlating with a deflagration point of 202 °C (Meyer et al., 2005).

3.2. Impact sensitivity analysis (BAM impact apparatus)

The recorded H_{50} values in centimetres from the impact sensitivity tests using the BAM Impact Apparatus and the Bruceton up-and-down test procedure are presented in Table 1 and Fig. 7. Analyses of bench-mark test samples using recently produced relevant samples of TNT and PETN are listed in Table 1 as BMS-1 (TNT) and BMS-2 (PETN) and visualized in Fig. 7 as red horizontal lines.

It is important to note that drop-weight impact tests are only a screening tool for handling sensitivity, and that interpretation of the results can be difficult (Manner et al., 2020). As measurements can also be affected by test conditions, location and the various analysis methodology, consistency among sample testing is critical (Marrs et al., 2021). As such, the results obtained may vary due to differences in the way the experiments are conducted and reported and with respect to the type of impact sensitivity apparatus used. However, when all influencing factors are considered, it appears

Table 1
Description of ordnance category, country of origin, explosive, condition, location, impact weight and the corresponding drop-height (H_{50}) with standard deviation.

Sample	Object category	Country of origin	Condition	Location	Explosive	Weight (kg)	50 % drop height (cm)
1	Grenade, hand	United Kingdom	Intact	On land	TNT	5	69.4 cm ± 1.187 cm
2	Grenade, hand	United Kingdom	Intact	On land	TNT	5	56.7 cm ± 1.110 cm
3	Grenade, hand	United Kingdom	Intact	On land	TNT	5	59.6 cm ± 1.139 cm
4	Grenade, hand	United Kingdom	Intact	On land	TNT	5	54.5 cm ± 1.101 cm
5	Grenade, hand	Norway	Partially open	On land	TNT	5	66.8 cm ± 1.212 cm
6	Charge, explosive	Germany	Intact	On land	TNT	5	50.5 cm ± 1.110 cm
7	Charge, explosive	Germany	Intact	On land	TNT	5	46.2 cm ± 1.116 cm
8	Charge, explosive	Germany	Intact	On land	TNT	5	66.8 cm ± 1.139 cm
9	Charge, explosive	Germany	Intact	On land	TNT	5	56.2 cm ± 1.156 cm
10	Charge, explosive	Germany	Intact	On land	TNT	5	47.3 cm ± 1.083 cm
11	Charge, explosive	Germany	Intact	On land	TNT	5	61.6 cm ± 1.225 cm
12	Charge, explosive	Germany	Intact	On land	TNT	5	61.3 cm ± 1.143 cm
13	Grenade, hand	Germany	Intact	On land	TNT	5	66.8 cm ± 1.139 cm
14	Projectile	Germany	Intact	On land	TNT	5	56.9 cm ± 1.133 cm
15	Grenade, hand	Russia	Partially open	On land	TNT	5	47.3 cm ± 1.104 cm
16	Grenade, hand	Russia	Partially open	On land	TNT	5	64.9 cm ± 1.255 cm
17	Projectile	Russia	Intact	On land	TNT	5	57.9 cm ± 1.143 cm
18	Grenade, hand	Germany	Intact	On land	TNT	5	68.1 cm ± 1.168 cm
19	Mine	Germany	Open	In water	TNT	5	64.9 cm ± 1.255 cm
20	Mine	Germany	Open	In water	TNT	5	47.3 cm ± 1.139 cm
21	Mine	Germany	Open	In water	TNT	5	59.6 cm ± 1.139 cm
22	Mine	Germany	Open	In water	TNT	5	75.0 cm ± 1.104 cm
23	Mine	Germany	Open	In water	TNT	5	47.3 cm ± 1.139 cm
24	Mine	Germany	Open	In water	TNT	5	66.8 cm ± 1.139 cm
25	Mine	Germany	Open	In water	TNT	5	65.6 cm ± 1.243 cm
26	Projectile	Germany	Intact	In water	PETN	2	32.5 cm ± 1.143 cm
27	Projectile	Germany	Intact	In water	PETN	2	42.2 cm ± 1.139 cm
28	Projectile	Germany	Intact	On land	PETN	2	43.0 cm ± 1.098 cm
29	Grenade, rifle	Germany	Intact	On land	PETN	2	25.0 cm ± 1.166 cm
30	Grenade, rifle	Germany	Intact	On land	PETN	2	32.5 cm ± 1.255 cm
31	Grenade, rifle	Germany	Intact	On land	PETN	2	21.1 cm ± 1.212 cm
32	Grenade, rifle	Germany	Intact	On land	PETN	2	25.9 cm ± 1.143 cm
33	Grenade, rifle	Germany	Intact	On land	PETN	2	26.6 cm ± 1.156 cm
34	Projectile	Germany	Intact	On land	PETN	2	37.6 cm ± 1.139 cm
35	Mine	Germany	Open	In water	PETN	2	23.7 cm ± 1.104 cm
36	Mine	Germany	Open	In water	PETN	2	29.9 cm ± 1.139 cm
37	Mine	Germany	Open	In water	PETN	2	29.9 cm ± 1.212 cm
38	Mine	Germany	Open	In water	PETN	2	30.7 cm ± 1.143 cm
39	Mine	Germany	Open	In water	PETN	2	26.6 cm ± 1.104 cm
40	Mine	Germany	Open	In water	PETN	2	29.0 cm ± 1.143 cm
41	Mine	Germany	Open	In water	PETN	2	26.6 cm ± 1.139 cm
42	Mine	Germany	Open	In water	PETN	2	21.1 cm ± 1.104 cm
43	Mine	Germany	Open	In water	PETN	2	27.8 cm ± 1.100 cm
44	Mine	Germany	Open	In water	PETN	2	21.1 cm ± 1.060 cm
45	Mine	Germany	Open	In water	PETN	2	29.9 cm ± 1.139 cm
46	Mine	Germany	Open	In water	PETN	2	21.1 cm ± 1.139 cm
47	Mine	Germany	Open	In water	PETN	2	27.4 cm ± 1.143 cm
48	Mine	Germany	Open	In water	PETN	2	23.7 cm ± 1.139 cm
49	Projectile	Germany	Intact	In water	PETN	2	27.2 cm ± 1.116 cm
50	Projectile	Germany	Intact	In water	PETN	2	24.8 cm ± 1.179 cm
BMS-1	Bench-mark test sample				TNT	5	59.6 cm ± 1.212 cm
BMS-2	Bench-mark test sample				PETN	2	29.0 cm ± 1.143 cm

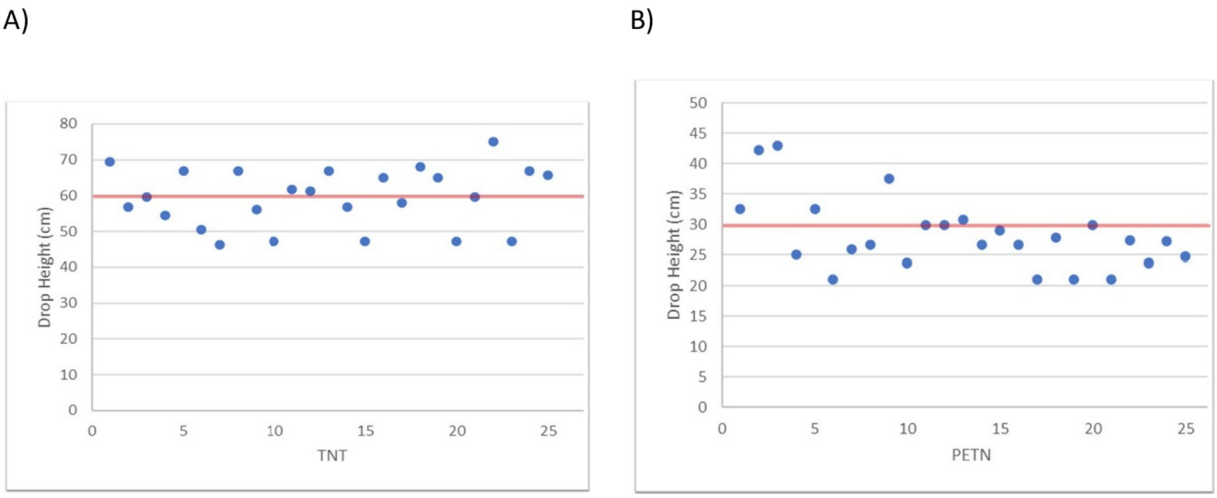


Fig. 7. 50 % drop height (H_{50}) in centimetres for A) TNT and B) PETN. The X-axis represents the sample number, and bench-mark samples of recently produced TNT and PETN are shown as red horizontal lines.

that there is consistency between the results obtained by this test and results in the literature on comparable explosive compositions. For example, NATO STANAG 4489 lists typical anticipated results in Joule for the testing of impact sensitivity of various explosives with the BAM Impact Machine (NATO, 1999). The applicable listed values are: TNT – 30 J and PETN – 5 J. This study demonstrates that the H_{50} impact energy in Joule for the tested explosives is as follows: for TNT, between 23.1 and 37.5 J, with a mean of 29.72 J (the correlating test sample result was 29,8 J), and for PETN, between 4.2 and 8.6 J, with a mean of 5.6 J (the correlating test sample result was 5,8 J). This demonstrates that the test results are consistent with the expected values for comparable explosive compositions, taking into account variations in composition (e.g., the presence and/or percentage of metals, binders, phlegmatizers, other energetic material or compositions thereof, etc.), as well as test conditions and analysis methodology.

4. Summation and discussion

Most recorded incidents of unplanned explosions in ERW come as a result of a sudden unintended incident or external stimuli. This can originate as the result of a "natural" incident, such as a lightning strike, forest fire, structural collapse of shipwrecks or the shifting of ordnance in the tide; as the result of deteriorating containers and packaging, etc.; or as the direct result of human interaction (e.g., touching or moving the ordnance or otherwise subjecting the energetic materials to heat, friction, impact, etc.). Furthermore, ERW are coming into increasing contact with human activities, like development and fishing. Some decades ago, for example, trawlers would rarely trawl below 120 m; now, they can trawl in depths of 1500 m (Monfils, 2005). Increased development and utilization of both land and sea can lead to infrastructure being built in explosive-contaminated areas. Sometimes this is even done knowingly, reassured by an assumption that the ammunition does not pose any significant risk. However, the forces generated by the use of construction equipment, such as excavators, hydraulic hammers, crushing machines and drills, are generally sufficient to detonate most kinds of explosives under certain circumstances and are regularly linked to accidental detonations of undetected explosives (Dahl, 1998). Analyses of some accidental explosions have shown that the most frequent causes of these accidents are subjective in nature, resulting from the disregard of necessary safety precautions (Suceska, 1995). Similarly, at sea, both shipping and construction activity, such as dredging and other seabed interventions (e.g., cable and pipeline installations and piling works), can produce more than enough impact energy to initiate an underwater explosion of high explosives and/or explosive objects, potentially resulting in a sympathetic mass-detonation of dumped ammunition or ammunition confined within a sunken vessel (Zhuang et al., 2016).

This study demonstrates that all analysed high explosives extracted from ERW are still in good condition, and that impact sensitivity does not seem to have been significantly reduced over the last eight decades. In fact, the study shows that the impact sensitivity of the ageing explosives generally correlates with what is recorded in the literature. The study does, however, also demonstrate that the impact sensitivity (H_{50}) of the tested explosives in some cases could be over 20 % greater, compared to both what are considered standard values for equivalent explosives and the results obtained from the relevant quality control sample (see Table 1).

As the explosives remain in nature, special concern is raised regarding the leaking and bioaccumulation of toxic constituents and their potential to contaminate living organisms, as well as the surrounding soil and groundwater. Unlike other contaminants, they cannot be reduced by land measures, and only removal of the source can reduce the contamination (Bełdowski et al., 2020). Furthermore, as corrosion of munitions persists, the increased deterioration of the munitions' casings may lead to a greater emission of harmful constituents in the future, leading to ecological consequences of yet unknown proportions (Beck et al., 2022). Concern is also raised that dumped munitions are open to terrorist access and potential misuse (NATO, 2010). Some agencies and organizations therefore advocate that all ERW should be cleared, as far as practically feasible (OSPAR Commission, 2009). A prerequisite for this would in any case be that the risks involved are identified to a satisfactory degree, and that the subsequent risk assessments are based on strong background knowledge. This would require comprehensive research into relevant ERW, including potential variations in the ageing of explosives as a result of environmental, chemical or technical differences, etc.

5. Conclusions

The thermal and impact sensitivity results obtained in the analysis showed no indications of deterioration of high explosives in explosive remnants of war that could denote any significant reduction in performance and/or decreased impact sensitivity. Consequently, there is no evidence in this study to support a claim that, if left alone, the ammunition will slowly become harmless over time. The study did show that the high explosives are still in good condition, and that impact sensitivity does not seem to have been reduced over the last eight decades. Further research into possible variations, as a result of environmental, chemical or technical differences, will be required, in order to gain further knowledge on ageing ERW.

It is important to note that this study is limited to only the analysis of TNT and PETN and does not include either primary explosives or

other high explosives or explosive compositions, some of which could be expected to be significantly more impact-sensitive than the explosives included within this study.

CRediT authorship contribution statement

Geir P Novik performed writing - original draft and conceptualization.

Funding

This research is funded by the Norwegian Defence Research Establishment. The funding source had no involvement in the research and/or preparation of this article.

Declaration of competing interest

Geir P. Novik reports financial support was provided by Norwegian Defence Research Establishment.

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