TECHNICAL NOTE

Elihu C. Ihms[1] and Dennis W. Brinkman,[1] Ph.D.

Thermogravimetric Analysis as a Polymer Identification Technique in Forensic Applications

ABSTRACT: This paper investigates the potential of thermogravimetric analysis (TGA) as a tool for determination of different species of polymers. Materials analyzed include polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC), polystyrene, polypropylene, nitriles, and nylon. Analyses showed excellent discriminating results even when samples were contaminated with silicates, organics, moisture, and char. The techniques developed were designed with a forensic-type analysis in mind, such as analysis of blast fragments and arson debris. Techniques were developed that gave satisfactory results even when sample sizes were less than five milligrams.

KEYWORDS: forensic science, thermogravimetric analysis, polymers, plastics

Plastics that are recovered from scenes of high destruction, such as fires or explosions, are often not in a state conducive to a chemical analysis (1). In the case of a blast scene, for example, the plastic casing of the timer can be shredded and/or melted. In some cases, the bomb casing is plastic and components of the explosive may remain. Other items of interest involved in a blast scene include identification of any camouflaging (such as a duffel bag) and nearby items. Discovery of the types of plastics and components present can establish a list of likely materials used by the bomber (2). In arson cases, the appearance of the plastic is often changed by the high temperatures present, and the residue displays significantly different properties from that of the original polymer (3). Additionally, these samples are often present with large amounts of carbon char included not only on the surface, but incorporated into the melted plastic.

Thus, qualitative identification of polymers by typical methods such as Fourier transform infrared spectroscopy (FTIR) or mass spectrometry (MS) can be especially difficult due to the inclusions of dirt, glass, char (4), and other foreign particles in samples taken from the scene. To minimize the error induced from these contaminants, and when separation is not possible, a method less affected by these interferents is needed.

TGA, or thermogravimetric analysis, has long been an accepted analysis method for polymers in industry (5,6). Its advantages are also easily seen from a forensic point of view. First, the required sample size is relatively small. Our study has shown that easily repeatable results can be obtained when sample sizes are no larger than five milligrams. Secondly, very little sample preparation is required, which translates to fast analysis times. TGA displays very low sensitivity to contaminants commonly found in forensic samples of this type and exhibits repeatable thermogravimetric data

even when the sample is highly degraded. If the given defining temperatures are distinct enough, it has been shown (7) that TGA can even characterize polymer mixtures. Many modern TGA instruments come with optional secondary analysis components, such as FTIR or mass spectrometers, to characterize the gaseous phase degradation products (8). These would provide even greater identification capabilities, although this paper will demonstrate that TGA by itself is a powerful tool.

The primary drawback of TGA is that it is destroys a portion (≤ 5 mg) of the collected evidence. Samples are reduced to a carbon char, with the eluted gases being either dissipated into the atmosphere or passed on to another instrument.

Methods

Materials

Emphasis was placed on common and easily obtainable polymer types and forms:

CPVC:	cream-colored 1/4 in. (0.635 cm) water pipe
PVC:	white $1\frac{1}{2}$ in. (3.8 cm) water pipe
Low-density Polyethylene (LDPE):	Nalgene™ 125 mL wash bottle (marked LDPE)
Nylon:	Nylon Rope, Lehigh Cat: ND650
Polypropylene:	Standard amber prescription vial (marked PP)
Polystyrene:	Aldrich (Milwaukee, Wisconsin), Cat: 18,243–5
Tygon™:	3/8 O.D. Tygon™ (formula R-3603)
Nitrile:	Fisher® nitrile gloves, Cat: 19-050-221C
Natural latex:	Pasteur pipette bulb. Fisher, Cat: 14-065B

[1] Department of Chemistry, Indiana Wesleyan University, 4201 South Washington, Marion, IN 46953.

Sample Preparation

Samples were cut from representative sources with a sharp scalpel in roughly rectangular forms. An attempt was made to obtain fragments weighing 7 mg or less. Nylon rope samples were cut longitudinally and coherent fibers were trimmed to a manageable length. Nitrile material was recovered from the laboratory gloves by cutting sections from the thickened wristband.

Degraded polypropylene samples were created by charring five sample squares to varying degrees in a propane flame.

Samples were placed into the center of the platinum analysis pan with tweezers, except in the case of the polystyrene spheres. These were simply poured onto the pan from a sheet of folded weighing paper.

Calibration

Calibration of the instrumentation can take two forms, explicit and implicit calibration. An internal standard can be generated by using a pure organic compound with a known decomposition temperature. Using several compounds having a range of decomposition temperatures, a function relating apparent values to true values can be generated. Because we were concerned with demonstrating repeatability in this paper, extensive calibration was not performed, other than what was needed to maintain precision. This was done by periodically running a triplet set of CPVC samples and comparing mean values with previous analysis values.

TGA Parameters

Analysis was performed on a DuPont™ 951 TGA using a 9900 interface unit. A Thermal Analyst™ 2200 (TA Instruments, New Castle, DE) microcomputer running TA Instruments software version 8.10B (2.3A) was used to collect and analyze data. A DuPont™ Gas Switching Accessory was used to control flow rates of ultra-high purity (UHP) nitrogen.

Samples were analyzed using the following protocol:

Nitrogen flow rate: 100 mL/min (UHP; 99.999% min)
Time constant: 1 s
50% suppression

Temperature program:

COMMAND	TEMP	TIME
1. Equilibrate	100°C	...
2. Ramp 20°C/min	800°C	35 min
3. Isothermal	800°C	3 min
Total: 38 min + equilibration time		

Data were analyzed using the General Analysis Utility, V 4.1 provided with the system. Thermogram plot parameters were as follows:

AXIS	VALUE	SCALE
X-axis:	Temperature (°C):	0–900°C
Y-axis:	Mass (%):	0–100%

First derivative thermogram plot parameters:

X-axis:	Temperature (°C): 0–900°C	
Y-axis:	Mass % derivative with respect to temperature	

Relative maxima in the first derivative plot were found with the "Peak Max" software utility and labeled with the temperature at that point.

Results and Discussion

Identification of Defining Temperatures

Each sample data file was processed using the labeling function of the General Analysis Utility software package. Peaks were generated by taking a derivative of raw mass loss data with respect to temperature, and plotting this derivative versus temperature. These peaks showed temperatures of maximal mass loss rates, and were used to determine defining temperatures (T_D). Local bounding areas around apparent peaks were set manually (see Fig. 1, which shows start/stop boundaries for two adjacent peaks) and the program's peak detection algorithm was applied. The points of relative maximum mass changes detected by the labeling program are considered "Defining Temperatures" or T_Ds. For most polymers, there is a single, well-defined point at which the majority of the sample mass is lost. There is also a general peak geometry that stays consistent for each type of polymer. In some cases, most notably that of CPVC, there is more than one peak. These are labeled with an additional subscript, such as T_{DA} or T_{DB}.

In the case of clear LDPE, a "shoulder" peak was at times apparent close to the base of the major T_D. In two out of the five sample sources, a definite point was observed, and a temperature value label was applied. These values are recorded in Table 1.

Differences in relative rates of mass loss are apparent upon observation of the first derivative graph, such as with polypropylene, in which the breakdown rate gradually accelerates and then precipitously drops (Fig. 1).

Multiple replicates of each polymer type were run, often on separate days and at different ambient temperatures. The maximum spread seen between the various T_D values was always less than 1.5% (Table 1).

Repeatability

The excellent precision of a carefully executed sample set can be seen in Fig. 2, which shows an overlay of four nitrile replicates. There is the potential for excellent repeatability when using this method. This is dependent on several factors:

1. Heating rate: It has been shown (7) that there is a definite shift to apparently higher decomposition temperatures as heating rates are increased. If heating rates are not consistent, this technique will not yield reliable results.

2. Pan placement: In most cases, it is not advisable to remove the platinum pan from the balance arm. In the 951 TGA unit, the pan basket is suspended by a small loop of platinum wire which rests in a groove milled around the end of the quartz balance arm. A minute shift in the placement of this arm, or the position of the loop in the groove, is sufficient to cause upwards of 5% deviation from the zeroed mass of the empty pan. For this reason, it is advisable to place the sample in the pan while it is still suspended. Failure to properly place the pan often leads to negative baselines and incorrect percentages of thermally stable binding/contaminating material.

3. Instrument zero: Most samples leave behind a significant amount of char. For example, amber polypropylene used in prescription drug vials leaves behind a significant amount of a tan-colored residue. In some cases, it is feasible to mechanically remove the char, such as when PVC is analyzed. It is often impossible to scrape the pan clean while retaining it on the balance arm. In these cases a "burnout" program that holds the pan at a high temperature for an extended amount of time
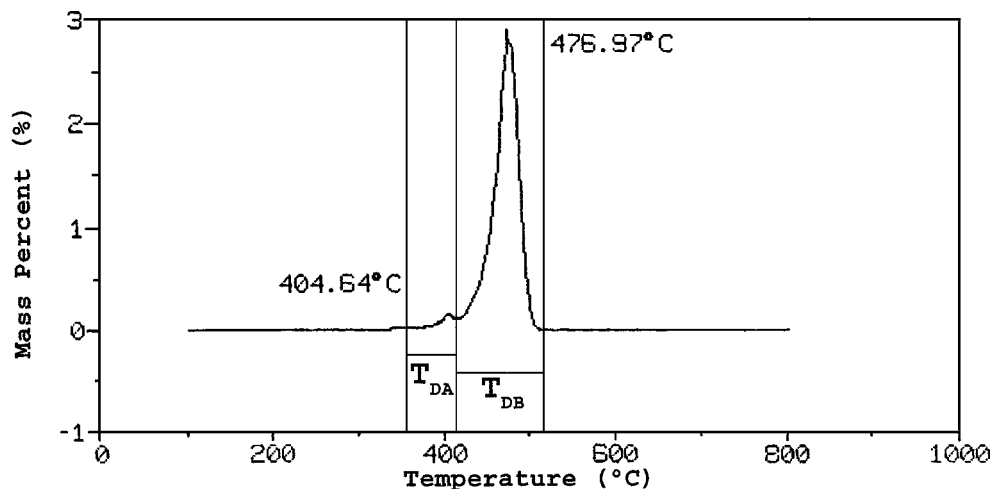
FIG. 1—*First derivative polypropylene thermogram with boundary lines. This thermogram shows the distinct peaks associated with first derivatives of mass loss. Additionally, boundary boxes are shown around peaks of interest, demonstrating the use of the "peak select" function of the TGA software.*

TABLE 1—*Defining temperatures for some selected polymers.*

Substance	T_{DA} °C		Substance	T_{DA} °C	T_{DB} °C
Polystyrene	449.3		**CPVC**	339.4	483.9
"	445.8		"	341.8	485.3
"	447.7		"	341.9	480.1
			"	344.5	494.4
Mean:	447.6		"	341.9	489.2
RSD (%):	0.39				
			Mean:	341.9	486.6
Nitrile	480.6		*RSD (%):*	0.53	1.12
"	485.9				
"	486.8		**LDPE**	N/A	491.3
"	485.4		"	439.1	502.0
			"	N/A	502.7
Mean:	484.7		"	N/A	492.6
RSD (%):	0.58		"	430.8	501.3
Latex	407.2		*Mean:*	435.0	497.98
"	404.2		*RSD (%):*	1.35	1.11
"	406.9				
"	406.1				
Mean:	406.1				
RSD (%):	0.33				
Polypropylene	477.0				
"	474.0				
"	477.7				
"	472.9				
"	478.4				
Mean:	476.0				
RSD (%):	0.51				

is utilized. Instrument zero is critical when the percent of thermally stable binder is to be determined, such as when mass percent of glass fiber reinforcement is being measured (7). This becomes unimportant when large amounts of thermally stable contaminates are already present.

4. Thermocouple placement: In the 951 TGA unit, a flexible thermocouple can be positioned at several points near the sample pan. The effects of moving this thermocouple during a string of replicates can be disastrous, as seen in Fig. 3. These shifted curves are the result of three different sample analyses, all with different thermocouple placements. An effort must be made to keep thermal variables to a minimum during replicates.

5. Purge flow rate: This value must be kept constant. Random errors incurred by pulses in this flow appear as sharp dips in the thermogram. If no purge gas is used at all, a buildup of evolved gases often condenses on the balance arm and pan, ruining reproducibility. If excessive purge rates are used, an overall "rough" appearance is imparted to the resulting graph. For the 951 unit, optimal purge rates can vary from 100 mL/min to 1 L/min, depending on the substance being analyzed. Experience has shown that soft, more flexible polymers, such as latex and nitriles, generate a large amount of a condensing gas, and higher purge rates must be used.

6. Mechanical placement: The TGA unit must be kept free from mechanical vibration, preferably mounted on a marble vibration-dampening slab. This is especially critical when sample sizes are minute.

As can be seen from the data in Table 1, which lists several experimental values for various polymers, sufficient resolution exists to make definite statements about the identity of all but the most degraded samples.

Qualitative Determination of Polymeric Identity

The methods developed for this paper were able to distinguish heavily charred (approximately 80% char by mass) samples smaller than 5 mg. Additionally, contaminants such as plant matter, sand, and moisture did little to mask the identification power of the defining temperatures of the polymers. It has also been shown that many polymers have distinct enough defining temperatures so as to make immediate identification relatively easy. This can be seen conclusively in Figs. 5 and 6.

Figure 4 shows three raw-data thermograms: CPVC, LDPE, and latex. Interestingly, the overall shape of the thermogram of natural latex looks like that of LDPE. Although definite differences in graph shapes and locations are present, a derivative graph must be used to unequivocally distinguish between them. This graph is useful, however, to show residual nonvolatile mass, such as the approximately 30% residual in the CPVC sample.
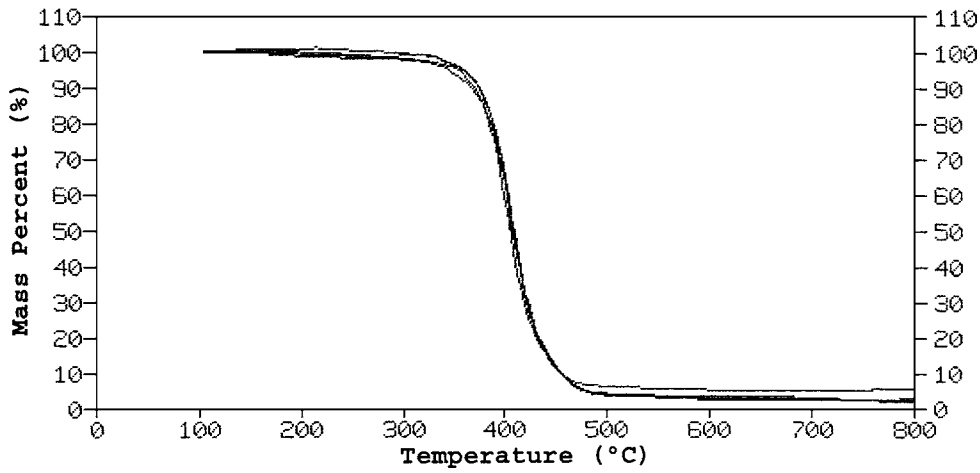
FIG. 2—*Nitrile sample reproducibility overlay. This overlay of four separate nitrile graphs displays the excellent reproducibility achievable with TGA analysis.*
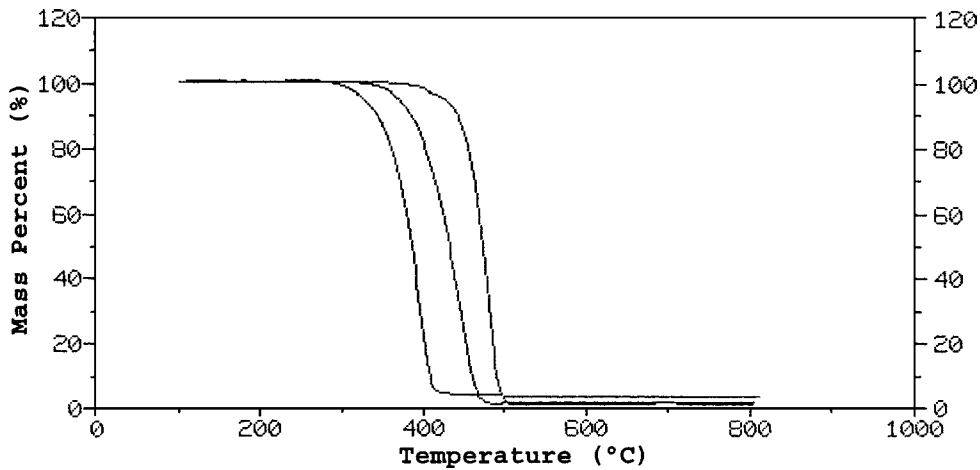

FIG. 3—*Error induced by thermocouple placement. This overlay of three separate latex sample thermograms shows the disastrous effects of a shift in thermocouple placement. As the thermocouple is moved away from the sample location, and closer to the oven wall, perceived T_Ds are drastically increased.*
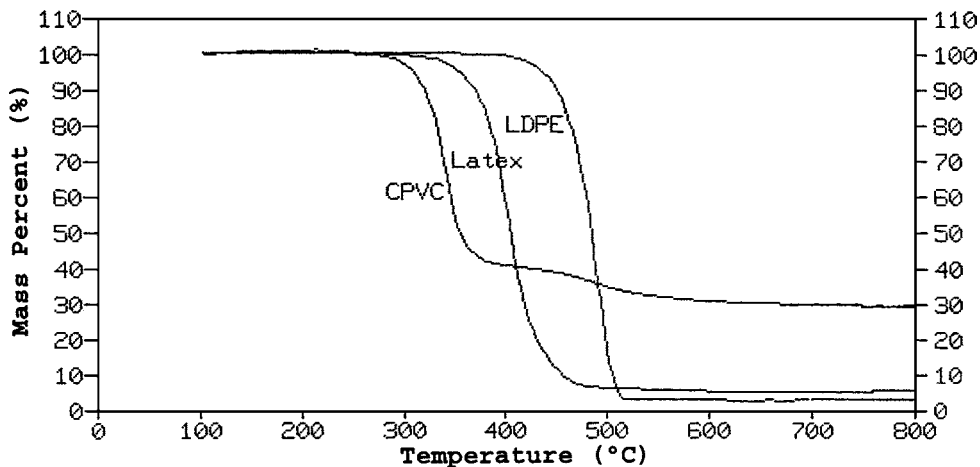

FIG. 4—*Overlaid thermograms of CPVC, LDPE, and latex. This overlay of three thermograms of different polymers displays the obvious qualitative difference in thermogram curve shape. It also shows the relatively high percentage of stable filler/binder in our CPVC sample.*
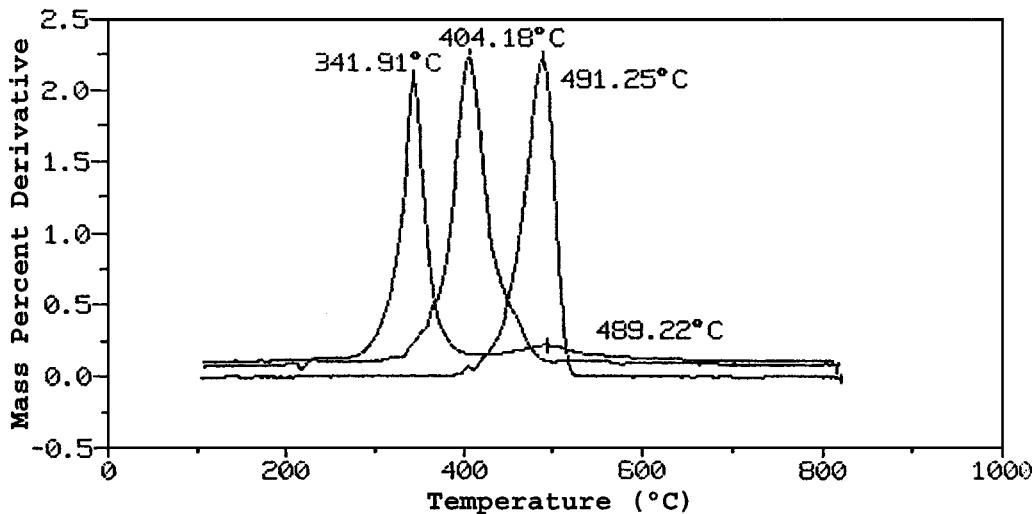
FIG. 5—*First dervative graph of CPVC, and latex. This overlay quantitatively shows the difference available in the first derivative graph of thermo-gravimetric data. The three separate compound T_Ds are immediately discernable.*
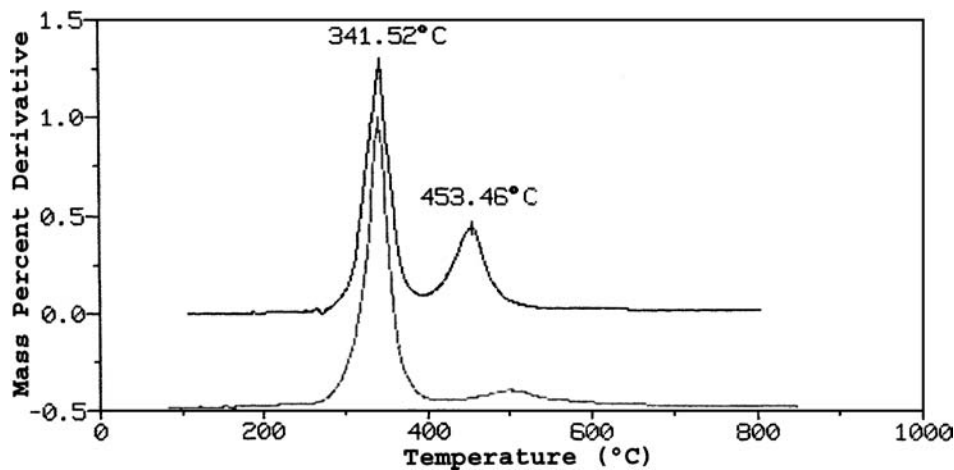

FIG. 6—*First derivative graph of CPVC samples, with and without hemp rope present. This thermogram shows the effect of a simulated plant matter (in this case, modeled by hemp rope) on the thermogram of CPVC. The hemp breakdown temperature is the lesser T_D at 453°C. The downshifted gray plot is a standard non-contaminated sample of CPVC. Notice the complete masking of the second peak by the hemp peak.*

Figure 5 shows the derivative of the previous thermogravimetric data with respect to temperature. This reduces the data to their pure form: the defining temperatures. We can now say numerically that there is a definite difference between the samples, and these standards may now be used to identify an unknown, no matter how contaminated or thermally degraded. Note that any refractory material left over has no effect on the shape or position of the first derivative graph.

Influence of Thermally Unstable Materials

The effect of thermally unstable materials present in conjunction with the polymer can be seen in extra mass losses in the thermogram that are not due to the polymer in question. This can be due to moisture (which can be negated by selecting a high initial equilibration temperature), or the presence of bioorganic substances such as grass or plant material. During the heating process, these components will be reduced to a carbon char and their inorganic constituents. Problems can occur when the decomposition temperatures for these contaminants intrude into the temperature ranges associated with the desired polymer. In these cases, a judgment must

be made as to the major contributor to the mass loss: whether it is a contaminant or a defining temperature of the plastic itself. As an example of this effect, Fig. 6 shows what happens when a section of hemp rope (simulating plant material) is analyzed with CPVC. In this case, the hemp rope degrades *after* the large T_{DA} (341.5°C) of the CPVC, and completely masks its T_{DB} (486.5°C).

Influence of Previously Degraded Sample Material

Defining temperatures are where the polymer itself begins to quickly break down. The recovered polymer may exist already in a partially degraded state, in which case the degradant itself will follow a predictable mass loss curve. As stated before, the polymer may experience several stable intermediate states in which the mass stays relatively stable for a specific temperature range.

This is one of the main reasons why thermogravimetric analysis is so well suited for thermally degraded samples. Since the analysis process requires the breakdown of the sample as a function of temperature, the unchanged portion of the sample will degrade until the entire sample is homogenous, at which point the entire sample will deteriorate equally. This does assume, however, that

the material does not form quasi-stable intermediates in response to rapid heating (which might be found in a bomb casing fragment). Should portions of the material become completely charred, it will appear just as a baseline value along with the rest of the background material, such as sand, and cause no interference.

Influence of Thermally Stable Materials

Thermally stable contaminants may be thought of as baseline material, i.e., a percentage of the sample that is not degraded. The effect on a thermogram is that of a mass percentage remaining that is higher than 0% at the end of the run. Silicates like sand or glass are immediately obvious, but carbon and most inorganic components will remain until the sample cell is flushed with an oxidizing gas. For the most part, background materials may be ignored, except for the possibility of a matrix effect. In some cases in industry, polymer types can be differentiated by stable binder/filler content. This may be of limited use in the forensic scene, since samples often are contaminated with materials of similar properties.

This showcases the third major advantage to using TGA as a forensic method. Most of the contaminants that are present in a sample from a blast scene would be material from the local environment (such as sand or grit) blasted into the softened plastic fragment. These have little or no effect on the breakdown chemistry of the polymer, but would definitely cause problems with a traditional analysis method like FTIR.

A possibility exists that areas of contamination may act as a catalyst site for localized deterioration, such as "hot spots" present on the surface of sand particles, but this has not been observed in our testing.

Conclusion

When the repeatability and precision of these analysis techniques are coupled with the ease of use and the minimal sample preparation involved, it becomes clear that TGA is a powerful analysis tool for samples that would otherwise be nearly unidentifiable.

Further investigation into the breakdown chemistry of the polymers, especially the stable intermediates formed at high temperatures, will do much to make this analysis protocol an even more effective tool for the well-equipped forensic laboratory.

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Additional information and reprint requests:
Dennis W. Brinkman, Ph.D.
Department of Chemistry
Indiana Wesleyan University
4201 South Washington Street
Marion, IN 46953