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THE DETECTION OF IGNITION TEMPERATURES OF VARIOUS MATERIALS BY PHOTOTHERMAL ANALYSIS

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ABSTRACT

The ignition temperatures of various common materials were detected by means of a photothermal analysis apparatus. The sample is heated in a tube furnace which is programmed at a linear heating rate; a photomultiplier tube located at the end of the furnace tube is used to detect the ignition process. This technique is potentially useful and is most advantageous when used to supplement DTA or TG data. The instrumental factors which influence the ignition temperature, such as heating rate, furnace atmosphere, and so on, were investigated. Factors such as the sample surface area, mass, density, and others can affect the reproducibility of the curves even if the instrumental factors are held constant.

INTRODUCTION

Thermally induced emission of visible radiation has been observed in association with combustion processes for many centuries. However, measurements relating light emission with the programmed temperature of a sample have only recently been utilized in thermal analysis. One such technique for obtaining this type of information is that of thermoluminescence (TL) which has been used for many years in geological and archeological dating and in dosimetry[1]. This technique can, for example, determine the mineralogical composition of limestones or be used to date archeological artifacts such as pottery sherds, and so on. More recently, David[2] described a modified TL technique which he named *photothermal analysis* (PTA). Not only could the light emission of a sample be detected and recorded but the differential thermal analysis (DTA) curve as well. He applied this technique to various inorganic materials and to polymers.

To detect combustion processes and smoke evolution, Loehr and Levy[3] described an apparatus in which the smoke released from a sample, contained in a thermobalance, could be detected photometrically. Thus, a recording of the mass-loss of the sample and the evolution of smoke could be detected simultaneously. Mickelson[4] photographically observed the combustion of polymers treated with various flame retardants.

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The ignition temperatures of various materials have been determined for many years by indirect thermal analysis methods. In DTA, for example, ignition of the sample is indicated by the appearance of a large, exothermic peak. Using the technique of thermogravimetry (TG), a very rapid mass-loss is generally indicative of the ignition of the sample. We wish to describe here an apparatus in which the ignition temperature of a sample is detected photometrically, using the techniques of photothermal analysis. The sample is heated in a furnace which is programmed at a linear heating rate; a photomultiplier tube connected at the end of the furnace is used to detect the ignition process. The term "ignition temperature" used here is the temperature at which the first light emission, due to the combustion of the sample, is detected. There are many variables which have an influence on the photometric curve so obtained and several of these are elucidated using various commonly available materials.

EXPERIMENTAL PART

Materials

The wood splints, tobacco, matches, cotton cloth samples, and tissue paper used in this study are materials which are commonly found in the laboratory and were used with no purification or analysis. These substances were of unknown composition and were used only to demonstrate the potential application of the technique. Whatman No. 1 filter paper, used in the heating rate study, was thought to be relatively reproducible in composition. The ammonium dichromate used was Baker Analyzed reagent quality while the gunpowder employed was duPont SR-7625 smokeless powder.

Apparatus

The apparatus employed is illustrated schematically in Fig. 1.

The sample is placed on a flat 8 mm by 12 mm nickel sample pan which is

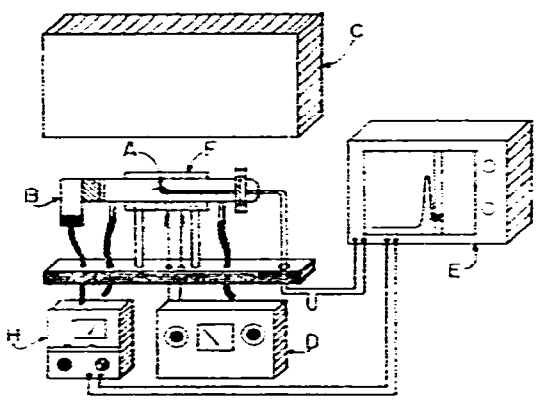

Fig. 1. Apparatus employed for ignition temperature detection. A, sample holder and thermocouple; B, photomultiplier tube and housing; C, enclosure; D, temperature programmer; E, x–y recorder; F, furnace; H, power supply for photomultiplier.

welded directly to a Chromel-Alumel thermocouple junction. The thermocouple is held in place by means of a 5 mm in diameter two-holed ceramic tube which is sealed into a Pyrex end-tube that can be attached to the furnace by an O-ring joint and clamp. The furnace consists of a 25 mm by 250 mm Vycor tube with a Pyrex window sealed at one end and the O-ring joint on the other end. Small inlet and outlet tubes at each end of the furnace tube permit the control of the atmosphere surrounding the sample. The furnace heater element consists of a 17.4 ohm Nichrome wire heater wound around the Vycor tube and covered with asbestos insulation. The end of the furnace containing the Pyrex window is fitted into a metal housing containing a 1P28 photomultiplier tube. The complete furnace–photomultiplier combination is mounted on a metal base. All wire leads are routed through small holes in the base and emerge from under the instrument. Tygon inlet and outlet hoses attached to the furnace are also routed through the bottom of the base. This entire system is then covered with a wooden box which is painted black on the inside surfaces.

The photomultiplier tube is connected to a control unit manufactured by the American Instrument Company. The output signal from this unit is fed into the y-axis of a Hewlett–Packard x-y recorder. The thermocouple lead, with a 0 °C junction in series with it, is attached to the x-axis input. The heating rate of the furnace is controlled by a motor driven variable transformer type temperature programmer.

Operating procedure

The operating procedure used to determine the ignition temperature depends to a large extent on the nature of the sample. Typically, 4 to 5 mg of sample is employed which is placed in contact with the bottom of the sample pan. For samples such as paper or powdered materials, this type of sample packing presents no problem. However, large, voluminous samples such as tobacco must be compacted as close to the bottom of the sample pan as possible to get the best results. Sample mass, surface area, and placement in the container are held as constant as possible during repetitive runs.

Once the sample is placed on the pan, it is introduced into the furnace and sealed with the O-ring joint and clamp. The furnace is then flushed for approximately five minutes with the appropriate gas and the flow rate adjusted to the proper value. The cover is placed over the apparatus and the photomultiplier tube control unit is activated. The voltage on the tube is 800 volts and the sensitivity control set at 100%. After adjusting the heating rate to the desired value (from 11 to 100 °C/min^{-1}), the heating cycle is initiated and the recorder activated to obtain the PTA curve.

There is usually little difficulty in determining the ignition temperature since most samples give rapid responses at ignition. A minimum of four runs was made for each substance, with all parameters held constant, and the ignition temperature is taken as an average of the runs. The error in the temperature is taken as the difference between the average ignition temperature and the upper and lower temperature extremes. This degree of error depends upon the physical properties of the sample and therefore varies depending on the substance studied.

RESULTS AND DISCUSSION

The primary interest of this investigation was to determine the ignition temperatures of various common materials under a given set of experimental conditions. It is recognized, of course, that the combustion of a substance, such as filter paper and other materials, is an exceedingly complex process. Only the gross features of this process are detected here, i.e., the approximate temperatures at which combustion begins.

To determine the effect of heating rate on the ignition temperature, samples were run at several different heating rates with all other parameters such as sample mass, surface area, placement on the pan, and furnace atmosphere held reasonably constant. The sample chosen for this part of the study was filter paper which was used because it is relatively homogeneous, easy to reproduce its surface area, and gives good reproducibility of the ignition temperatures.

TABLE 1

IGNITION TEMPERATURES FOR FILTER PAPER AT VARIOUS HEATING RATES

Air atmosphere at a 11.5 ml min^{-1} flow rate; sample mass of 4.5 mg.

Heating rate (°C min^{-1})	*Ignition temperature (°C)*
11	none
22	350 ±8
29	355 ±8
55	367 ±8
90	377 ±8
100	383 ±8

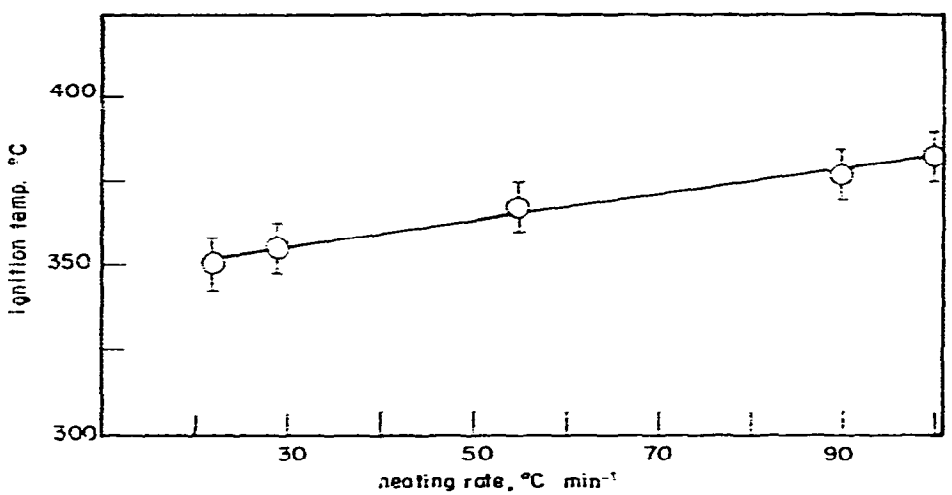

Fig. 2. Relationship between ignition temperature and heating rate for filter paper in an air atmosphere.

The effect of heating rate on the ignition temperatures is given in Table 1. As the heating rate is increased, the ignition temperature also increased. This relationship is approximately linear, as shown in Fig. 2. However, this does not imply that this relationship is true for all substances. The heating rate effect should be determined for each individual material which is to be studied. Also, there seems to be a lower heating rate limit below which the sample chars without ignition. For filter paper, this lower limit was somewhere between 11 and 22 °C min^{-1}. For other materials, this lower limit may be either at a higher or lower heating rate. For wood samples there was no ignition detected at a heating rate of 29 °C min^{-1} and an ignition response of only 50% of the time at 55 °C min^{-1}. In general, all samples ignited at heating rates of 100 °C min^{-1} or higher.

The ignition temperatures of other common materials are summarized in Table 2. Most of the materials studied, such as is illustrated by the filter paper, gave

TABLE 2

IGNITION TEMPERATURES OF COMMON MATERIALS AT 100 °C min^{-1} IN AIR

Material	*Ignition temperature* (°C)
Filter paper	367 ±8
Cotton cloth	346 ±4
Paper match head	239 ±3
Poly (2-hydroxy-3-methylbenzoic acid)	210 ±15
Cigarette tobacco	439 ±12
Pipe tobacco	432 ±10
Smokeless gunpowder	151 ±2; 204 ±2[a]
Wood splint	468 ±10

[a] See text for explanation.

a photometric curve as shown in Fig. 3. The curve was essentially flat until the ignition temperature was reached; at this point, a large output response of the photomultiplier tube was observed. Some materials, such as ammonium dichromate, ignited at short intervals over a wide temperature range, as shown in Fig. 4. Individual crystals appeared to ignite and were detected by the photomultiplier tube and recorded as a series of rapid pulses. Another material with an unusual photometric curve is smokeless gunpowder. About one-half of the runs gave a small photomultiplier response at 151 ±2 °C, then a larger response at 204 ±2 °C. The remainder of the runs gave only the response at the higher temperature.

Two effects were noted during the operation of the instrument which appear to limit its usefulness. If ignition begins on the side of the sample opposite the photomultiplier tube, the pan rapidly heats up before a response is detected and the ignition temperature will be too high. This is observed as a sudden jump of the recorder pen in the x-direction followed by the photomultiplier response. A second limitation is the background emission of the furnace tube; at temperatures above 500 °C, the emission from the furnace tube is so large that the sample emission cannot be detected.

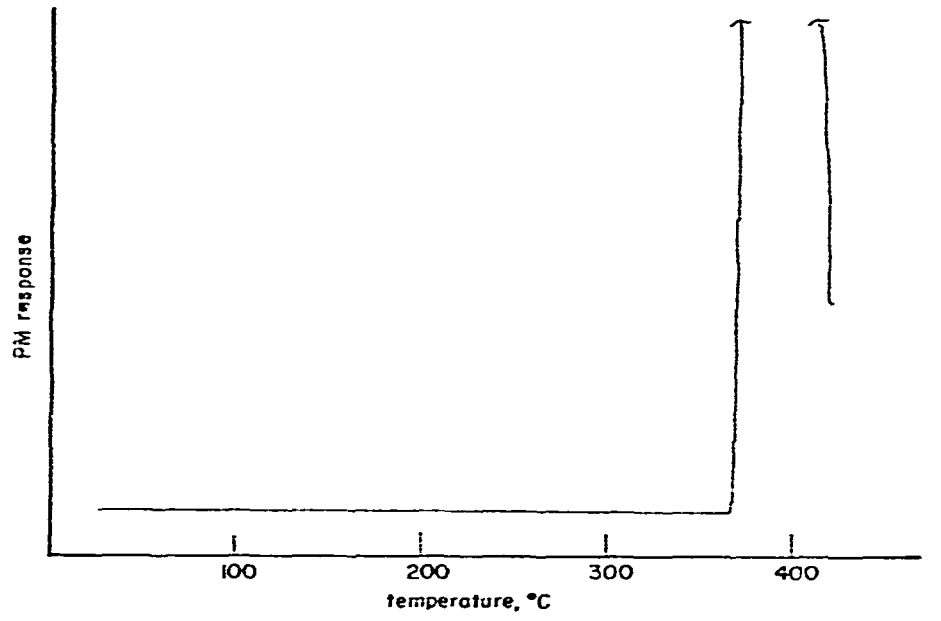

Fig. 3. Photometric curve for the ignition of filter paper in air at a heating rate of 55 °C min^{-1}.

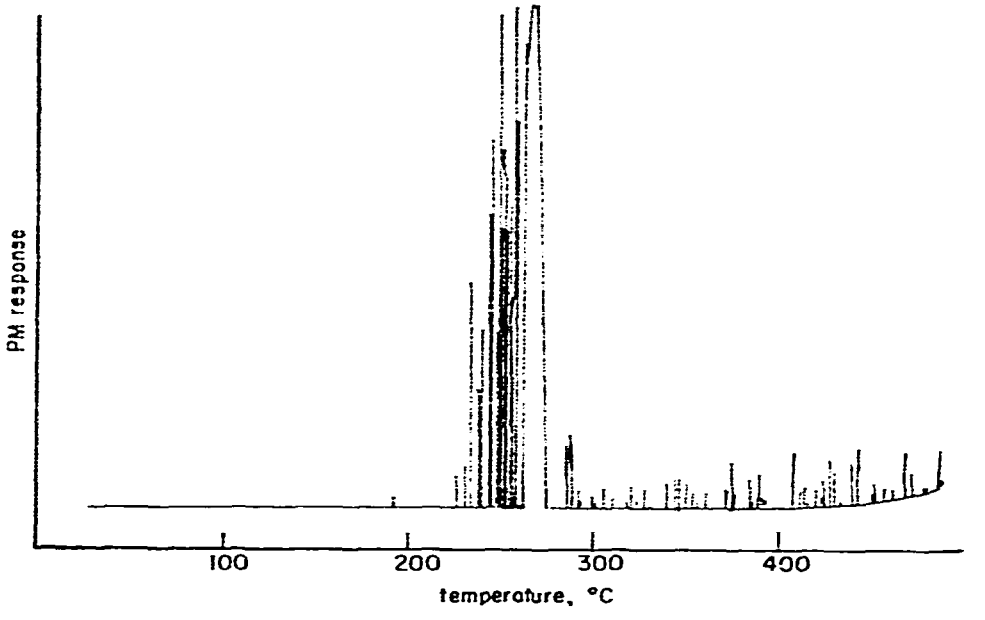

Fig. 4. Photometric curve for the decomposition of ammonium dichromate at 55 °C min^{-1} in air.

CONCLUSIONS

The technique of photothermal analysis is a potentially useful, although somewhat limited tool which has numerous applications in thermal analysis. The nature of the information gained through this technique is such that it is most advantageous

when used in conjunction with another thermal technique, such as DTA or TG. The simplicity of the procedure makes it adaptable to existing thermoanalytical instrumentation as a complementary technique with only minor instrument modification in most cases. However, as this study has shown, some caution should be exercised in the interpretation of the PTA curves since the instrumental parameters and the physical state of the sample influence the curve which is generated.

The major instrumental factor which affects the ignition temperature is the heating rate. Generally, as the heating rate increases, the ignition temperature increases according to an approximately linear relationship. Also, some materials were observed to char without ignition if the heating rate was too slow. Therefore, a fast heating rate, usually greater than 50 °C min^{-1}, is recommended for most studies.

A second instrumental factor, the furnace atmosphere, was observed to exert a much smaller effect on the ignition than the heating rate. The ignition temperature was always lower in pure oxygen than in air, as was expected. However, this effect never amounted to more than 10 °C for any of the materials studied.

The reproducibility of the curves seems to be primarily dependent on the physical characteristics of the sample. Factors such as sample surface area, sample mass, homogeniety of the sample, sample density, and the placement of the sample on the pan can affect the reproducibility of the curve even if the instrumental factors are held constant. Although not all of these factors was investigated individually, general trends were observed for the materials used. Generally, the higher the density of the sample, the higher the ignition temperature. Also, the greater the surface area exposed, the lower the ignition temperature. The sample mass seemed to have little or no effect on the ignition temperature and the effect of inhomogeniety in the sample could not be determined. Since all of these factors, and possibly others which were not considered, are different for different materials, multiple determinations of the ignition temperature curves must be made so that a statistical average can be taken. In view of the great number of variables, the reproducibility of the ignition temperatures to within 10 °C in most cases is rather surprising.

ACKNOWLEDGEMENT

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