Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THE THERMAL ANALYSIS–HYDROGEN FLAME IONIZATION DETECTOR SYSTEM FOR CHARACTERIZING ORGANIC MATERIALS*

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(Received February 26th, 1970)

ABSTRACT

The combination technique of thermal analysis–flame ionization detection (TAFID) offers attractive new possibilities for the precise measurement of the volatilization patterns of a wide variety of organic materials. Advantages over other methods are due chiefly to the sensitivity, specificity, and small sample requirement of the flame detector. Essential features of apparatus design are a close coupling of the detector to the sample furnace and provision for operating the detector at high temperatures in order to avoid condensation and thus allow quantitative measurements. Advances that have been made in instrumentation of the system provide speed and convenience.

Recent improvements in techniques and apparatus will be discussed. The wide applicability of this approach to thermal analysis will be illustrated by a number of methods developed for specific purposes, including the characterization of various polymers, oils, bitumens, rubber compositions, and other organic materials.

INTRODUCTION

During the past few years an evolved gas analysis technique employing the hydrogen flame ionization detector (FID) has been developed into a highly effective system for characterizing organic materials. Such a combined thermal analysis–flame ionization detector (TAFID) system has been employed to measure the thermal stability and trace volatiles content of polymers[1,2], the volatility of oils and bitumens, and the vapor pressure of organic compounds[3]. Many other applications have been explored and appear promising[4].

The advantages of the TAFID system are due chiefly to a number of favorable characteristics of the flame detector. Its high sensitivity and wide range of linear response, together with its specificity and uniformity of response to organic carbon, make it uniquely well suited for the quantitative analysis of organic materials.

In order to utilize the flame detector in a thermal-analysis system that is sensitive,

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*Presented at the Symposium on Recent Advances in Thermal Analysis, American Chemical Society Meeting, Houston, Texas, U. S. A., February 23–27, 1970.

quantitative, and widely applicable, it was necessary to overcome a number of problems of apparatus design and technique. It is the purpose of this paper to review the requirements of a well-designed TAFID system, and to describe some improvements that have been made recently. Also a discussion is given of performance characteristic in conjunction with use of the system for various applications.

APPARATUS REQUIREMENTS

The basic system, shown schematically in Fig. 1, consists of a small sample furnace joined to a high-temperature flame ionization detector. Also included is a gas-flow scheme to supply carrier gas (usually nitrogen), hydrogen and air for the flame detector, air for burning out residues in the furnace and air for rapidly cooling the furnace. The carrier gases and the gases for the flame detector are purified by passage through Molecular Sieve 13X. Auxiliary components are: a temperature programmer, a suitable amplifier for the detector, and a two-channel 1-mV recorder for monitoring both detector signal and sample temperature as indicated by the thermocouple. A detailed description of the system used in our studies has been given previously[2,3]; therefore, only a general discussion of apparatus features will be given here.

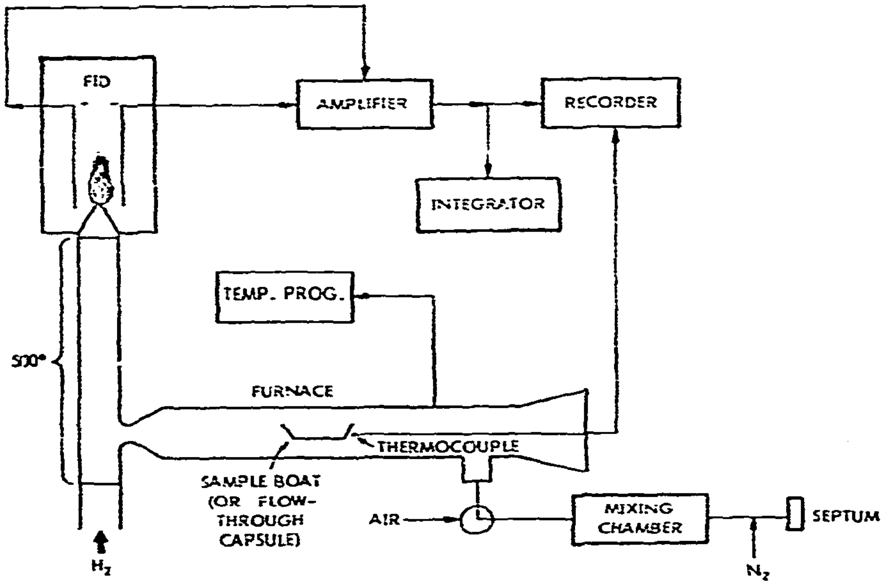

Fig. 1. Schematic diagram.

The sample furnace and FID jet are constructed of Vycor tubing as a single unit. The unitized construction and the high temperature of the FID, normally 500 °C, are essential features for preventing condensation losses, thus permitting complete recovery of volatiles by the detector. The furnace is heated with resistance wire, either by manual control of the voltage applied or by the temperature programmer. The flame jet also may be heated by resistance wire, as reported previously[2], or it may be heated by means of a stainless-steel block, as described by Stapp and Carle[5]; the latter design is simpler and more rugged. In constructing the high-temperature flame detector, special precautions must be taken to avoid loss of signal.

Provision is made for injecting standard gas samples from a syringe, via a septum inlet, for convenient calibration of the detector response. A mixing chamber in the nitrogen line to the furnace dilutes the gas standard so that it is more amenable to quantitative peak area measurement. *n*-Butane is generally used as the standard gas.

The sample boat is of aluminum, platinum or gold; it is held in a stainless steel wire frame attached to a sheathed thermocouple. In a recent improvement of this probe, made to permit rapid isothermal tests, it is constructed so that the supporting rod can slide through the joint at the inlet of the furnace. In this way the sample can be held at the cool inlet while the baseline is established, and then injected at the desired temperature. A flow-through type of probe is used for vapor pressure measurements, as well as for other special applications in which good gas-sample contact is especially desired. This probe consists of a small stainless steel capsule (0.1-ml capacity) through which any desired fraction of the total carrier gas can be directed. Details of this probe and of the necessary carrier gas flow controls have been described previously[3].

All of the analysis discussed in this report were made under the following conditions: (*1*) nitrogen carrier gas: 30 ml/min; (*2*) hydrogen to the FID: 25 ml/min; (*3*) air to the FID: 800 ml/min; (*4*) FID temperature: generally 500°C.

The FID (modified Varian–Aerograph) was normally employed with an amplifier sensitivity corresponding to 3×10^{-10} Amp. = full scale on the 1-mV recorder. The signal was attenuated as necessary to keep the tracing on scale.

PERFORMANCE OF THE SYSTEM

Important performance features and analytical capabilities of the system are discussed below and these are illustrated with a number of specific applications that have been developed. Included in the discussion are several interesting new applications.

Sensitivity

The lower limit of detection of the flame ionization detector is of the order of 1×10^{-4} micrograms of carbon per minute. However, as found in previous work on the thermal stability of polymers[2], it is hardly feasible to utilize this high sensitivity because of the heating blank obtained even with a well cleaned system (burnout with air at 550°C). In a temperature-programmed test from room temperature to 500°C with an empty pan the base line gradually rose to a final FID signal corresponding to 0.01 µg/min, equivalent to 0.001%/min with a 1-mg sample. This sensitivity is about 100 times greater than that ordinarily obtained by thermogravimetric analysis. The high sensitivity of the detector makes it possible to obtain meaningful thermal analysis curves with as little as a few micrograms of material. Vapor pressure measurements can be made below the level of 1 mtorr, as described previously[3].

The sensitivity of the system is illustrated by the example of Fig. 2, in which a moderately large peak was obtained for 0.3% of an additive in polypropylene, using only 0.5 mg of sample.

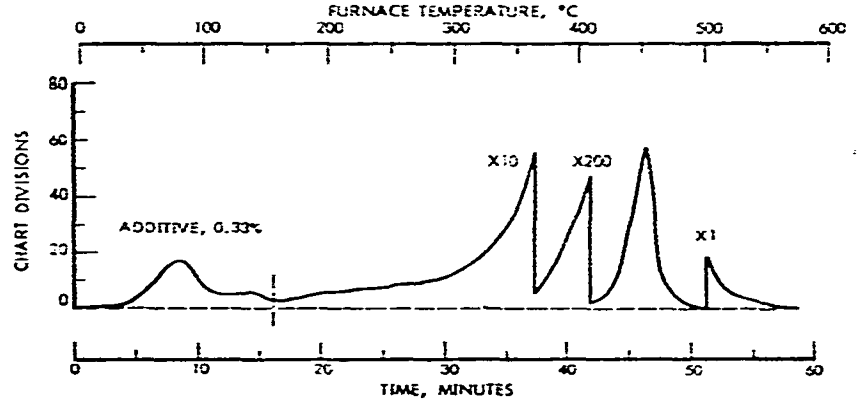

Fig. 2. Additive in polypropylene (0.5 mg of polymer film).

Quantitative analysis

Yield-temperature data are determined with virtually no holdup due to condensation of volatiles. As already mentioned, this is made possible by the high-temperature capability of the FID, its unitized construction with the Vycor furnace and the air-burnout feature which keeps the system clean. Using a detector temperature of 500 °C, the recovery of pyrolysis products from various hydrocarbon polymers was found to be 100 ±3%; at FID temperatures of 200–400 °C substantial amounts of condensation were found to occur[1,2]. Any residual material remaining after a test can be conveniently weighed on a microbalance.

The detector designed for the system responds linearly to volatiles-evolution rates corresponding to as much as 0.5 mg of carbon/min. The yields of organic carbon, as indicated by thermal volatilization curves, can be determined by applying a single calibration factor, for example that for butane. Yields may be expressed as rates of evolution (signal height) or integrated amounts (peaks areas). If it is desired to convert from yields of carbon to amount of a particular substance it is necessary to apply an appropriate calibration factor for that substance. Such factors generally can be calculated to a good approximation relative to that for butane, from response data in the literature, for example the data of Sternberg *et al.*[6]. For greater accuracy the response for a particular material can be determined simply by vaporizing a weighed amount in the system to determine peak area (or integrator counts) per mg. The problem of calibration factors is simplified by the fact that all hydrocarbons and hydrocarbon groups give about the same response per carbon atom. Carbon singly bonded to oxygen gives about half the normal response, and if doubly bonded to oxygen gives no response.

Resolution

Higher resolution is possible than in TGA because of the smaller samples that can be used. The system is capable of giving, in effect, approximately a one-plate distillation. The advantage of small sample size is illustrated by the curve in Fig. 3 for 25 μg of 900 mole weight polystyrene deposited in the sample pan from a benzene solution. Several peaks are observed corresponding to the solvent, monomer, dimer, trimer, *etc.*, present in the sample. In a similar test with 0.5 mg of sample only the first two peaks were observed, and even less resolution would be expected with the still larger quantities normally used in TGA.

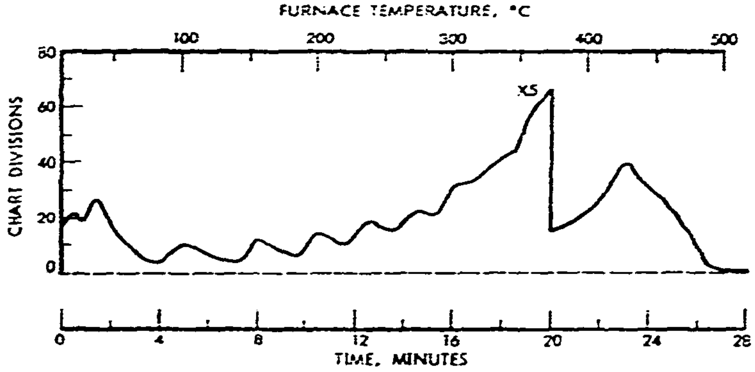

Fig. 3. Curve for polystyrene (900 mol. wt., 25 μg sample).

Possible use of the system for analyzing polymer formulations is illustrated by the example in Fig. 4, in which almost a complete separation of four components was achieved.

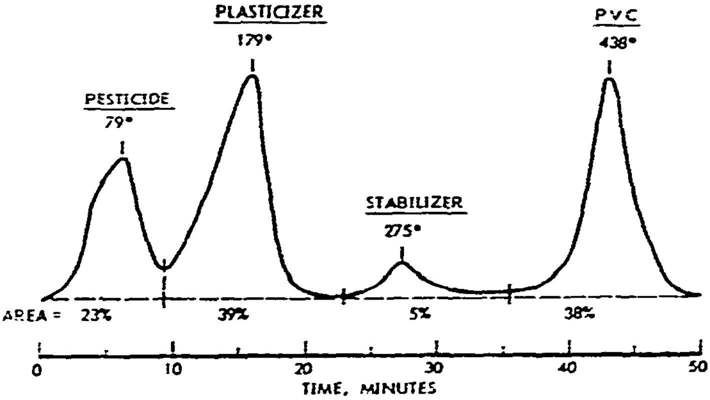

Fig. 4. Curve for a polyvinyl chloride formulation (0.4 mg sample, 10 °C/min).

In the case of oils, asphalts, process streams, and other organic materials, thin films of material can be distilled in the sample pan to obtain useful data on relative volatility[3,4]. The thermal analysis curves permit a precise comparison of trace quantities of light ends and heavy ends in various products.

Rapid isothermal technique

The retractable type of sample probe makes the system well-suited for isothermal operation. In this technique the sample is initially located at the cool inlet of the furnace while the detector flame is lighted and the baseline adjusted; the sample is then pushed into the furnace at the desired temperature. This mode of operation is advantageous for the rapid comparative testing of various materials, such as for quality control purposes. A further advantage is that trace volatiles are generated more rapidly and therefore can be detected more sensitively and precisely.

An example of this type of test is shown in Fig. 5, which is the curve obtained for 5 mg of a rubber composition. In this analysis a weighed sample (microbalance) is thrust into the furnace at 300 °C to volatilize the oil extender rapidly, following which the sample is quickly heated to decompose the rubber. The peak areas are evaluated by applying suitable calibration factors. Residual carbon-black filler is determined by making a final weighing. In addition to speed of analysis, a high degree of precision is made possible by using the detector signal to indicate when a pre-selected end point has been attained in each of the heating stages.

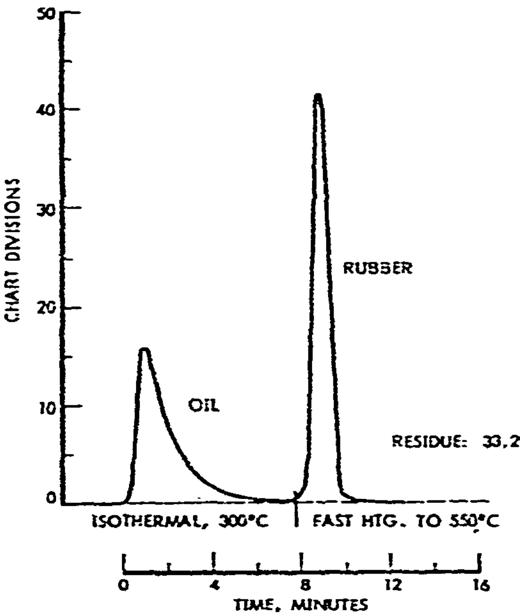

Fig. 5. Curve for a rubber composition (5 mg sample).

Specificity

The flame detector is specific for reduced carbon and does not respond to water, carbon oxides, nitrogen oxides, and other substances normally associated with inorganic materials. Accordingly the system is useful for obtaining thermal analysis curves specifically for the organic portion of compositions that are only partially organic or contain water.

Although water itself does not respond in the FID, it does affect the response factor of organic carbon, as demonstrated by Hill and Newell[7]. Using argon as the carrier, they observed a gradual decrease in response with increasing water vapor concentration up to 10%, at which point the response had been reduced by about 30%, and appeared to be levelling off. In substantial agreement with these results, our system gave a 25% lower butane response when 30% water vapor was introduced into the nitrogen carrier gas. These results indicate that water-containing samples can be analyzed in the TAFID system with only a moderate decrease in sensitivity. We have found that the reduced carbon response can be taken care of readily by calibration.

Non-responsiveness of the detector to water is an important advantage for a number of applications. In one example, reported earlier[2], asphalt–water emulsions were analyzed to obtain volatility curves for the organic portion only. By this means it was possible to determine that a particular emulsion for use as a paving material had been contaminated with a relatively low-boiling material.

Application of the technique to air- and water-pollution studies appears highly promising, since trace organics can be determined with virtually no interference from associated inorganic substances. Carle has obtained a curve for organic material collected on a glass filter pad from contaminated air[5]. Similar analyses could be made of organic material adsorbed from polluted water by a suitable inorganic adsorbent; or the analysis might be made directly on the water sample. Initial studies on the determination of trace organics in water appears promising and the work is being actively pursued.

Oxidative thermal analysis

The system can be used for oxidative decomposition studies because the presence of oxygen in the carrier gas has only a minor effect on the response of the flame-ionization detector[6]. Effectiveness of the system for this type of measurement is illustrated by the curves shown in Fig. 6 for two polypropylene samples. These tests were made with 0.5 mg of thin polymer film (2-mil thickness) in a platinum sample

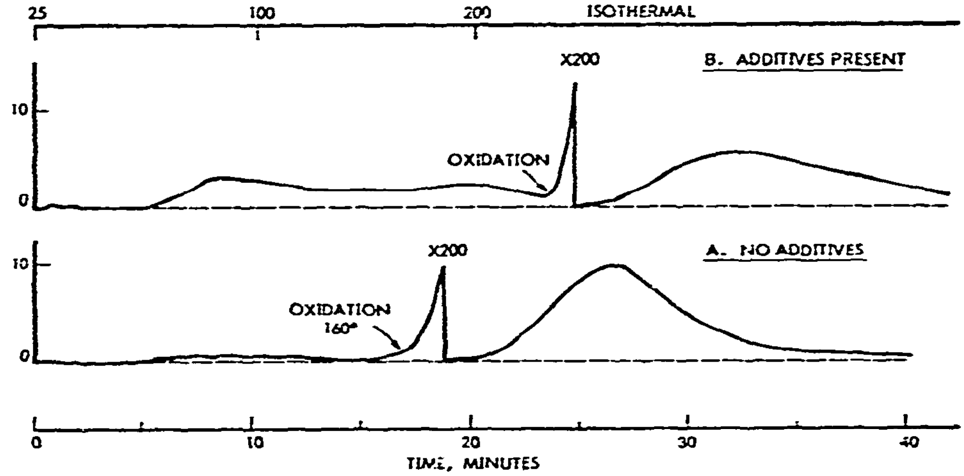

Fig. 6. Oxidative stability of polypropylene (0.4 mg, air carrier gas, 30 ml/min).

pan, using air instead of nitrogen as the carrier gas. The sample temperature was programmed at 10°C/min to 200°C and then held at that temperature. The flame detector was maintained at 210°C.

The onset of oxidative decomposition is indicated by the point on the curve (Fig. 6) at which a sharp increase in volatiles production is observed. With pure polypropylene this point was reached at 160°C, whereas with the polymer containing additives, oxidative attack was delayed until the sample had been heated for about 4 min at 200°C. Also rates degradation can be determined from the curves. This technique appears promising for the sensitive and precise measurement of the effectiveness of various oxidation inhibitors, not only in polymer formulations, but in other products where resistance to oxidation is an important property.

CONCLUSIONS

The thermal analysis–flame detection system described is well-suited for the sensitive and quantitative determination of yield *vs.* temperature information for a wide variety of organic materials. Effective one-plate resolution is obtainable because of the small sample size that may be used. The specificity of the detector to organic carbon makes possible the analysis of organic material in samples containing water and other inorganic components.

The system is capable of high speed of analysis, owing to the small sample requirement and the low thermal lag of the furnace which permits rapid heating and cooling. The isothermal mode of operation provides especially rapid and convenient measurements, for example, of volatility or trace organic content.

As in other thermal analysis methods, a combination with mass spectrometry would be highly desirable for identification of the organic volatile material as it is evolved. This addition would be especially useful in the TAFID system because of the relatively high degree of resolution that can be obtained.

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