

## APPLICATION OF THERMAL ANALYSIS METHODS TO THE STUDY OF UNSTABLE AND METASTABLE MATERIALS\*†

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### ABSTRACT

The application of thermal analysis methods to the study of unstable and metastable materials is discussed. Specific DTA and TG techniques are described which have been successfully used to measure small reactivity changes and induced physicochemical changes in primary and secondary explosives. Data obtained by these techniques have been correlated to the more engineering-type tests currently used. Comparisons between the two types of tests are made, and arguments for the justification for routine application of thermal analysis to unstable and metastable materials is presented.

### INTRODUCTION

This paper presents a discussion of the feasibility of applying thermal analysis methods, for accurate and reliable measurements, to determine small reactivity changes in unstable materials as they age. These analytical techniques will also be discussed as possible methods for determining physicochemical changes that occur in metastable materials through the action of external stimuli, such as electromagnetic radiation, pressure, and temperature. Thermal analysis methods appear capable of detecting small changes which occur in a wide variety of materials that degrade with age or through interactions with their environment, such as photographic film, storage batteries, dry cells, explosives, propellants, pharmaceuticals, food, rubber, fuels, and oils, to name just a few.

As illustrations of the successful application of thermal analysis methods to the study of unstable materials, discussions will be given of some recent studies where these methods were used to determine the thermal reactivity changes of aged explosives<sup>1,2</sup> and also crystallographic and thermal reactivity changes produced in explosives by irradiation with ultra-violet light<sup>3</sup>.

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According to Copp *et al.*<sup>4</sup>, there are two main variants in routine tests for determining the thermal reactivity of explosives. In the first method the explosive is heated in a suitable container, with ignition occurring above some limiting temperature which is dependent on the heating rate. Provided a standard rate of heating is used, the ignition temperature gives qualitative relative information on the sensitivity of the material. In the second method, the container of the explosive is suddenly plunged into a bath maintained at a constant temperature, and the time interval before ignition or detonation occurs is measured. Krien<sup>5</sup> has studied the application of differential thermal analysis (DTA) and thermogravimetry (TG) in the examination of explosives. In his work he had to choose low rates of heating (0.5–5°C/min) for thermogravimetry (balancing problems) with the resultant flattening of the DTA peaks. In recent years, DTA and/or TG have been used to characterize, or provide a "fingerprint" of many different explosives according to their thermal reactions<sup>6–10</sup>.

For the explosive studies to be discussed here a simultaneous DTA–TG technique was used, wherein the resulting curves were analyzed for both peak temperatures of any exothermic processes and sensitivity factors of the exotherm. A shift to higher temperatures for the peak of the exotherm indicates a decreased thermal sensitivity. The sensitivity factor of the exotherm is defined as the height to half width ratio ( $h/w_{1/2}$ ) where an increase in this number indicates an increase in thermal sensitivity.

It will be demonstrated that thermal analysis techniques can be used to provide quick, safe and reliable data on the reactivity of unstable chemicals. Further, it will be shown that these data can be correlated to the more usual type of gross engineering tests. For example, the shock sensitivity of explosives is very often characterized by a test where the figure of merit is defined as the height from which a specified weight must fall on a confined explosive for a 50% probability of detonation. To provide a meaningful correlation between the thermal analysis tests and the less sophisticated shock test required that the sensitivity and accuracy of the usual shock test be improved. A discussion of the improved analytical procedure developed in this study will be presented because it adds to the credibility of the final correlation and because it has a wide application in the area of destructive testing, being not limited solely to explosives.

## EXPERIMENTAL

A Mettler simultaneous DTA–TG thermoanalyzer was used for the thermal analyses in these studies. Because of the hazards involved in handling explosives, small sizes are desirable (*e.g.* 1–10 mg). The sensitivity of the instrumentation used was such that the small samples presented no problem. Since the Mettler thermoanalyzer is equipped with a transparent quartz furnace it is possible to distinguish, visibly, between decomposition and detonation.

In a typical analysis, the test sample of explosive and the reference  $\text{Al}_2\text{O}_3$  were loaded into adjacent platinum cups of 3-mm diameter and 4-mm height. These same platinum cups act as one junction of the temperature sensing thermocouples. A circular platinum shield surrounding the cups provides uniform temperature condi-

tions at the measuring head, and also functions as the furnace control thermocouple. Both the test sample and reference material were loosely packed in the crucible to a sample weight of 2.0 mg. After the quartz furnace was placed over the samples, the entire measuring head and balance unit were evacuated to approximately  $10^{-3}$  Torr and then filled with dry nitrogen or helium purified by passing through  $\text{CaCl}_2$  granules, concentrated  $\text{H}_2\text{SO}_4$ , KOH pellets, and  $\text{P}_2\text{O}_5$  towers. The addition of columns packed with heated copper turnings for drying and oxygen removal had no effect on the DTA curves reported here and were therefore not used. During a test run, a steady flow of dry gas was maintained around the samples at flow rates of 10 liters per h.

The irradiation source used in the photochemical studies was a Hanovia low pressure mercury lamp whose main output is two lines, at 2537 and 1849 Å. The intensity of the lamp was varied by placing calibrated neutral density filters between the sample cell and the lamp. For longer wavelengths a General Electric AH-6 high pressure, water cooled, mercury arc was used.

During irradiation the samples were contained in a Pyrex cell fitted with a flat quartz window and connected to a vacuum line. A typical sample size weighed about 100 mg; the area of irradiation was about  $3\text{ cm}^2$ . The samples were irradiated at room temperature in a vacuum of  $10^{-3}$  Torr for approximately 1.5 h.

The drop test instrument employed to measure the shock sensitivity of the explosives used a steel ball weighing 2 kg. In operation, the ball is suspended by an electromagnet a known distance above the cup containing the material under test and released by cutting power to the magnet. In all cases, the point of impact was within 0.1 in. of the center of the cup.

Most sensitivity testing is carried out using cups with a firing pin diameter of about 0.25 in. This cup size typically requires samples weighing 50 mg. Because only a small amount of explosive material was available for this study (typically 50–100mg), new sample cups were designed and used which gave satisfactory results with samples as small as 5 mg. The base of the cups and the tops were machined from hardened steel. The firing pin was a short force fit insert of 0.125-in. drill rod ground to the proper length.

At any one time no more than 10 cups were filled with  $5.0 \pm 0.2$  mg of material. The drop tests were carried out in the same order as the cups were filled so that each sample would be exposed to the ambient atmosphere for approximately the same time. After the tests the cups were washed and then sand blasted to guarantee that no material from previous runs would be left in the cups. The tests were carried out using the Bruceton staircase technique, *i.e.*, the 2 kg ball would be raised or lowered depending on whether the previous test resulted in no fire or a fire, respectively.

## RESULTS AND DISCUSSION

### *Thermal changes due to irradiation*

1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) is a secondary high explosive that exhibits four polymorphic forms<sup>11</sup> which are structurally different and

of different explosive sensitivity. The thermal properties of unirradiated and UV irradiated crystals of the  $\alpha$ ,  $\beta$ , and  $\gamma$  forms of HMX were studied with the simultaneous DTA-TG technique<sup>3</sup>. The technique enabled a comparison to be made between the effects arising from crystal conformational changes and those effects related to changes in the thermal stability, or sensitivity of the irradiated solid.

For the unirradiated  $\beta$  polymorph of HMX, the DTA, using a flowing (10 l/hr) helium atmosphere and a 6°C/min heating rate shows an endotherm at 194°C representing the  $\beta$  to  $\gamma$  phase change, and a decomposition exotherm at 282°C. UV irradiation results in the displacement the  $\beta$ - $\gamma$  endotherm from 194 to 180°C ( $\Delta T = 14^\circ\text{C}$ ) and the exotherm from 282 to 277°C ( $\Delta T = 5^\circ\text{C}$ ). The TG curves show that at 260°C the unirradiated  $\beta$ -HMX has not lost any weight whereas the irradiated sample shows a weight loss of 6 to 7%. The observed shifts in endotherm and exotherm temperatures and also weight loss are all linearly dependent on the radiation dosage.

The DTA curve for the  $\alpha$ -polymorph shows two endotherms, the first occurring at 183°C perhaps representing an  $\alpha$ - $\gamma$  transformation and the second at 199°C representative of the  $\gamma$ - $\delta$  transformation. The fast decomposition is characterized by an exotherm at 282°C. Irradiation shifts the first endotherm from 183 to 178°C ( $\Delta T = 5^\circ\text{C}$ ) with the second endotherm remaining unchanged. The decomposition exotherm which occurs at 282°C is now lowered to 252°C ( $\Delta T = 30^\circ\text{C}$ ). More important is that irradiation produces two additional exotherms, one at 135°C and a second at 170°C. These are both associated with a simultaneous weight loss, signifying that the weight loss is not due to absorbed or occluded species but due to the decomposition of  $\alpha$ -HMX, probably initiated at the sites of the nuclei formed by irradiation. Finally the TG curves show that while at 240°C unirradiated  $\alpha$ -HMX does not lose any weight, the irradiation sample has lost 23% by weight. Similarly for  $\alpha$ -HMX the irradiation effects, as mentioned earlier for  $\beta$ -HMX, are a linear function of the irradiation dose.

The  $\gamma$ -polymorph of HMX exhibits an endotherm at 188°C, the  $\gamma$ - $\delta$  transformation, and the decomposition exotherm at 282°C. On irradiating the following effects are evident: 1. lowering of the endotherm temperature from 188 to 185°C ( $\Delta T = 3^\circ\text{C}$ ); 2, shifting of the exotherm temperature from 282 to 226°C ( $\Delta T = 56^\circ\text{C}$ ); 3, appearance of two new exotherms at 130 and 170°C, both associated with weight loss processes; and 4, a weight loss of 30% at 220°C as compared to 0% for the unirradiated sample. These irradiation effects are also a linear function of the irradiation dose as was observed for  $\alpha$ - and  $\beta$ -HMX. It is apparent that the behavior of irradiated  $\gamma$ -HMX is very similar to that of irradiated  $\alpha$ -HMX.

A comparison of the irradiation effects in the  $\alpha$ ,  $\beta$ , and  $\gamma$  polymorphs is shown in Table I. It is evident that the largest change in the transition temperature for a phase transformation occurs in the  $\beta$  polymorph ( $\Delta T = 14^\circ\text{C}$ ), followed by  $\alpha$ - ( $\Delta T = 5^\circ\text{C}$ ), and then  $\gamma$ -HMX ( $\Delta T = 3^\circ\text{C}$ ). Defining the lowering of the transformation temperature as a photon induced sensitization, then this sensitization which is in the sequence  $\beta > \alpha > \gamma$  follows the ordering of the densities,  $\beta > \alpha > \gamma$ , as well as the ordering of the thermal stabilities,  $\beta > \alpha > \gamma$ .

The changes resulting from irradiation of HMX given in this section could have been based on single DTA-TG analyses per irradiated sample. To have obtained a comparable amount of information using isothermal kinetic and X-ray analysis techniques would have involved a significantly greater expenditure of effort. Even then, the existence of the phenomena which were responsible for the additional exotherms in irradiated  $\alpha$ - and  $\gamma$ -HMX might have been missed.

TABLE I  
COMPARISON OF THE IRRADIATION EFFECTS ON THE DIFFERENT HMX POLYMORPHS

Phase	Shift in the endotherm	$\Delta T$ ( $^{\circ}C$ )	Shift in main exotherm	$\Delta T$ ( $^{\circ}C$ )	Additional exotherms	Temperature for 30% weight loss
$\beta$	194 $\rightarrow$ 180	14	282 $\rightarrow$ 277	5	None	275 $^{\circ}C$
$\alpha$	183 $\rightarrow$ 178	5	282 $\rightarrow$ 252	30	135, 170 $^{\circ}C$	237 $^{\circ}C$
$\alpha$	199 $\rightarrow$ 199	0				
$\gamma$	188 $\rightarrow$ 185	3	282 $\rightarrow$ 226	56	130, 170 $^{\circ}C$	205 $^{\circ}C$

#### Reactivity changes due to aging

The reactivity changes in an aged, primary explosive, lead azide ( $PbN_6$ ), were studied using a variety of TG and DTA techniques<sup>1</sup>. The lead azide was stored under different atmospheres, and changes in reactivity as a function of age and storage temperature were determined. These reactivity changes (changes in sensitivity) were investigated in three different ways: (a) by thermogravimetry, which can differentiate between decomposition and detonation, as a function of heating rate; (b) by the DTA method of the shift in temperature of the exotherm peak; and (c) by the DTA method of the sensitivity factor, defined as the height of the exotherm over the half-width.

The application of thermogravimetry as a reliable and accurate method for determining the thermal sensitivity of lead azide by differentiating between a detonation and a fast decomposition can be seen in Tables II and III.

TABLE II  
DETONATION AS A FUNCTION OF CRITICAL MASS OF  $PbN_6$ <sup>a</sup>

Mass (mg)	Visual criterion	Mass loss (mg)	Inference: temperature of reaction ( $^{\circ}C$ )
1.0	Decomposition	0.25	< 1515
1.6	Decomposition	0.35	< 1515
2.0	Decomposition	0.50	< 1515
3.0	Detonation	3.0	> 1515
4.0	Violent detonation	4.0	> 1515

<sup>a</sup>Heating rate, 15  $^{\circ}C/min$ ; atmosphere, flowing He, 10 l/h.

TABLE III  
 DETONATION OF  $\text{PbN}_6$  AS A FUNCTION OF CRITICAL HEATING RATE\*

Heating rate ( $^{\circ}\text{C}/\text{min}$ )	Visible criterion	Mass loss (mg)	Sensitivity (height/half-width)	Inference: temperature of reaction ( $^{\circ}\text{C}$ )
10	Decomposition	0.50	$10/3.5 = 2.9$	<1515
15	Decomposition	0.55	$15/2.0 = 7.5$	<1515
25	Detonation	2.0	$25/1.0 = 25.0$	>1515

\*Sample mass, 2.0 mg; atmosphere, flowing He, 10 l/h.

Table II shows that a critical mass is required to proceed from decomposition to detonation (keeping the heating rate and other experimental variables constant), and reveals that during decomposition only 25–30% of  $\text{PbN}_6$  is lost, corresponding to total loss of the azide groups. A 100% loss is observed during detonation. Therefore, at a constant heating rate the sample which requires the minimum weight to detonate is the most sensitive and *vice versa*. This is in complete agreement with earlier knowledge that a critical mass is required for detonation<sup>5</sup>.

When the heating rate is varied from a low to a high value (Table III), the reaction goes from decomposition to detonation with a 25–30% weight loss for decomposition and a 100% weight loss for detonation. Since the results in Tables II and III show that the critical mass is very much dependent on the heating rate, if a constant mass is maintained, then the heating rate can be used to differentiate between lead azide samples of varying sensitivities. The lower the heating rate at which a given mass of  $\text{PbN}_6$  detonates, the higher its sensitivity, and *vice versa*.

By using this method of thermogravimetry in conjunction with the DTA methods the aging characteristics of lead azide were successfully determined. The fourth column of Table III gives the sensitivity of the DTA exotherm associated with the weight loss, as calculated from the ratio of the height of the exotherm to its half-width. As a function of heating rate, the DTA sensitivity is seen to change from a low arbitrary value to a high one as the reaction changes from a decomposition process to one of detonation.

In the aging study a small exotherm occurring around 120 $^{\circ}\text{C}$  in DTA curves was observed during the first 4 weeks of aging, after which it was never observed. This is proposed as being associated either with a crystal phase change, or more likely, with the initial gas evolution peak as found in the rate of gas evolution vs. time plots<sup>1,2</sup> for the thermal decomposition of  $\alpha\text{-PbN}_6$ .

The main exotherm which is symmetrical during the first two weeks becomes broadened and unsymmetrical except in the case of the  $\text{PbN}_6 + \text{Cu}$  system. This implies that water and  $\text{CO}_2$  react with  $\text{PbN}_6$  forming a basic salt. The sensitivity of the system  $\text{PbN}_6 + \text{H}_2\text{O} + \text{CO}_2$  goes through a cyclic process of an increase, a decrease, and an increase in sensitivity during the 15-week period of aging. By comparing these results with those of the system  $\text{PbN}_6 + \text{H}_2\text{O} + \text{CO}_2 + \text{Cu}$ , it appears that copper

densitizes in the first 4 weeks, after which a sensitization is observed. The desensitization is tentatively attributed to a relatively large concentration of metal which acts as a heat sink, and the sensitization is attributed to colored ions of Cu diffusing into the basic lead salt.

As was the case for the HMX study, the use of thermal analysis greatly facilitated the detection of small changes which occurred, in this case, during the aging process. The observed growth in asymmetry in the main decomposition DTA peaks suggests subtle changes in the decomposition mechanism. Such changes could easily be missed using isothermal techniques.

*Correlation of thermal analysis data to engineering test data*

The data obtained in a study to determine whether there were any aging effects in the two secondary high explosives pentaerythritol tetranitrate (PETN) and cyclotrimethylenetrinitramine (RDX) are summarized in Table IV. Each material was analyzed using the thermal sensitivity factor (decomposition exotherm height to half-width ratio), and the shock sensitivity test. As discussed in the Introduction, a more sophisticated analysis of the impact test data was used instead of the standard engineering method.

TABLE IV  
COMPARISON OF THE THERMAL SENSITIVITY AND THE SHOCK SENSITIVITY OF PETN AND RDX

PETN			RDX		
Manufacturing date	Sensitivity factor ( $h/w_2$ )	Drop height (in.)	Manufacturing date	Sensitivity factor ( $h/w_2$ )	Drop height (in.)
8/63	4.3	8.2	6/63	8.0	12.1
10/63	3.9	8.6	2/64	7.9	13.8
11/63	4.0	8.2	9/64	5.6	27.2
1/64	5.5	6.6	4/65	7.2	19.0
2/64	5.6	6.2	9/65	8.0	13.8
4/64	7.3	4.0	2/66	7.9	13.5
6/64	5.3	6.7	5/66	8.2	13.3
7/64	6.1	5.6	12/66	7.4	15.4
8/64	5.2	6.6			
9/65	5.8	4.8			
10/65	5.9	5.7			
11/65	4.1	8.7			
12/66	4.7	8.3			
6/68	3.9	8.3			
10/68	4.9	7.4			

Most impact test data are presently analyzed and obtained using the Bruceton Staircase method<sup>13</sup>. In this method the height is varied by a fixed increment, with the height being increased if the previous test were a success and decreased if the previous

test were a failure. The value of  $h_{0.5}$ , the height where the probability is 0.5 for a firing, is calculated by either

$$h_{0.5} = \frac{\sum i X_i^2}{\text{successes} / \text{successes}} - I/2 \tag{1a}$$

or

$$h_{0.5} = \frac{\sum i X_i^2}{\text{failures} / \text{failures}} + I/2 \tag{1b}$$

where  $i$  is the number of successes or failures at height  $X_i$  and  $I$  is the height increment. Procedures for evaluating  $h_n$  where  $n$  is other than 0.5 and confidence limits for the calculated value of  $h_n$  are extant<sup>13</sup>. This analysis of Bruceton Staircase data is based on several mathematical approximations which are valid only for a moderately large number of tests and also depends on a particular form for  $P(X)$ , the probability of a failure at height  $X$ .

To overcome these limitations the problem was considered from first principles. The probability of a given sequence of failures and successes is given by

$$P = \prod_i p_i(X_i) \prod_j [1 - p_j(X_j)] \tag{2}$$

(the subscript  $i$  is used here and henceforth for failures and the subscript  $j$  for successes). It has been shown that for a wide variety of explosives  $P_i(X_i)$  has the form  $\exp(-KX^m)$  where  $K$  and  $m$  depend on the material<sup>14</sup>. For many secondary explosives  $m$  is approximately 4, whereas the Bruceton analysis effectively assumes that  $m$  is 2. Using this result it is found that

$$P(K) = \exp\left(-K \sum_i X_i^4\right) \prod_j [1 - \exp(-KX_j^2)] \tag{3}$$

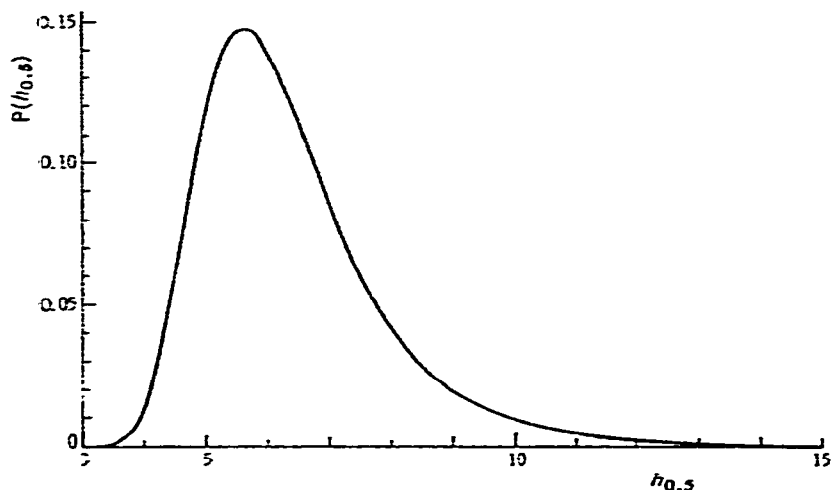


Fig. 1. Plot of the probability for a particular sequence,  $P(h_{0.5})$  vs.  $h_{0.5}$ . The curve is for two failures at 5.29 in., and two successes at 6.24 in.  $h_{0.5}$  (mode) = 5.6064;  $h_{0.5}$  (median) = 6.088; and  $h_{0.5}$ (Bruceton) = 5.79.



Since  $h_n$  (the height at which the probability of a success is  $n$ ), is given by  $[(1-n)/K]^{0.25}$ , the fundamental problem is resolved into determining the optimal value of  $K$  on the basis of the data. An *a priori* reasonable appearing hypothesis is that the proper value of  $K$  is the value for which  $P(K)$  is a maximum (*i.e.*, the mode). Consideration of Fig. 1, shows, however, that this is not the case. In this Fig., the probability for a particular sequence is plotted vs.  $h_{0.5}$ . The asymmetry is quite typical for such curves and shows that use of the mode to determine  $K$ , would result in too small a value of  $h_{0.5}$ . A statistically sounder technique for determining  $h_{0.5}$  is to use the value of  $h_{0.5}$  for which it is equally likely that the correct value is either larger or smaller than the calculated value (*i.e.*, the median). This criterion necessitates solving for  $h_{0.5}$  the equation

$$\int_0^{h_{0.5}} P(K) dX = \int_{h_{0.5}}^{\infty} P(K) dX \quad (4)$$

An additional desirable piece of information is a measure of the reliability of the value of  $h_{0.5}$ . This can be expressed as either the probability that  $h_{0.5}$  is within a specified range,  $\pm a$ , or as the confidence limits on  $h_{0.5}$  (*i.e.*, the limits on  $h_{0.5}$  for a specified probability). Since the latter is of more general usefulness, it was determined. The confidence limits were calculated by solving for  $X_{0.5} \pm a/2$ , equations such as

$$P_a = \int_0^{X_{0.5} \pm a/2} P(K) dX / \int_0^{\infty} P(K) dX \quad (5)$$

Because of the asymmetry of  $P(X)$ ,  $X_{0.5} - a/2$  is not usually the same as  $X_{0.5} + a/2$ .

Although this analytical procedure is discussed in terms of the drop test, it should be noted that the test is homomorphic to many other classes of destructive testing, thus the analysis given herein is of more general applicability than it would otherwise appear.

A computer program has been written which calculates, for a given sequence,  $h_{0.5}$  based on the mode, median, and Bruceton method and also calculates  $P_a$  for given values of  $a$ . The program is in the basic language for use on time sharing computers.

Both the thermal sensitivity factors and the drop heights in this study show no indication of any aging trend for the two explosives (Figs. 2 and 3). The scatter in the data is attributed to either lot-to-lot variations in the manufactured material or else to the particular time-temperature history experienced by the sample. Information on these two variables is not available. The direct correlation between the data from the two types of tests (thermoanalytical and engineering) is very evident in these Figs. The solid line in the Figs. is the average value for both sets of data. A decrease in the value of the thermal sensitivity factor  $h/w_{1/2}$ , indicating a decrease in sensitivity, is always accompanied by an increase in the drop height. Similarly, an increase in  $h/w_{1/2}$ , indicating an increase in sensitivity, is always accompanied by a decrease in drop height. This is what should actually occur. The correlation is further illustrated by Figs. 4 and 5. For the two explosives in this particular study a linear relationship

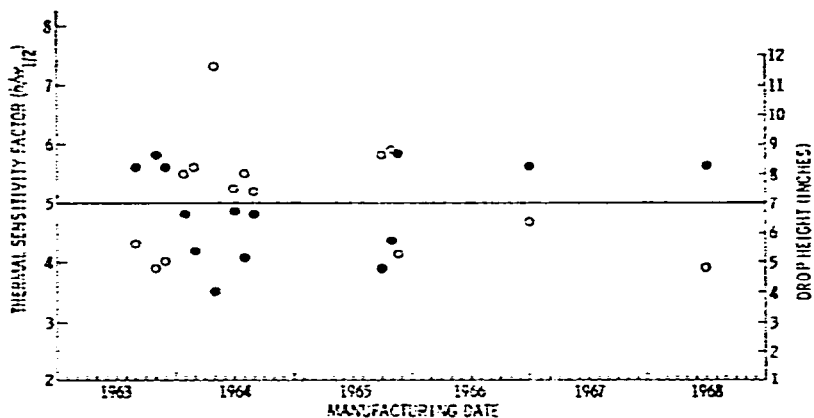


Fig. 2. Plot of the PETN thermal sensitivity factor and drop height *vs.* age. (O), thermal analysis; (●), shock sensitivity (drop height).

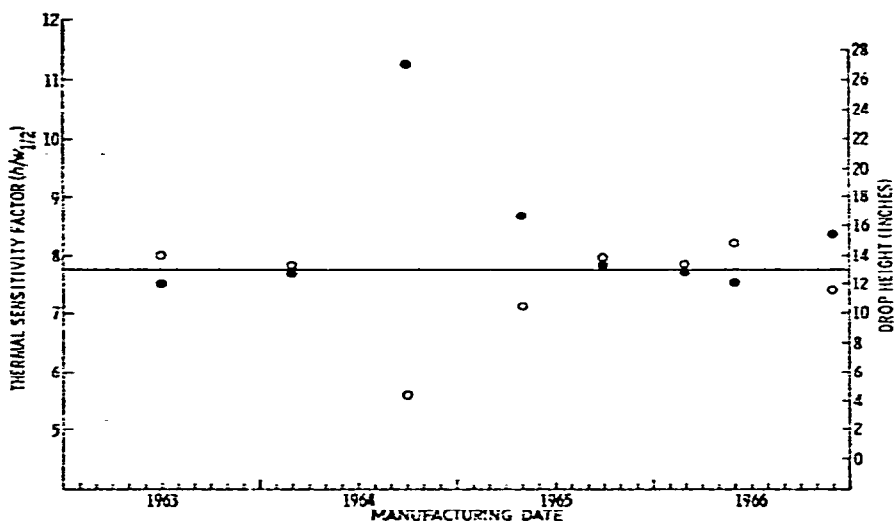


Fig. 3. Plot of the RDX thermal sensitivity factor and drop height *vs.* age. (O), thermal analysis; (●), shock sensitivity (drop height).

between the two types of tests exists. The establishment of a direct correlation between the two types of tests gains further importance when the testing procedures of each type are compared.

Only one small sample (2.0 mg) is needed for each data point in thermal analysis. Even with the modified drop test apparatus used in this study, which requires very much smaller amounts of sample per drop than the standard method (5 mg as opposed to 50 mg), a total of 50 mg of material are needed to give reasonable accuracy, *i.e.*, ten individual tests. Thermoanalyzers are now available that perform simultaneous DTA-TG, so that for one small sample much more information is obtainable than in the standard engineering test. The difference in the amount of time required to get

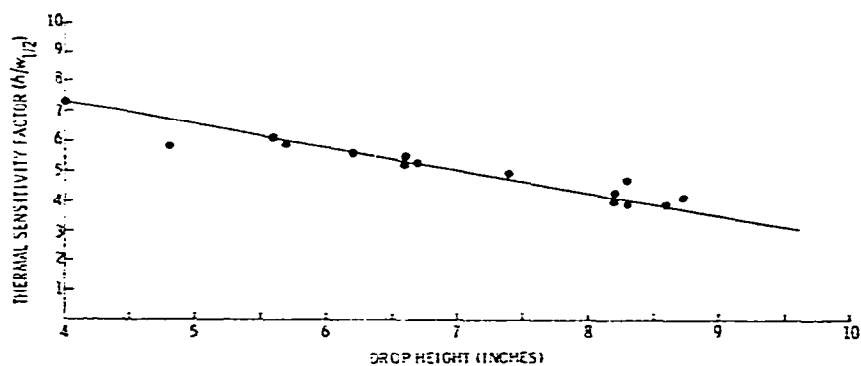


Fig. 4. Plot of the PETN thermal sensitivity factor *vs.* drop height at each manufacturing date

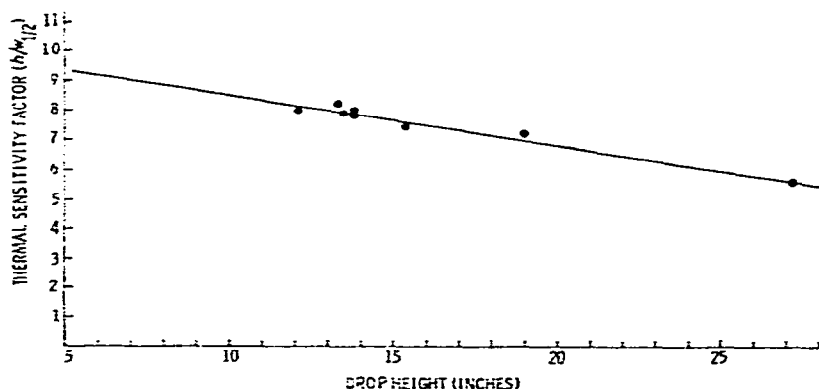


Fig. 5. Plot of the RDX thermal sensitivity factor *vs.* drop height at each manufacturing date.

a data point in each type of test is extremely large. Also, it has been our experience that the ambient conditions (temperature, relative humidity) under which the drop tests are conducted strongly influence the test results. The environment in thermal analysis tests is much easier to control between consecutive analyses. Further, the lack of standardized engineering test hardware seriously hampers the comparison of test information between investigators. Provided all experimental parameters in a DTA and TG test are specified, the test should be able to be duplicated by another investigator on another instrument with the same results obtained.

#### CONCLUSIONS

Thermal analysis methods such as DTA and TG can be applied for reliable and accurate measurements of small reactivity changes in unstable materials and of small physicochemical changes induced in metastable materials by external stimuli. It has been explicitly shown how specific DTA and TG techniques have been successfully used to determine the thermal reactivity changes in explosives aged in different atmospheres and to determine the crystallographic and thermal reactivity changes

produced in explosives irradiated with ultraviolet light. Also, the correlation of the data from these techniques to the more "engineering-type" tests currently used on explosives has been shown. The results of these studies are sufficient justification for recommending and extending the use of sound thermal analysis techniques into studying other unstable materials. The use of thermal analysis in place of routine engineering tests will save time, be much safer, and also provide more precise information.

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