

# *HEMs: Characterization and Evaluation*

## *10.1 Introduction*

In any research area concerned with new chemical compounds, characterization and evaluation of the synthesized compounds, including intermediates, are of vital importance. High-energy materials (HEMs) cannot be an exception. Characterization is essentially an identification process whereas evaluation refers to the measurement of certain special characteristics of the synthesized compounds. For instance, a newly synthesized energetic compound is “characterized” by a systematic process involving chromatography (to ensure the purity of the compound), spectroscopy, and any such method to make sure of its molecular structure so that the chemist knows what exact compound he has synthesized. On the other hand, the chemist would “evaluate” the new compound for certain specific performance parameters or performance potentials. For example, a newly synthesized explosive molecular compound may be evaluated for calorimetric value (thermochemical potentials), velocity of detonation (VOD; detonation potential), or friction/impact sensitivity figures (mechanical sensitivity potential).

With the advent of highly sophisticated instrumental analytical techniques, the characterization and evaluation techniques related to HEMs have come a long way over the years. Chromatography, spectroscopy, and thermal analysis techniques are the mainstay for characterization and evaluation of HEMs. It might be interesting to note that certain techniques that are as old as a century or several decades are still being followed today when it comes to the evaluation of certain characteristics of HEMs. The vacuum stability test for explosives and certain propellants, friction and impact sensitivity tests for almost all HEMs, and shock sensitivity tests for explosives may look a little archaic or even outdated; however, all of these tests are time-tested, highly reliable, and totally indispensable. Apart from these, there may be highly specific tests for a particular explosive. For instance, for nitrocellulose (NC), the Bergmann and Junk test chemically measures the amount of oxides of nitrogen evolved on heating a gram weight of NC for a specific period at a specific temperature. The amount of oxides of nitrogen evolved (evaluated titrimetrically) indicates the extent of instability of NC. This chapter does not include such tests, but it gives a general approach to the characterization and evaluation of HEMs.

## 10.2 Chromatographic Techniques

Chromatographic techniques are a group of analytical techniques used for the separation of components from a mixture using differences in their distribution between two phases (stationary and mobile phase). Many chromatography techniques are available today for characterization purposes (e.g., thin layer chromatography (TLC), gas chromatography (GC), high-performance liquid chromatography (HPLC) etc.). These techniques are used for identification, separation, characterization, and quantification. Let us discuss only the techniques that are frequently used for the characterization of energetic materials.

### 10.2.1 Thin Layer Chromatography

TLC is a quick, simple, ready-to-use, inexpensive tool typically used in laboratory synthesis practices. It gives the quick answer to the synthesis chemist whether he/she is going in the correct direction or not. This is usually not considered a characterization technique, but it gives an idea about the number of components in a reaction mixture. TLC is used to confirm the presence of unknown substances in comparison to the standard known substance using the relative front ( $R_f$ ), which is the ratio of the distance traveled by the solvent front to the distance traveled by the substance under examination. TLC is also used to monitor the course of the reaction and gives an idea about the conversion of reactant to product. TLC experiments are generally performed with reactant, product, and possible byproduct in a single run.

A TLC plate is a thin sheet of solid adsorbent (usually silica or alumina) spotted with known and unknown substances. This plate is eluted with a proper solvent (often binary mixtures based on the polarity) liquid. Once the solvent reaches the top of the plate, the plate is removed from the developing chamber, dried, and the separated components of the mixture are visualized in an ultraviolet (UV) lamp. Identical compounds possess similar  $R_f$ , and dissimilar compounds deviate up or down.

### 10.2.2 Gas Chromatography

In GC, the mobile phase is an inert gas and the stationary phase is a liquid or solid. Thus, in GC, separation of components in a chemical mixture is achieved on the basis of differences in the partition coefficient of solutes in the gas phase and stationary phase. In GC, the time gap between the injections of the sample (zero time) and the peak maximum of substance is called its retention time (RT). It is the characteristic property of the compound, and it varies from compound to compound. The greater the affinity of the compound for the stationary phase, the more the compound will be retained by the chromatographic column and will be eluted later than the one having less affinity for the stationary phase. The major limitation of GC is that the compound analyzed should

possess reasonably high vapor pressure. Low-melting explosives (e.g., trinitrotoluene and 2,4-dinitroanisole (DNAN)) and compounds with high vapor pressure (volatile substance and liquids) mostly can be analyzed by GC. The main advantage of GC is that the analysis is faster and accurate.

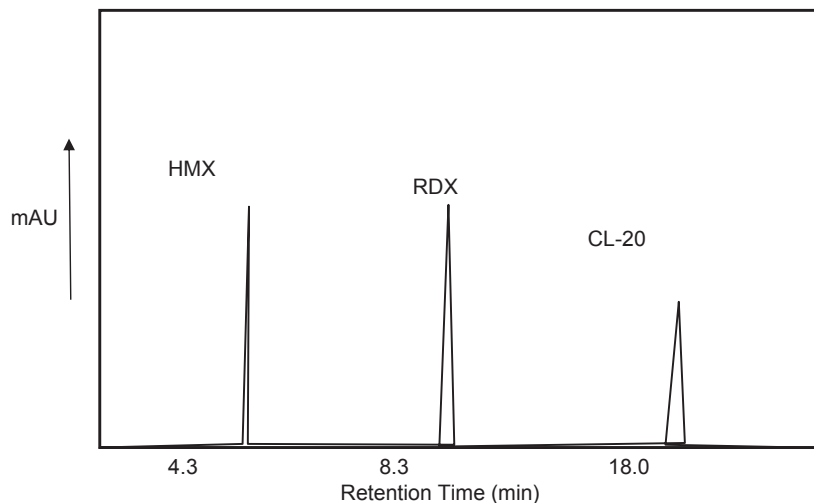
### 10.2.3 High Performance Liquid Chromatography

In contrast to GC, HPLC uses a liquid as the mobile phase, and liquid phase (coated on inert solid support), solid adsorbent (e.g., silica or alumina), or ion-exchange resin is used as the stationary phase. The separation of constituents in HPLC is based on the interaction of the individual components, and the stationary phase and components are retained to a different extent, which causes the separation. For example, those samples that have stronger interactions with the mobile phase than with the stationary phase will elute from the column faster and thus have a shorter RT. Likewise, those who do have strong affinity to the stationary phase will stay in the column for longer duration.

HPLC is superior to any other liquid chromatographic techniques in terms of separation efficiency. The analysis of mixtures can be done faster with HPLC because of the increased flow rate using high-pressure pumps.

Reverse-phase HPLC is the method of choice for the detection and quantification of explosive molecules. In the analysis of nitro compounds, a UV detector is mainly used. In this technique, several components can be identified and quantified in a short time.

Many explosives and their intermediates have been analyzed by HPLC. An example of an HPLC chromatogram is shown in [Figure 10.1](#). It can be seen that the order of the elution



**Figure 10.1**  
HPLC Chromatogram of Nitramine Explosives.

is (1) HMX (4.3 min), (2) RDX (8.3 min), and CL-20 (18 min) with the following instrumental parameters: mobile phase, water/methanol (60:40); flow rate, 1.2 mL/min; injection volume, 10  $\mu$ L; and column, C-18.

### 10.3 Spectroscopic Techniques

Spectroscopy is a well-known analytical technique for the identification of functional groups in chemical substances. In spectroscopy, a certain portion of the electromagnetic spectrum (UV, visible (VIS), or infrared (IR)) interacts with matter and the resultant spectrum is interpreted to diagnose the molecular structure of the chemical substance.

#### 10.3.1 UV/VIS Spectroscopy

UV radiation (wavelength varying from 200 to 400 nm) is the part of electromagnetic radiation that can promote the electrons of a molecule from their ground state to an excited state. The VIS portion of the spectrum lies between 400 and 800 nm. UV and VIS spectrometers typically are available together. Both regions correspond to energy level characteristics of excitation of  $\pi$  and nonbonding electrons and are most often associated with molecules containing conjugated double bonds. This spectroscopic method provides only limited information to the chemists. Fortunately, most of the explosives molecules possess groups containing  $\pi$  electrons and  $n$  electrons and are UV active. For example,  $-\text{NO}_2$  groups present in explosive CL-20 appear as a broad peak at 230 nm in the UV spectrum. Some more examples are given in Table 10.1.

#### 10.3.2 IR Spectroscopy

The IR region of the electromagnetic spectrum ( $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ ), which corresponds to changes in vibrational energies within molecules, is very helpful for the identification of functional groups in chemical characterization. Not all possible vibrations within a molecule will result in an absorption band in the IR region. For a molecule to be

**Table 10.1: Some UV Active Explosives.**

Compound	$\lambda_{\text{max}}$ (nm)	Compound	$\lambda_{\text{max}}$ (nm)
NB	269	1,3-DNB	242
1,3,5-TNB	227	2,4,6-TNT	232
Picric acid	378	Picramide	333
RDX	213	HMX	228
CL-20	230	Nitroguanidine	265

$\lambda_{\text{max}}$ , wavelength at maximum intensity; NB: nitrobenzene; DNB: dinitrobenzene; TNB: Trinitrobenzene

Table 10.2: IR Absorption Frequencies.

Groups	IR Peak ( $\text{cm}^{-1}$ )	Groups	IR Peak ( $\text{cm}^{-1}$ )
C—H	2850–3000	—NO <sub>2</sub>	(1) 1510–1560 (2) 1330–1370
O—H	3000–3400	C≡N	2220–2260
N—H	3100–3450	—N <sub>3</sub>	2200
C=O		—NO <sub>3</sub>	1350–1380
Aldehydic	1680–1740		
Ketonic	1665–1725		

Note:  $\text{cm}^{-1}$  is the unit of wave number, which is the reciprocal of wavelength in cm.

IR active, the vibration must result in a change of dipole moment during the vibration. The IR absorption frequencies of some of the typical functional groups found in most explosives are given in Table 10.2.

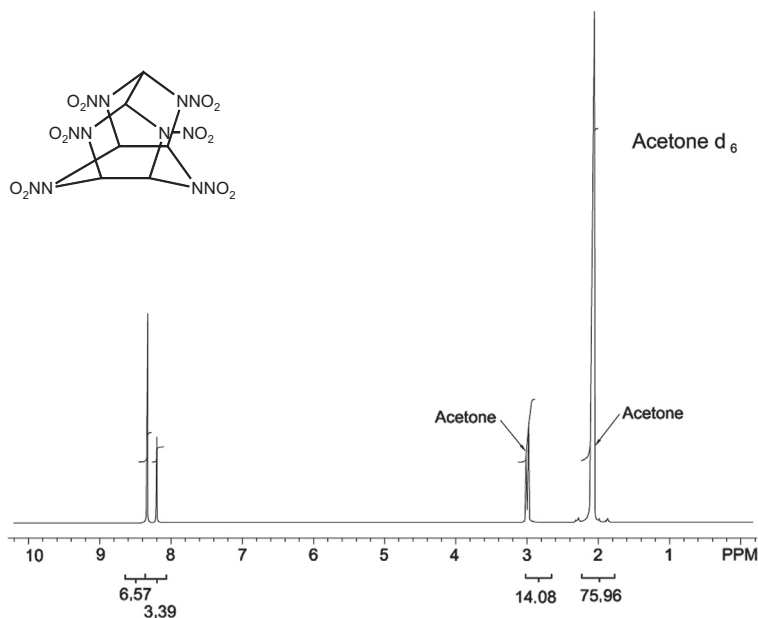
Explosive samples are generally analyzed by mixing a small quantity of sample and a mineral oil nujol to give a paste, which is then applied between two sodium or potassium chloride plates. The plate is then fitted into the IR instrument and analyzed. Another method of analysis is by mechanically pressing the finely ground sample and pure potassium bromide (KBr) into a transparent disc in a die under pressure. Later, the KBr disk containing the sample is placed in a sample holder ready for scanning in an IR machine.

Nowadays, Fourier transform IR (FTIR) spectrophotometers are used for the analysis. Analysis is faster in FTIR, and it takes a few seconds to record the spectrum. Another advantage is that a very small quantity of substance is sufficient to record a reasonably good spectrum.

### 10.3.3 Nuclear Magnetic Resonance Spectroscopy

In a molecule, every spinning proton acts as a tiny magnet. Therefore, molecules containing atoms such as H<sup>1</sup> and F<sup>19</sup>, which have an intrinsic magnetic moment, can interact with an external magnetic field giving rise to nuclear spin energy levels. When molecules containing one or more hydrogen atoms are placed in a magnetic field, the magnetic moment of the proton gets aligned. For a proton, the quantum theory permits only two orientations that differ in energy, the energy separation being proportional to the strength of the magnetic field. In typical experiments, the energy gap is so adjusted that 60 megacycles ( $6 \times 10^7$  cP) of electromagnetic radiation (corresponds to radiofrequency (RF) of the electromagnetic spectrum) is able to cause transition between the energy levels.

The utility of the magnetic resonance method arises from the fact that the local molecular environment of a hydrogen atom in a molecule slightly perturbs the energy gap, thus



**Figure 10.2**  
NMR Spectrum of CL-20.

modifying the frequency of the absorbed radiation. For example, in a molecule of ethanol ( $\text{CH}_3\text{—CH}_2\text{—OH}$ ), the H atoms present in  $\text{CH}_3$ ,  $\text{CH}_2$ , and OH have different molecular environments and they produce their own characteristic shifts in the RF absorption called “chemical shifts.” Measurement of chemical shifts yields accurate information about the total number of H atoms as well as the type of H atom (e.g., C—H, O—H, N—H, etc.), helping the chemist to elucidate the molecular structure of a given compound.

Nuclear magnetic resonance (NMR) spectroscopy is an important tool for structural elucidation during the synthesis and analysis of HEMs. A typical such NMR spectrum of the explosive CL-20 is given in [Figure 10.2](#).

### 10.4 Thermal Evaluation of Energetic Materials

The thermal evaluation of energetic materials is an important area in assessing the performance and suitability of the material for various applications. In thermal evaluation techniques, a small quantity of energetic material under investigation is subjected to programmed heating, and the response from the sample is recorded with respect to temperature.

Thermal evaluation techniques enable one to obtain better insights on the following aspects: thermal stability, shelf life, compatibility, safety aspects, transition temperature,

heat capacity, melting temperature, crystallization kinetics, hazard evaluation, aging and thermal history effects, quality control, dehydration, dehydration kinetics, heat of transition, phase transition, glass transition, etc. The important techniques generally used are as follows:

1. Differential thermal analysis (DTA)
2. Differential scanning calorimetry (DSC)
3. Thermogravimetric analysis (TGA)
4. Simultaneous thermal analysis (STA)

#### 10.4.1 Differential Thermal Analysis

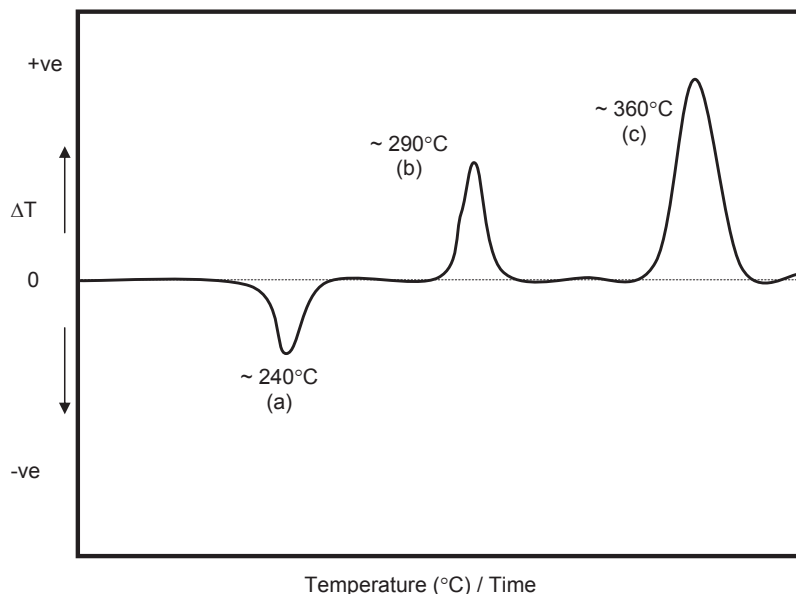
DTA is the simplest form of a thermal analysis technique. The principle of DTA is based on subjecting the sample (e.g., ammonium perchlorate [ $\text{NH}_4\text{ClO}_4$ , AP]) and an inert reference material (mostly aluminum oxide) to a simultaneous temperature program and recording the differential temperature (i.e., difference between the temperature of the sample and that of the reference, i.e.,  $\Delta T$ ) with respect to the temperature. A few milligrams each of the sample and reference are taken in separate platinum cups connected to Pt or Pt/Rh temperature sensors. The entire setup is kept in a heating furnace, and the sample and reference materials are heated at a specified heating rate (e.g., at  $10^\circ\text{C}/\text{min}$ ). The difference in temperatures of sample and reference ( $\Delta T$ ) is recorded on the ordinate and the temperature (or time, because the rate of heating is a constant) is recorded on the abscissa.

As long as no reaction (chemical reaction and physical changes such as melting, phase changes, etc., which involve heat changes) takes place in the sample,  $\Delta T$  is zero. If the sample undergoes an endothermic change (e.g., melting), then its temperature goes lower than the temperature of the reference and  $\Delta T$  is recorded as negative. Conversely, if the sample undergoes an exothermic reaction (e.g., oxidation), then its temperature will be higher than that of the inert reference material and  $\Delta T$  is recorded as positive. A DTA thermogram (Figure 10.3) is given for AP and the possible explanations are given (based on other evidences).

- a.  $\Delta T$ : -ve; endothermic ( $240^\circ\text{C}$ ) Phase change of AP (orthorhombic to cubic)
- b.  $\Delta T$ : +ve; exothermic ( $290^\circ\text{C}$ ) First stage oxidation of AP
- c.  $\Delta T$ : +ve; exothermic ( $360^\circ\text{C}$ ) Complete oxidation of AP resulting in its deflagration

#### 10.4.2 Differential Scanning Calorimetry

DSC is the most important thermal evaluation technique. In DSC, a known quantity of sample and a reference are subjected to programmed heating and the difference in energy inputs into the sample and reference is measured as a function of temperature. The DSC

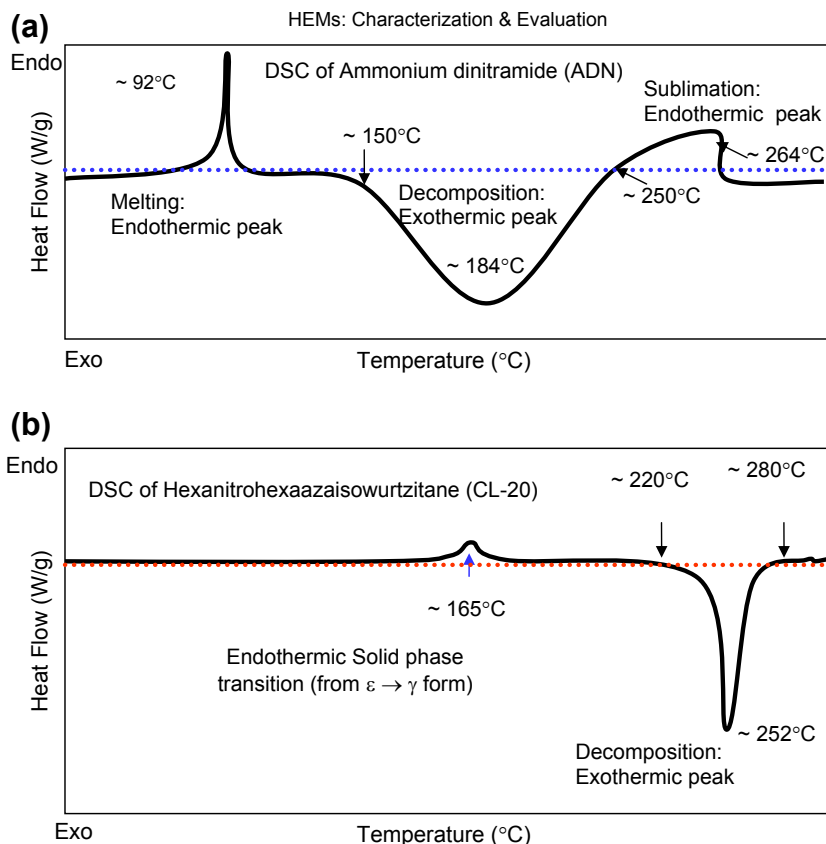


**Figure 10.3**  
DTA Thermogram of Ammonium Perchlorate (AP).

technique is more quantitative, accurate, and faster than the DTA method. In DSC, the temperature of the sample and reference is not allowed to vary. For instance, during simultaneous temperature programming, if the sample undergoes an exothermic reaction, (thereby becoming hotter than the reference), then the reference is given the heat output (which can be accurately measured) such that it also attains the temperature of the sample; conversely, in an endothermic reaction of the sample, heat output is given to the sample. In a DSC thermogram, the heat output is plotted against the temperature. [Figure 10.4](#) shows the DSC thermograms of ammonium dinitramide (ADN) and CL-20. A DSC thermogram of ADN shows two endothermic events and one exothermic event. The first endothermic peak is due to the melting of ADN (92 °C), and the second peak corresponds to the exothermic decomposition of ADN (150–250 °C with a  $T_{\text{max}}$  of 184 °C) to various decomposition products (mainly ammonium nitrate). Ammonium nitrate formed during the decomposition sublimates (endothermic peak at 264 °C) in the third step.

CL-20 exists in various polymorphs such as  $\alpha$ ,  $\beta$ ,  $\delta$ ,  $\epsilon$ ,  $\gamma$ , etc., but the  $\epsilon$  form of CL-20 is more stable at ambient temperature than other polymorphs. The DSC thermogram of the  $\epsilon$  form of CL-20 shows one small endothermic and a significant exothermic peak ([Figure 10.4\(b\)](#)). The  $\epsilon$  form of CL-20 absorbs heat energy and is transformed into the  $\gamma$  form of CL-20 at 165 °C. This event appears as an endothermic peak. During further heating, CL-20 exothermically decomposes (onset at 220 °C with a  $T_{\text{max}}$  of 252 °C) into various decomposition products and releases high heat output.



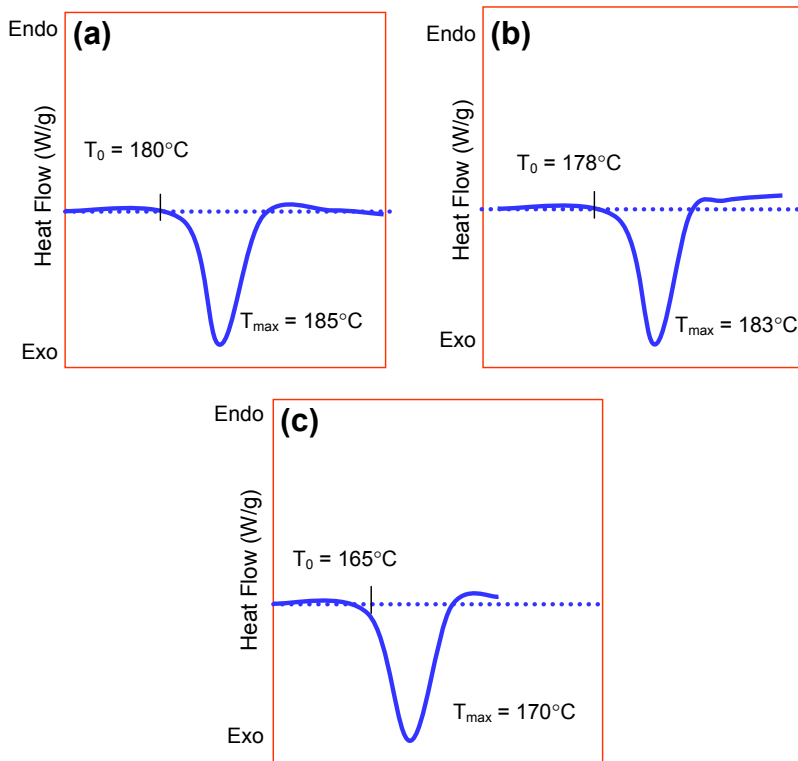
**Figure 10.4**

(a) DSC Thermogram of ADN and (b) DSC Thermogram of CL-20.

DSC study helps an HEM chemist to evaluate the compatibility of ingredients in an explosive formulation. The compatibility assessment is based on the principle that the addition of an ingredient (the compatibility of which with the explosive is being assessed) should not bring down the decomposition temperature of the virgin explosive by more than 5 °C. To conduct the assessment, the DSC thermograms are taken for the main explosive and for the explosive to which the ingredient is added to the extent required by the formulation. Let us propose to add either plasticizer A or plasticizer B as 5% of the formulation to NC (i.e., 95% NC + 5% plasticizer). The DSC thermograms taken (Figure 10.5) show that plasticizer A is compatible whereas plasticizer B is not.

### 10.4.3 Thermogravimetric Analysis

In the TGA thermal evaluation technique, a known quantity of the sample is subjected to programmed heating, and the weight loss pattern of the sample is measured as a function

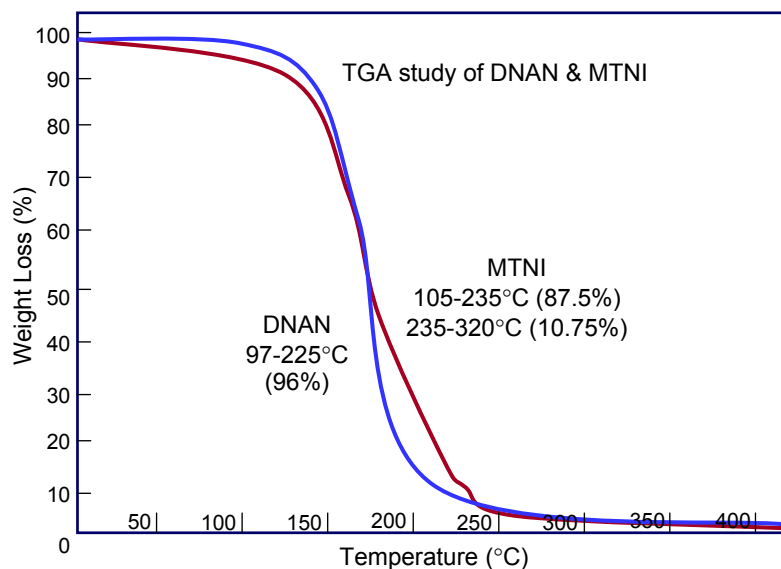


**Figure 10.5**

(a) DSC of NC, (b) DSC of NC + Plasticizer A (95:5), and (c) DSC of NC + Plasticizer B (95:5).

of temperature or time. The initial weight of the sample is considered as 100%, and the loss in weight is recorded as a percentage. As explosives are heated, they lose their weight through various processes such as dehydration, evaporation, or decomposition. It is interesting to note that some materials can gain weight by reacting with the atmosphere in the testing environment. The weight loss data are usually plotted on the y-axis and temperature/time on the x-axis. Thermogravimetric evaluation of explosives offers information about the thermal stability of explosives.

TGA of dinitroanisole (DNAN) and *N*-methyl-2,4,5-trinitroimidazole (MTNI) is depicted in Figure 10.6. DNAN loses its mass in a single stage in the temperature region of 97–225 °C with a mass loss of 97%. MTNI loses its mass in two stages. In the first stage, 87.5% mass is lost in the temperature region of 105–235 °C, and in the second step 10.5% is lost in the temperature region of 235–320 °C. Apart from obtaining an idea about the thermal stability of explosives, TGA may help in obtaining insight into the



**Figure 10.6**  
TGA of DNAN and MTNI.

possible decomposition mechanism of HEMs when combined with other techniques such as GC/mass spectrometry.

#### 10.4.4 Simultaneous Thermal Analysis

STA is a coupled technique in which a sample is heated in a programmed fashion and the thermal events are recorded simultaneously by using two different techniques (e.g., DSC and TGA or DTA and TGA). Simultaneous recording of TGA and DTA/DSC can provide better insight into the probable physicochemical mechanism involved during the decomposition/oxidation of the sample.

### 10.5 Sensitivity Tests of HEMS

The sensitivity of an HEM is its response to an external stimulus such as impact, friction, shock, and electrostatic discharge. Because the utmost care must be taken at every stage in the field of HEMs (e.g., formulation, processing, transportation, and storage), and one or more stimuli, as mentioned above, may be encountered by HEMs during any of these stages, the concerned HEM must be thoroughly tested for its sensitivity to most or all of the above stimuli. Because the sensitivity of HEMs varies depending on the nature of the HEM and the stimulus involved, in each case a reference HEM is taken to assess the relative sensitivity of a given HEM. For example, composition exploding (CE), which is 2,4,6-trinitrophenyl methylnitramine (Tetryl), is taken as a reference explosive with an

impact sensitivity of 70, and, on this scale, the relative impact sensitivity of other explosives is assessed. A brief mention is made in the following about the various types of sensitivity tests commonly used in the field of HEMs.

### **10.5.1 Impact Sensitivity**

Impact sensitivity is the ability of a substance to withstand a sudden blow without decomposing or igniting when impacted by the fall of a 2-kg hammer from a specific height. A 2-kg weight is released to impact the sample kept on an anvil and the result is noted. The impact distances are determined, and the results are analyzed by the Bruceton staircase method. In this method, one measures the 50% initiation level (the height at which 50% of the samples will detonate), compares it with that of a standard explosive (CE taken as 70), and reports it as the figure of insensitiveness (F of I). This height is called the median drop height of the sample.

$$\text{Figure of Insensitivity of the sample (F of I)} = \frac{\text{Median dropheight of sample}}{\text{Median dropheight of reference}} \times (\text{F of I of standard})$$

For example, if a high explosive and CE (standard) give median drop heights of 60 and 80 cm, respectively, in an experiment, the F of I of the explosive is given as

$$\text{F of I} = \frac{60}{80} \times 70 = 52.5$$

### **10.5.2 Friction Sensitivity**

Friction sensitivity is the measure of sensitivity to initiation of an HEM to relative frictional motion between two objects in contact. The sensitivity of an explosive is determined by subjecting a thin layer of explosive on a predetermined spot to a certain load through a loading arm and allowing the explosive to undergo standard frictional movement. The range of load for primary explosives is 10–1000 g and for other explosives is 0.5–36 kg. The observation of any effects (e.g., smoking, burning, or exploding) at a minimum particular load is taken as the sensitivity to friction of an explosive to that load.

### **10.5.3 Spark Sensitivity**

Repeated contact and separation of two dissimilar materials (one of them is insulator material) lead to accumulation of electric charge, which often gets discharged through lower potential materials in the surrounding. Hence, it is vital to measure the electrostatic

sensitivity of explosive stores to understand the hazards associated with that particular material. These data help in designing the safety measures required for reducing the electrostatic hazards in various operations such as mixing, sieving, handling, storage, etc. This assessment can be done by exposing a known quantity of a particular sample from low discharge energy to high discharge energy in an incremental fashion until the sample gets ignited.

### ***Suggested Reading***

- [1] J. Yinon, S. Zitrin, *Modern Methods and Applications in Analysis of Explosives*, John Wiley and Sons, 1996.
- [2] U. Teipel, *Energetic Materials Incorporation of Particular Components with Specialised Properties Allows One to Tailor the End Product's Properties*, Wiley-VCH Verlag GmbH, 2004.
- [3] W. Kemp, *Organic Spectroscopy*, second ed., Macmillan, 1987.
- [4] J.H. Michael, *Modern Spectroscopy*, fourth ed., Wiley, 2004.
- [5] J.P. Agrawal, R.D. Hodgson, *Organic Chemistry of Explosives*, first ed., Wiley, 2007.
- [6] J. Akhavan, *The Chemistry of Explosives*, third ed., Royal Society of Chemistry, 2011.

### ***Questions***

1. What is the difference between the characterization and evaluation of an HEM? Give an example.
2. What is the basic principle of chromatography?
3. Why is HPLC a preferred technique in the separation and analysis of HEMs?
4. Why are many HEM molecules active in the UV region?
5. Why do we get three clear, different NMR spectral peaks in ethyl alcohol?
6. Why are thermal analysis techniques very important in the field of HEMs?
7. What is the major difference between DTA and DSC?
8. What are the uses of the TGA technique in the field of HEMs?
9. What are the different types of sensitivity of HEMs and how are they measured?