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Quantitative Differential Thermal Analysis of Nitrocellulose Propellants

Gunpowder residues have long been important as evidence in the investigation of firearms cases, particularly in the reconstruction of crime scene events. Early work was based solely on the spatial distribution of unburned powder and its relationship to the distance between the target material and the weapon's muzzle. Current refinements have included mathematical analysis of these patterns and the identification of patterns of trace metal transfers of bullet lead, copper, and zinc, or primer lead, barium, and antimony by neutron activation, atomic absorption, or X-ray fluorescence.

Often the nature of the powder itself is ignored by the examiner; it is identified by its physical appearance or a simple chemical test as being gunpowder and dismissed without further analysis. Recently, thin-layer and gas chromatography (TLC and GC) techniques have permitted the examination and comparison of smokeless powders on the basis of the stabilizers used and their by-products [1,2].

The advent of stable and sensitive commercial differential thermal analysis (DTA) systems now permits the examination of single flakes of disk-type propellants, ranging in weight from 20 to 600 μg each, with minimal specimen preparation. The qualitative thermal properties, such as the temperatures of initiation, ignition, and completion, and the reaction rate, as well as the quantitative properties, such as heat of explosion, can then be established for each powder. Unknown powder residues collected from evidence materials can then be characterized as to their dynamic thermal properties in addition to the routine measurement of their static physical and chemical properties.

Procedure

Instrumentation

Preliminary DTA studies of smokeless powders revealed that energy released by the combustion of single flakes of such materials was on the order of 10 to 100 mcal, and that reproducible heating rates were essential to reliable results [3]. The DTA system used in these experiments was a Series 300 QDTA Thermalizer[®] (Fisher Scientific), shown in Figs. 1 and 2. This system provides sufficient sensitivity (maximum $dT/in.$: 0.03°C/in), one-millicalorie readability, reproducible and adjustable heating rates, small disposable sample pans, and provisions for rapid water cooling. Specimens were weighed on a Cahn Model G-2 Electrobalance[®] which provided 0.01-mg readability with

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FIG. 1—Quantitative DTA system with recorder.

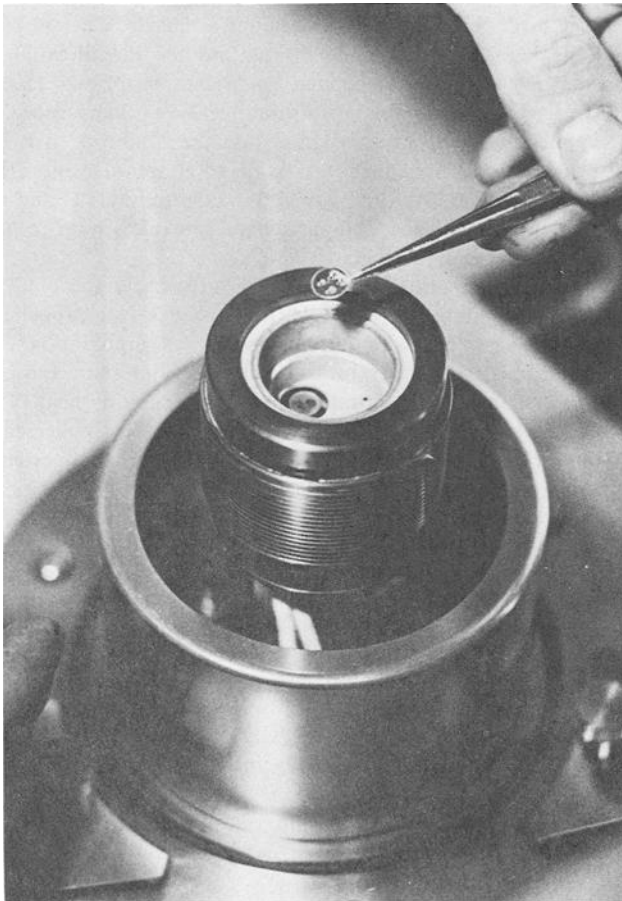


FIG. 2—Sample oven and typical sample pan.

100-mg capacity for weighing sealed sample pans at approximately 32 mg each.

Thermograms were recorded on a two-pen strip chart recorder. One pen recorded sample temperature T while the other recorded dT , the difference in temperature between the sample and an inert reference. The time-base recording of the dT signal permitted direct integration of the thermogram peak to yield a measure of the heat generated (or absorbed) by a given reaction [4]. Using thermochemical transitions of accurately known energy, the peak area was calibrated to the heat transfer and heat capacity properties of the particular instrument. (These properties, of course, vary from instrument to instrument.) It was then possible to calculate the energy of an unknown reaction directly.

Experimental Procedure

Single flakes of eleven of the most common, commercially available reloading powders and four types of factory-load handgun cartridges were selected for analysis. Until the advent of the very newest Winchester-Western ball-type reloading powders, the most common form of general purpose nitrocellulose propellant was the flat disk, roughly circular in outline. Other special purpose powders are of various geometric configurations: hollow cylinders for rifle loads, spherical balls for handgun and rifle loads, and irregular granules for handgun use. Since it was thought that the flat, circular disk form would offer the most opportunity for misidentification based on physical shape alone, especially when only a limited number of flasks were present, all of the powders analyzed here were of this form. Samples of each powder selected were identified as being single-base (nitrocellulose) or double-base (nitrocellulose and nitroglycerin) on the basis of their infrared (IR) spectrograms [5].

Each flake was weighed and sealed in a disposable aluminum sample pan using the sample encapsulator provided with the Fisher DTA system. Four symmetrically placed holes were punched in the lid of each pan to insure reproducible pressure levels by dissipating generated gases, thereby keeping the sample environment at atmospheric levels. For each powder, between seven and twelve individual flakes were selected at random and analyzed.

An empty sample pan was used as a reference. Temperature programming was carried out at 25°C/min from ambient (18 to 25°C) to 250°C, and a $dT/in.$ sensitivity of 0.09°C/in. was used to simplify interpretation. A continuous flow of water at 18°C was maintained through the cooling mantle of the sample chamber at 700 cm³/min. Zero points of T and dT were set per the manufacturer's recommendations. The resulting temperature output was checked against the fusion temperatures of calorimetric standards of tin, indium, and lead, and found to agree within $\pm 1^\circ\text{C}$.

Integration was carried out by one of two methods. All of the thermograms were photocopied and then the peaks were cut from the copies and weighed. This method was found to have a reproducibility error of approximately 4%, caused by distortion of the peak dimensions by the photocopying process and irregularities in the density and moisture content of the bond paper used in the copier. To minimize these effects, copying and weighing were carried out in three major data runs. Calibration thermograms of tin and indium fusions were copied and weighed with each set of propellant thermograms to provide a rough internal standard.

The second integration method involved the overlay tracing of the thermograms through Mylar® film, then cutting out these replicas and weighing them. Agreement between integrations of tin and indium thermograms carried out by this method was on

the order of 1%. Due to the substantially lower uncertainties obtained by this method, it was used as a double check on a number of the powders analyzed.

Results

Theory

Guncotton, the precursor of modern propellants, is essentially pure nitrocellulose and is dangerously unstable. Small amounts of HNO_3 or impurities can trigger the decomposition of the nitrocellulose by promoting the conversion of the ONO_2 radicals to NO_2 and heat. The NO_2 combines with water to form more HNO_3 . Successively more and more heat is generated until the entire lot explodes. Modern nitrocellulose propellants contain stabilizers, usually 1 to 2% diphenylamine, which react with excess NO_2 and prevent it from triggering further ONO_2 decomposition.

Since nitrocellulose functions as a propellant by generating large quantities of gases while undergoing an explosive burning process, its true behavior is pressure dependent. Due to the mechanical problems inherent in making a strong pressure vessel with sufficiently small thermal mass so as to retain sensitivity for very low energy combustions, very special apparatus is required for analysis under conditions that are normal for nitrocellulose propellant use [6]. Therefore, one must be content with evaluating a propellant's behavior at atmospheric pressure.

The explosive burning process mentioned above begins as a normal combustion when the temperature reaches 170 to 180°C. Heat generated by the combustion of the first "layers" accelerates the combustion of succeeding portions of the flake. The pressure generated by the production of NO_2 , CO , H_2 , and H_2O vapor causes the reaction to proceed faster and faster. At 500 psi, the combustion rate is approximately 0.5 in./s and rises to 3.5 in./s at 20,000 psi. [7]. The progressive burning feature of nitrocellulose makes the geometry of the individual flakes very important to the behavior of the propellant as a whole. Nonperforated disks burn from the outside in, and the surface participating in the reaction grows progressively smaller. Perforated disks or pellets maintain roughly the same surface area during combustion. As the "hole" becomes larger, the exposed surface area grows to compensate for the decreasing surface area of the outer perimeter. It is these two dynamic features of propellants, the effects of sample geometry and temperature stability, which are revealed by DTA.

Analysis

Examination of several typical thermograms in Fig. 3 reveals three major temperature transition points, all of which were recorded for each specimen. First, the initiation temperature T_i represents the slow beginning of combustion of the flake. This is characterized as the point where the dT signal leaves its baseline. Second, the onset temperature T_o of the most rapid portion of the decomposition represents generally the temperature at which self-sustaining levels of heat are being generated to accelerate the combustion rate. T_o is located on the thermogram by extrapolating this portion of the curve back to the baseline. Third, the peak temperature T_m represents the point at which the reaction is completed. The specimen quickly dissipates its accumulated heat, and the dT signal begins to return to the baseline. This maximum temperature is a close approximation of the temperature at which the exothermic reaction ceases in this system, since ballistic error is minimized by the small thermal masses of the sample pan and the thermocouple assembly, and the relatively slow exothermic peaks encountered.

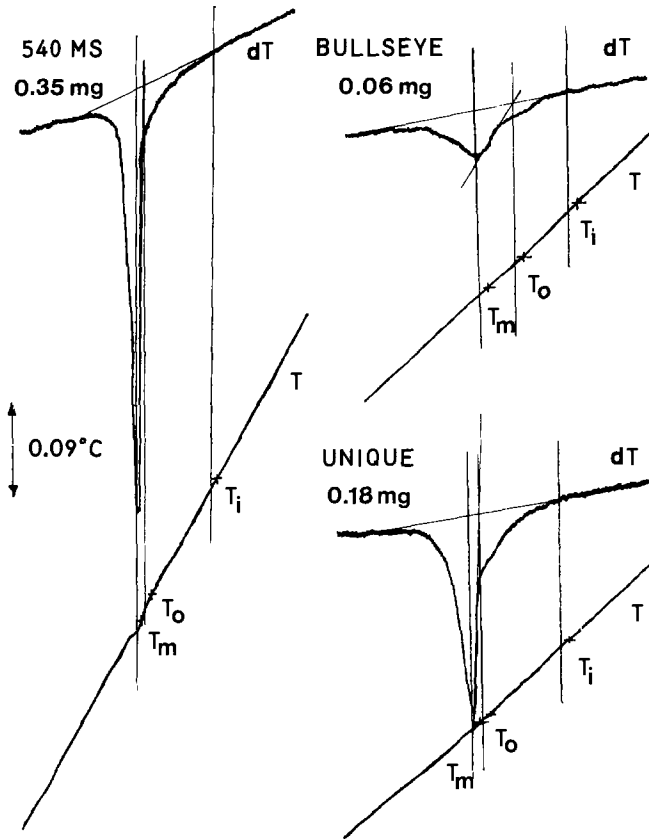


FIG. 3—Typical thermograms showing separate T and dT traces.

Two qualitative indices were calculated relating to the speed of the observed combustion. The first is a simple time-base criterion measured from time displacements on the thermogram. Elapsed times t between the onset of rapid combustion and completion and between initiation and completion were ratioed as:

$$\frac{dt}{t} = \frac{t_m - t_o}{t_m - t_i}$$

where t_i , t_o , and t_m are the time positions corresponding to the initiation, onset, and maximum completion temperatures described previously.

The quantity dt/t approaches unity as the reaction rate decreases and approaches zero as the reaction rate increases. This quantity is dependent upon heating rate and is recorded only as a rough criterion for evaluating the propellant reactions when a 25°C/min heating rate is used.

Also calculated was a temperature-based index of explosibility δ , where:

$$\delta = \frac{T_o - T_i}{T_m - T_i}$$

This quantity approaches unity as the reaction rate increases and approaches zero as the reaction rate decreases. Being temperature dependent, δ is less dependent on the heating rate than dt/t and is a measure of a propellant's chemical reactivity and the effects of flake geometry. Some discrepancies in the determination of δ will be caused by a fast heating rate, since irregularities in the heat transfer properties within the flake will be reflected in the thermogram. If true behavior is to be recorded by the index δ , it should be determined at several different heating rates and the results plotted. Extrapolation back to zero heating rate would then yield a true δ . In criminalistics applications where samples are extremely limited, one heating rate must suffice to minimize sample consumption.

Discussion

Table 1 demonstrates that many of the common smokeless powders have distinctive reaction temperatures. All of the individual flakes of a particular powder do not have exactly the same set of temperature values (initiation, onset, and completion). The values fall within a narrow range of $\pm 2^\circ\text{C}$ of the set's numerical average for most powders. The width of this range will reflect the stability of the powder and the nature of the batch mixture employed in the manufacture of the powder. Specimens which have been discharged from a weapon and recovered from the target material typically have a wider range of temperature values, indicating that reduced efficiency stems from partial combustion of the powder and its retardant coating.

Not all specimens of a particular powder exhibit the same reaction rate. Some powders, such as Herco[®], Green Dot[®], and Red Dot[®], include both fast- and slow-burning disks. Others, such as Unique[®], Remington-Peters (R-P) 12-gauge shotgun powder, and Winchester 540MS[®], exhibit very uniform combustion characteristics.

Both the ignition temperature and the reaction rate appear to be dependent upon specimen weight. The heavier a particular flake is within its weight range, the faster its combustion will be and the lower its temperature values will be. This, of course, follows from the typical burning pattern described previously. More massive flakes permit more prolonged self-sustaining combustion with the generation of more heat, thus accelerating the combustion of the remaining nitrocellulose. It was found that the temperature values of the lighter powders such as Bullseye[®] and the .22 rimfire powders were more dependent upon sample weight. When test-fired specimens of these powders represented very light individual flakes, T_m and T_c were significantly higher than the values for flakes of average weight.

Even larger variations were found in the heats of explosion calculated for each powder. The weight dependence of this value is shown in Figs. 4 to 6, where heat of explosion is plotted against specimen weight. Some powders, such as Red Dot[®], Unique[®], and .22 rimfire, demonstrate no clear relationship between sample weight and energy, however. In general, the more massive a particular flake is, within its typical weight range, the lower its heat of explosion will be.

It should be noted that the energies measured here are, in many cases, a fraction of the published heats of explosion for the same powder. Hercules 2400[®], for example, was measured at 290 to 665 cal/g, whereas the published value is 1150 cal/g [8,9]. Unique[®] was measured at 205 to 380 cal/g, compared with the published value of 1380 cal/g. These discrepancies are the result of the effects of pressure upon nitrocellulose combustion. Commercial determinations are made using several grams of powder and a bomb calorimeter. The resulting pressure levels permit complete combustion and thereby complete release of energy. This is corroborated by the relatively large amounts of

TABLE I—Temperature values and quantitative results for nitrocellulose powders.

Powder	T_1 , °C	T_0 , °C	T_m , °C	Weight, mg	$(dt/t)^a$	δ (Calculated)	Energy, cal/g		Description
							Range	Mean	
Alcan AL-7®	185 ± 4	198 ± 1	207 ± 2	0.08-0.14	0.18-0.67	0.59 (0.5-0.7)	300-530	490	single base; flat, nonperforated, rectangular wafers
Hercules Bullseye® Lot 1	183 ± 2	193 ± 2	206 ± 2	0.09-0.14	0.57-0.80	0.44 (0.4-0.5)	365-435	410	double base; flat, nonperforated, circular disks, light gray
Hercules Bullseye® Lot 2	184 ± 3	191 ± 2	206 ± 2	0.05-0.13	0.50-0.75	0.32 (0.2-0.4)	245-655	410	
Hercules Bullseye® Test-Fire	183 ± 3	193 ± 2	204 ± 2	0.04-0.09	0.40-0.75	0.48 (0.3-0.5)	345-645	350	
Hercules Green Dot®	177 ± 5	197 ± 3	201 ± 3	0.14-0.36	0.07-0.40	0.83 (0.4-0.9)	230-370	370	double base; flat, perforated, circular disks
Hercules Herco®	178 ± 4	198 ± 2	201 ± 3	0.14-0.43	0.04-0.40	0.87 (0.6-0.9)	240-670	255	double base; flat, perforated, circular disks
Hercules Herco® Test-Fire	177 ± 2	194 ± 2	201 ± 2	0.14-0.32	0.10-0.80	0.71 (0.5-0.9)	305-430	420	
Hercules Red Dot® Lot 1	181 ± 3	196 ± 3	205 ± 2	0.08-0.20	0.15-0.75	0.63 (0.3-0.8)	250-550	260	double base; flat, perforated, circular disks, light gray
Hercules Red Dot® Lot 2	179 ± 3	194 ± 2	205 ± 2	0.10-0.22	0.17-0.80	0.58 (0.5-0.9)	320-625	480	with red disks added for identification
Hercules Red Dot® Test-Fire	180 ± 4	194 ± 3	203 ± 3	0.06-0.30	0.20-0.45	0.61 (0.6-0.7)	275-445	370	
Hercules Reloder 7®	165 ± 4	184 ± 3	186 ± 2	0.39-0.60	0.07-0.13	0.91 (0.9-1.0)	230-375	270	double base; cylindrical, perforated pellets
R-P 12-gauge Shotgun	169 ± 4	193 ± 2	194 ± 2	0.27-0.43	0.08-0.12	0.96 (0.9-1.0)	185-285	285	double base; flat, nonperforated, circular disks
R-P .357 Magnum	185 ± 3	194 ± 1	203 ± 2	0.08-0.14	0.33-0.50	0.50 (0.5-0.6)	350-610	455	double base; flat, nonperforated, circular disks
Peters .22 Long Rifle	186 ± 2	194 ± 1	204 ± 2	0.09-0.22	0.30-0.60	0.44 (0.3-0.6)	210-435	320	double base; flat, nonperforated, circular disks, light gray
Peters .22 Test-Fire	193 ± 2	198 ± 2	209 ± 2	0.02-0.06	0.44-0.62	0.31 (0.3-0.5)	395-650	460	

TABLE 1—Continued.

Powder	T_i , °C	T_0 , °C	T_m , °C	Weight, mg	$(dt/dt)^a$	δ (Calculated)	Energy, cal/g		Description
							Range	Mean	
Federal .22 Long Rifle	182 ± 3	197 ± 1	203 ± 2	0.09-0.32	0.20-0.39	0.71 (0.3-0.7)	230-670	475	double base; flat, nonperforated, circular disks, light gray-green
Federal .22 Long Rifle Test-Fire	187 ± 3	198 ± 1	206 ± 2	0.07-0.15	0.28-0.70	0.58 (0.4-0.7)	240-365	300	
Questioned Powder	193 ± 4	199 ± 2	208 ± 3	0.02-0.09	0.25-0.60	0.40 (0.3-0.6)	215-660	NA	
Hercules 2400® Lot 1	181 ± 3	197 ± 2	201 ± 3	0.09-0.24	0.07-0.31	0.80 (0.6-0.9)	290-665	290	double base; flat, cylindrical pellets, light coating
Hercules 2400® Lot 2	176 ± 5	194 ± 4	197 ± 3	0.16-0.40	0.08-0.19	0.86 (0.6-0.9)	240-515	310	
Hercules Unique®	173 ± 2	195 ± 2	197 ± 2	0.20-0.39	0.08-0.16	0.91 (0.8-0.9)	205-380	255	double base; flat, nonperforated, circular disks, medium gray
Hercules Unique® Test-Fire	174 ± 4	192 ± 4	199 ± 4	0.15-0.24	0.12-0.60	0.72 (0.5-0.9)	300-475	350	
Unknown Powder Test-Fire	180 ± 4	195 ± 2	204 ± 2	0.10-0.31	0.12-0.62	0.61 (0.5-0.9)	240-520	310	flat, perforated, circular disks, light gray
Winchester 230 P®	182 ± 4	198 ± 3	205 ± 3	0.09-0.35	0.07-0.44	0.70 (0.6-0.9)	230-410	310	double base; flat, nonperforated disks, roughly circular, heavy black coating
Winchester 450LS®	182 ± 3	196 ± 2	206 ± 2	0.08-0.22	0.22-0.45	0.58 (0.5-0.7)	235-450	420	
Winchester 540MS®	166 ± 6	193 ± 2	194 ± 2	0.26-0.43	0.04-0.14	0.96 (0.9-1.0)	210-345	260	

^a At 25°C/min heating rate.

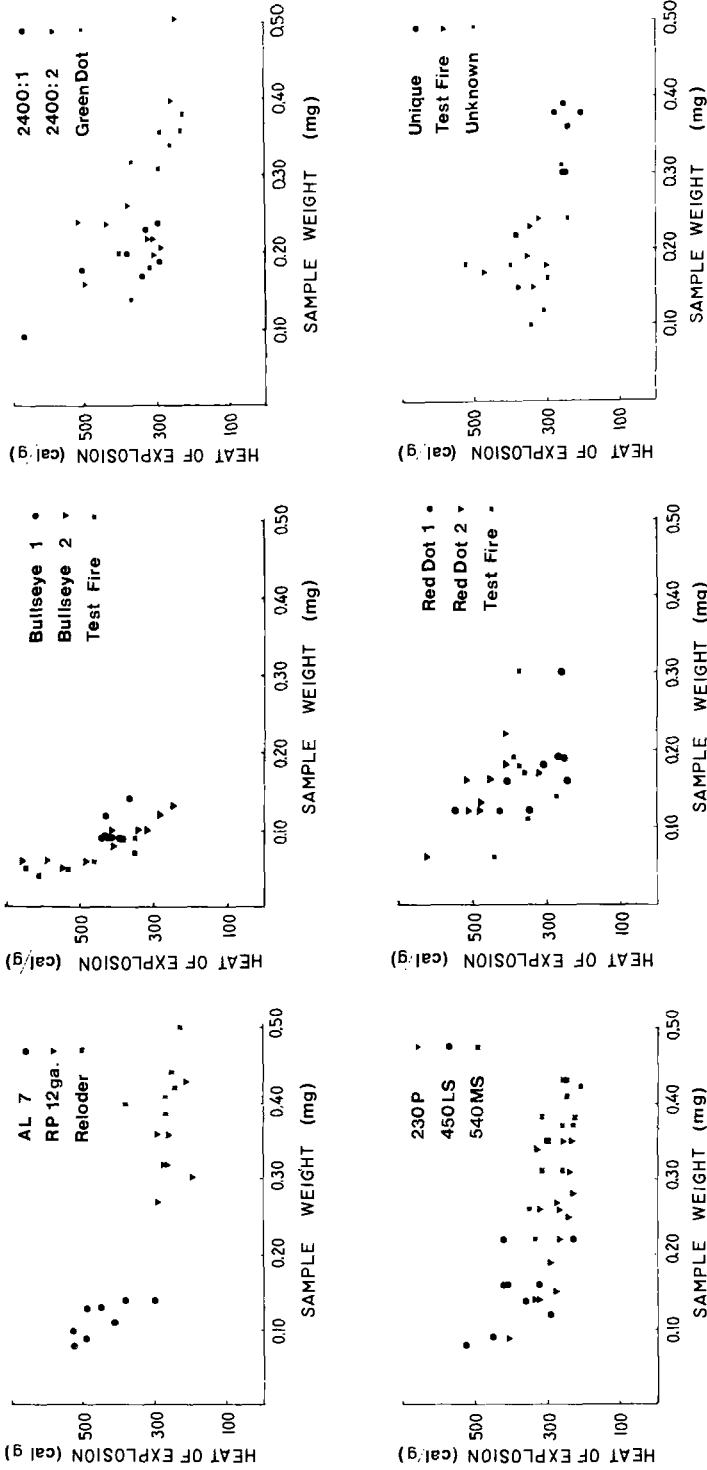


FIG. 4—Dependence of heat of explosion (energy released) on specimen weight.

FIG. 5—Dependence of heat of explosion on specimen weight: effects of lot variation and test-firing.

FIG. 6—Limited dependence of heat of explosion on specimen weight.

residue remaining after combustion at atmospheric pressure, typically 5 to 10% of sample weight, as compared with the virtually complete conversion to gases that occurs in normal firearms use.

Two lots of each of three reloading powders were sampled to examine the potential of DTA analysis in detecting lot-to-lot variations. The two lots of Hercules 2400® (from widely separate sources) exhibited significant differences in their temperature values, whereas their values for dt/t and δ were approximately the same for both. The two lots of Red Dot® were indistinguishable, as were two lots of Bullseye®, on the basis of both temperature and quantitative values.

One .38 Special caliber cartridge was prepared as an unknown using the recommended powder charge and was test-fired in a cleaned, .38 Special caliber revolver at a distance of 8 in. from cotton toweling, along with a series of similar cartridges loaded with Herco®, Red Dot®, Unique®, and Bullseye®. The unknown was subsequently successfully differentiated from Herco®, Unique®, and Bullseye® and was identified as Red Dot® on the basis of its qualitative (temperatures and reaction rates) and quantitative analytical results.

Summary and Conclusion

Quantitative differential thermal analysis (DTA) has demonstrated its usefulness in characterizing nitrocellulose firearms propellants obtained from reloading powders, factory ammunition, and test-fire targets. The commercial DTA system employed in this study provided sufficient sensitivity to accurately record the 10 to 100-mcal exothermic reactions encountered. Such state-of-the-art systems permit the determination of the thermal properties of single flakes of these powders, ranging in weight from 20 to 600 μg . These thermal properties include initiation and combustion temperatures, combustion rate, stabilizer and retardant effectiveness, and explosive energy.

Each powder presents considerable variation from flake to flake in all the observed thermal properties, making identification of single flakes nearly impossible. When a sufficient number (five to ten) of individual flakes are available, the powder can be characterized by the range of values measured for initiation temperature, combustion rate, and heat of explosion. Samples from several suspected sources can then be differentiated and compared with specimens from ammunition, clothing, or explosive devices. If the possible sources include powders which are of the same type, but which have been exposed to contamination or deterioration by unusual storage condition, the thermal properties observed will indicate the most likely source.

All thermal analysis results are somewhat instrument dependent. Therefore, interpretation of thermograms produced on other DTA systems must include allowances for variables such as the degree of sample containment and the heat capacities of the sample chamber. Quantitative DTA results are therefore best suited for comparative analyses between evidence materials and specimens from suspected sources, rather than as an absolute identification based on comparisons with published thermogram reference collections.

More extensive experimentation suggests itself in the areas of evolved gas analysis and the effects of prolonged or extreme storage conditions on the explosive properties of propellants. Further sampling and analysis should include rifle powders, ball-type powders, and other nitrocellulose-based materials of lower nitration percentages such as celluloid plastic, rayon, and lacquers.

Since DTA is able to reveal thermal and chemical properties that most other techniques do not, it has a wide variety of applications in evidence analysis [3]. As an

adjunct to physical and chemical means of determining the static properties of suspected explosives and propellants, DTA provides a unique means of examining dynamic thermal properties of these important evidential materials.

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