

## THERMAL REACTIONS BY AUTOMATED MASS SPECTROMETRIC THERMAL ANALYSIS\*

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### ABSTRACT

Combination of differential thermal analysis (DTA) with time-of-flight mass spectrometry and data storage on magnetic tape is used to study thermal decompositions.

A modified Du Pont 900 DTA cell is used for reactions at atmospheric pressure with evolved gas sampling into a small time-of-flight spectrometer.

For fast reactions a specially developed DTA cell is operated within the mass spectrometer and operates at high vacuum.

A combination of both operational modes yields pressure dependencies of chemical decomposition.

Examples studied include inorganic compounds and complexes, organometallics and organic chemicals such as fire retardants.

The data are presented as intensity/temperature curves for each observed fragment, which not only yields decomposition temperatures but also—by the curve shapes—information on the mode of decomposition.

### INTRODUCTION

When a scientist or engineer first gets involved with thermal analysis, he wants to know simply if anything happens to a particular sample on heating. Soon thereafter, however, the questions become more, more detailed and less easily answered. For example, it is fairly easy to recognize decomposition of a sample, but what is the nature of this decomposition, what are the products that are formed, how much decomposition does occur? If bubbling occurs, what is given off? Does the sample simply boil or is a different gas or mixture of gases released? How many products are there? Which products? When are they released, at what rate, at what temperature, how, etc., etc.? In other words, the classical analytical methods were not sufficient to answer all of these questions. Of course, one could always consult another analytical method and for identification of gases or vapors, mass spectrometry is a well-established

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lished tool. Using two analytical techniques on the same sample, however, poses a fundamental problem. It is often extremely difficult, if not impossible, to duplicate exactly the experimental conditions for the sample in two different analytical operations. Only if both analyses can be performed simultaneously on the sample can the results be unequivocally correlated.

Combining thermal analysis with mass spectrometry, one is faced with a disadvantage: mass spectrometric analysis is carried out in a high vacuum. This requires that either the thermal analysis is also carried out in vacuo or if performed outside the mass spectrometer, the resultant gas or vapor has to be introduced through a valve system. With respect to the test sample the first method seems to be more straightforward. However, most mass spectrometers are not capable of controlling or measuring exactly the sample temperature, since heat transfer in vacuum can only occur through radiation. Furthermore, temperature dependent chemical reactions may occur quite differently in vacuo than at ambient pressure. This apparent disadvantage, however, may actually be used as an additional analytical parameter as we will show later.

Other than mechanical difficulties, the main disadvantage of the second method is a delay in response between the thermal reaction and its mass spectrometric indication. Additionally, one can never be sure if the primary reaction product has not undergone further reaction by collision with the walls of the inlet system or even with the carrier gas.

We have used both methods for the following examples although at present we are using almost exclusively an internal DTA cell with operation under vacuum.

#### EXPERIMENTAL

The system which we have previously described<sup>1</sup> is shown in Fig. 1. To summarize, it consists of a modified Du Pont 900 thermal analyzer, a small time-of-flight

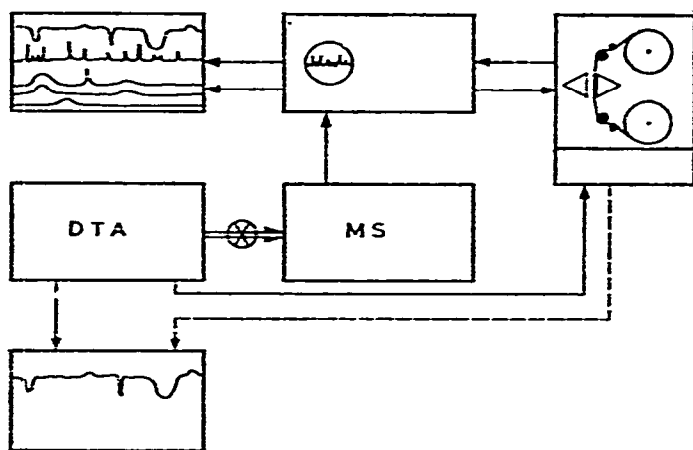


Fig. 1. Schematic of mass spectrometer-differential thermal analysis system.

mass spectrometer with attached scanning oscilloscope, a frequency modulated magnetic tape recorder and a *XY* recorder. The sample temperature is controlled and indicated by the DTA unit while the mass spectrum is continually displayed on the oscilloscope and recorded at a rate of approximately 10 complete spectra per second. On playback the intensity of each detected mass peak is plotted on the *XY* recorder as a function of increasing temperature.

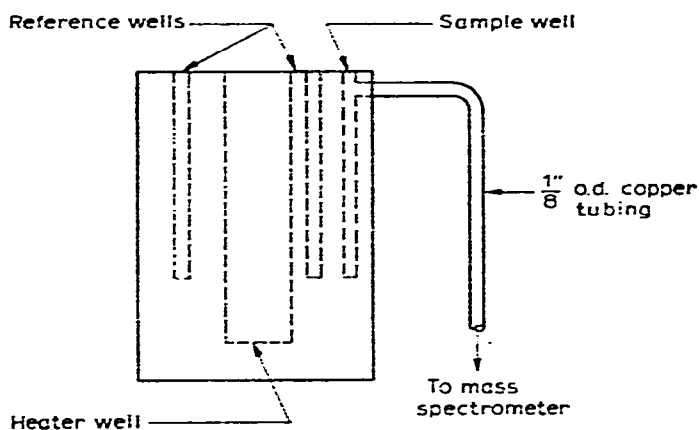


Fig. 2. External DTA cell modification for mass spectral analysis.

For external DTA operation the slightly modified Du Pont cell<sup>2</sup> is shown in Fig. 2, whereas for operations within the mass spectrometer this block has been miniaturized and mounted at the end of a push rod which is inserted through a vacuum seal. A wire wound radiative furnace had to be constructed which provided fast response to heat requirements whereas the capacity of the cell itself served to approximate linear temperature increase.

## RESULTS AND DISCUSSION

Control of the sample environment cannot be underrated in these operations as is shown with the following almost classical example. The decomposition of the monohydrate of tetramine copper sulfate has been investigated by several authors<sup>3-5</sup>. From the differential thermogram (Fig. 3) one might expect a stepwise release of ammonia and water ending up with essentially anhydrous copper sulfate. At high temperatures one might also expect a slight decomposition with formation of cupric oxide. However, when the sample is recovered at about 400°C from an inert atmosphere, it appears red, indicative of cuprous oxide or finely divided metallic copper. Plotting the intensity of the mass peaks obtained from the sample, decomposing at atmospheric pressure in an argon atmosphere, (Fig. 4) we obtained the diagram which we have discussed<sup>1</sup> in the past<sup>1</sup>. Briefly, during the early part of the decomposition water and 2 moles of ammonia are released followed by a separate release of an additional mole of ammonia whereas the final decomposition step involves a redox

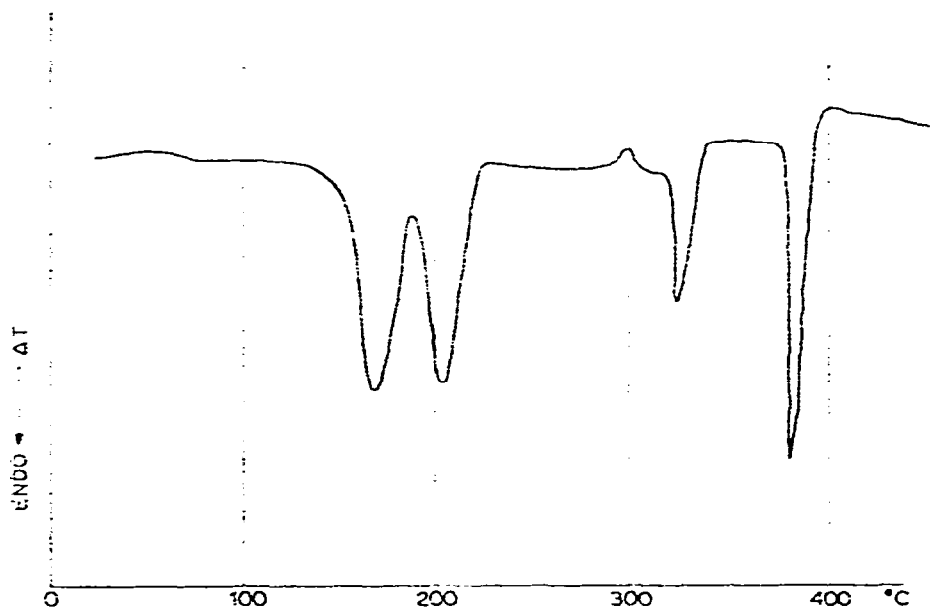


Fig. 3. Thermogram of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ .

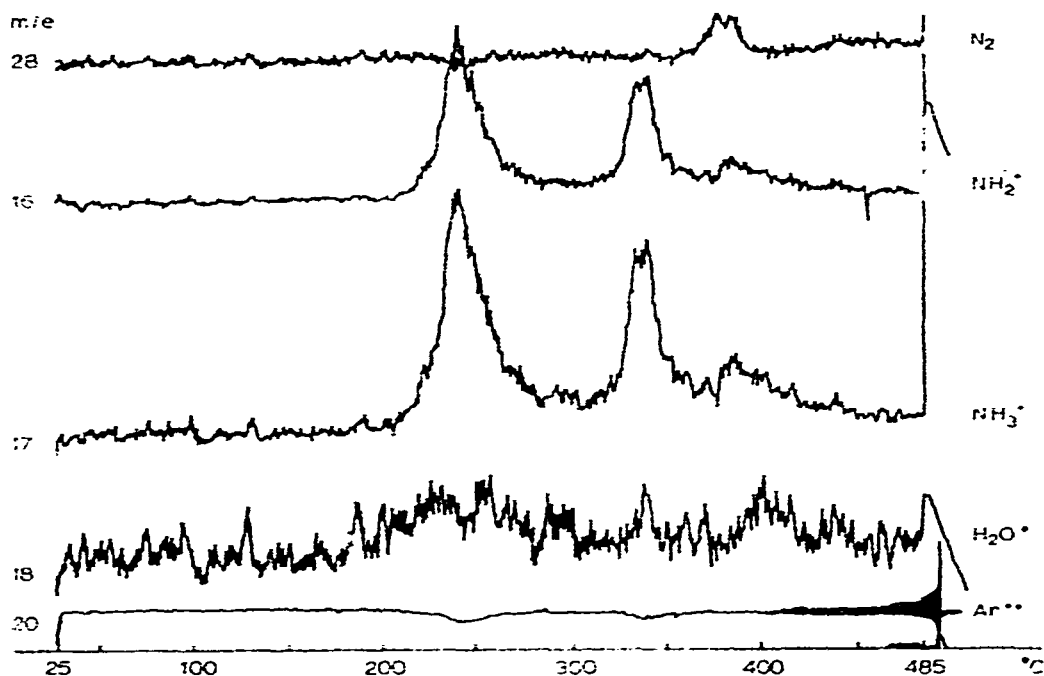


Fig. 4. Ion intensities versus temperature for the  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  decomposition in an argon atmosphere (external DTA cell).

reaction with formation of nitrogen, a small amount of ammonia, water, and sulfur dioxide. This is a typical result from the external DTA cell. The mass intensity peaks are fairly broad, the response is slow and slightly delayed and water is extremely hard

to recognize since it creeps along the walls rather than being carried freely in the gas stream and through the valve. Figure 5 dramatically shows the different behavior of the sample in vacuo and also clearly demonstrates the two different reactions, release of water and ammonia below 300°C and chemical reaction above this tempera-

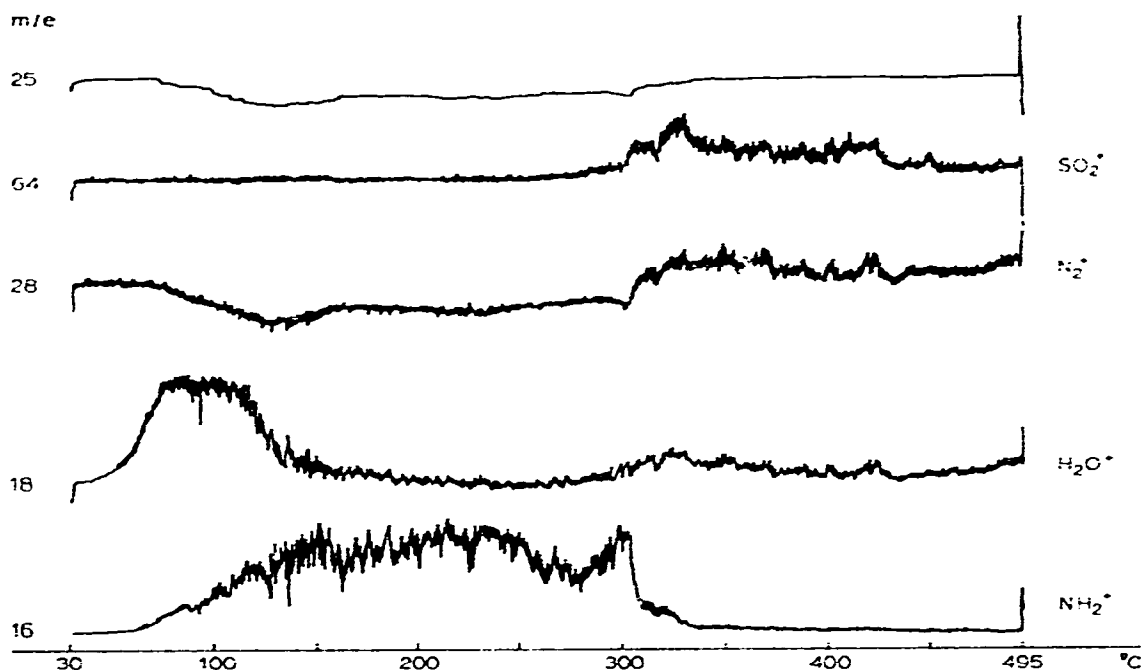


Fig. 5. Ion intensities versus temperature for the  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  decomposition at  $10^{-5}$  torr (DTA cell inside mass spectrometer); immediate heat.

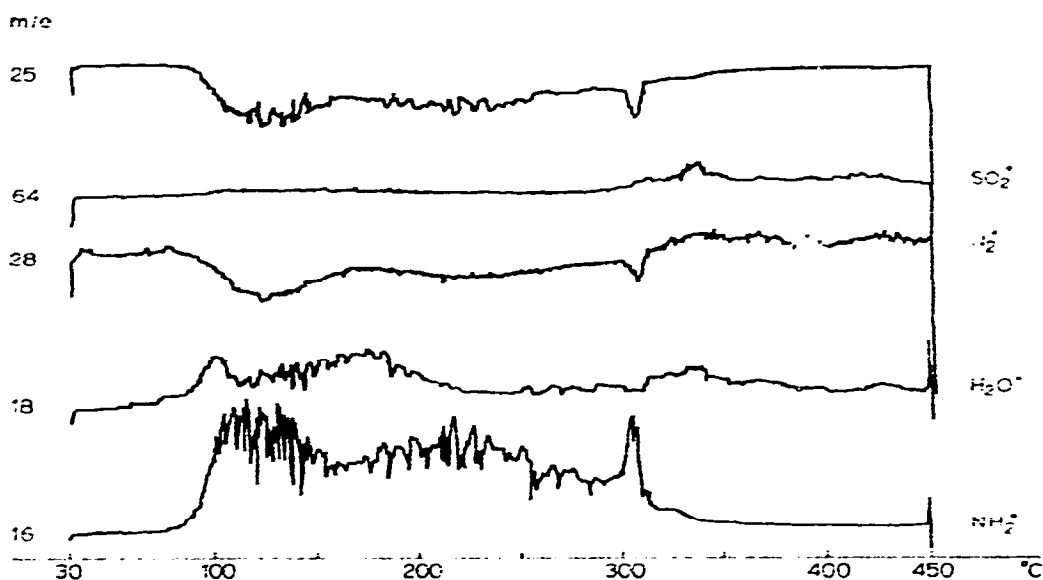


Fig. 6.  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  decomposition inside a mass spectrometer after 24 hours at  $10^{-5}$  torr.

ture. It is also significant that the release of water starts essentially at room temperature indicating very loosely held water of crystallization. Indeed, this is further documented by Fig. 6 where the sample had been pumped under vacuum for 24 hours and only a small amount of water remained.

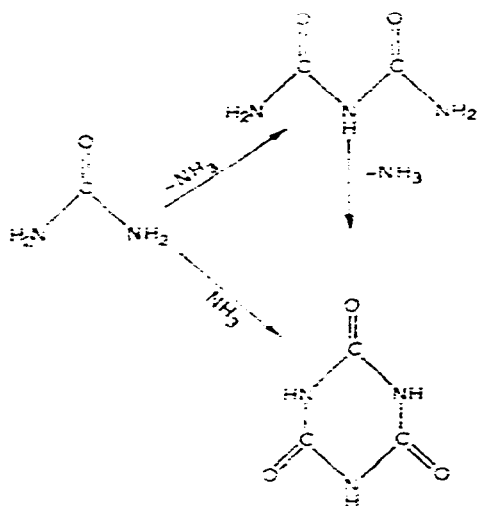


Fig. 7. Thermal condensation reactions of urea.

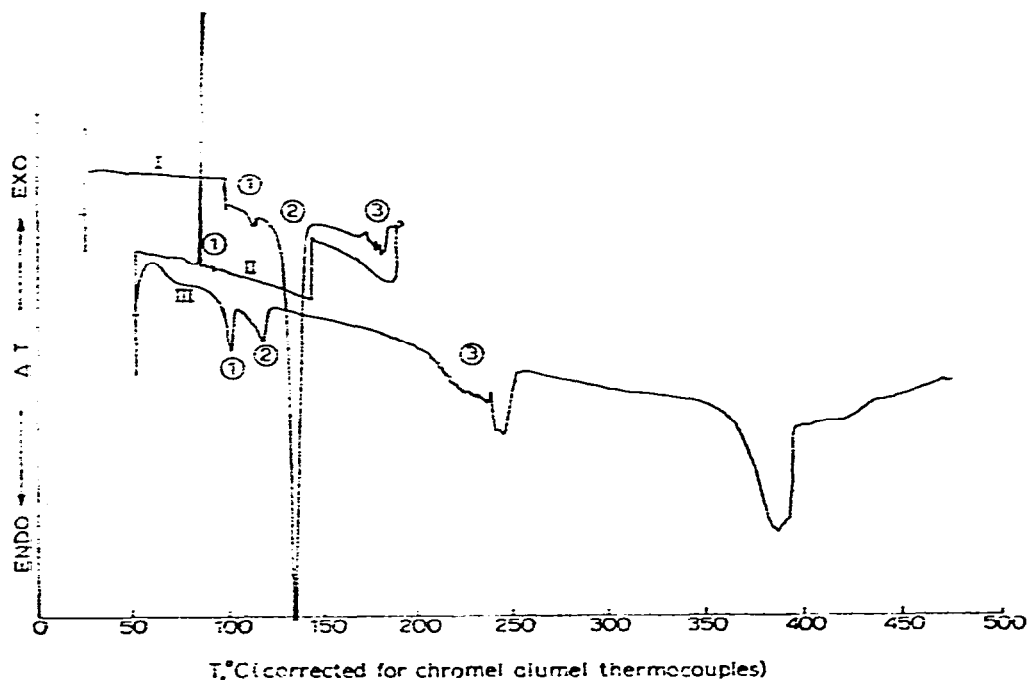


Fig. 8. Thermogram of urea: I, First heating: 2 = melting, 3 = decomposition with loss of  $\text{NH}_3$ ; II, Cooling with crystallization; III, 1 = partial melt, 2 = complete melt, 3 = decomposition with loss of  $\text{NH}_3$ , formation of white solid, 4 = sublimation with loss of  $\text{HNCO}$ , white solid residue.

This example demonstrates very clearly how deliberate changes in the analytical parameters can yield valuable information. The expected decomposition products have been identified. An unexpected reaction has not only been detected but the reaction products were determined. The pressure dependency of each of the reaction steps has been established and even structural information has become available as

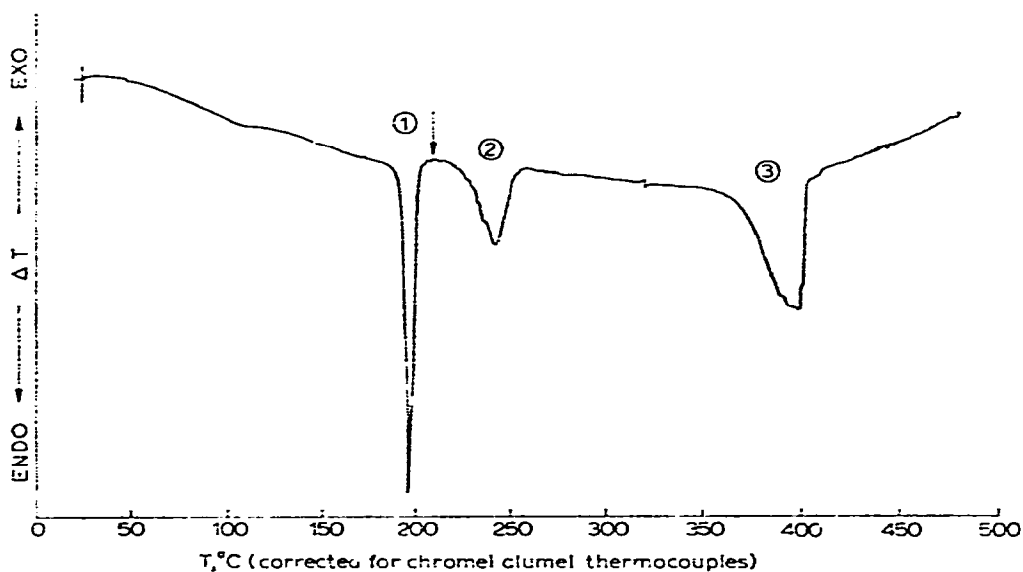


Fig. 9. Thermogram of biuret: 1 = melting, 2 = decomposition with loss of  $\text{NH}_3$ , formation of white solid, 3 = sublimation with loss of  $\text{HNCO}$ , white solid residue.

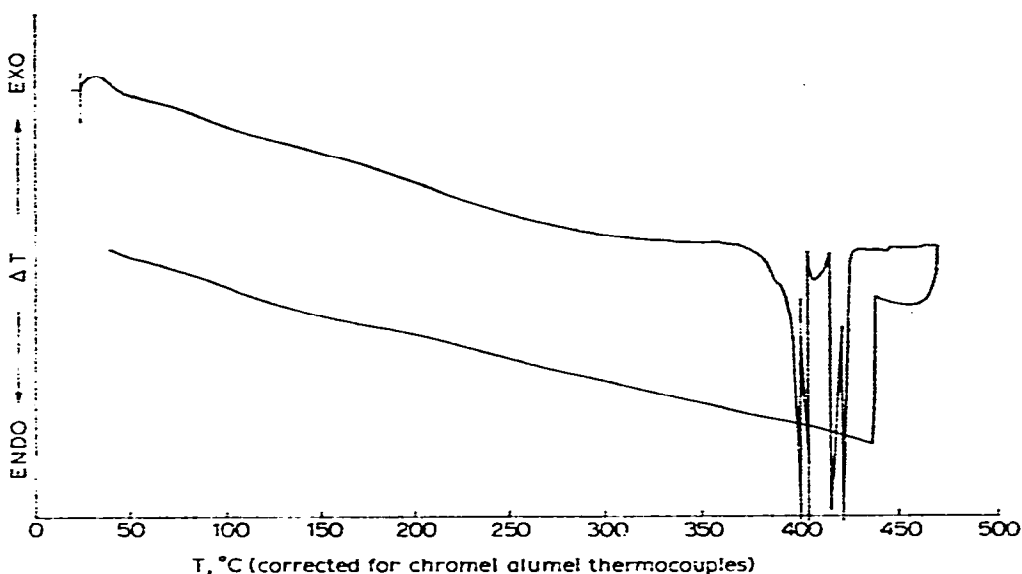


Fig. 10. Thermogram of cyanuric acid: 1 = Some melting and vapourization, but large amount of solid white residue.

indicated by the mode of release of water. The following example is typical for a system where an originally pure compound forms a secondary reaction product which in turn can undergo reaction or decomposition. The system is the condensation of

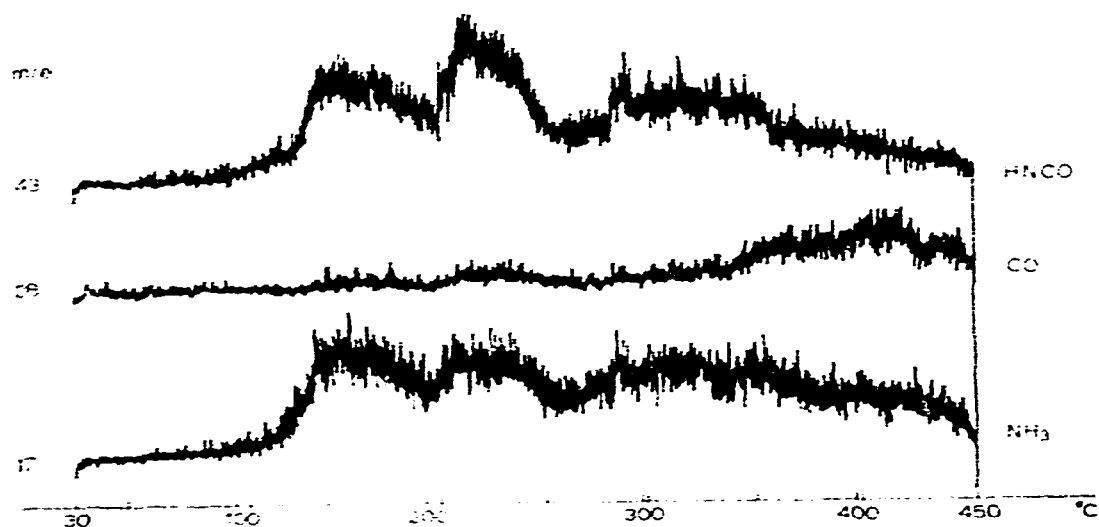


Fig. 11. Ion intensities versus temperature for urea thermolysis at  $10^{-5}$  torr.

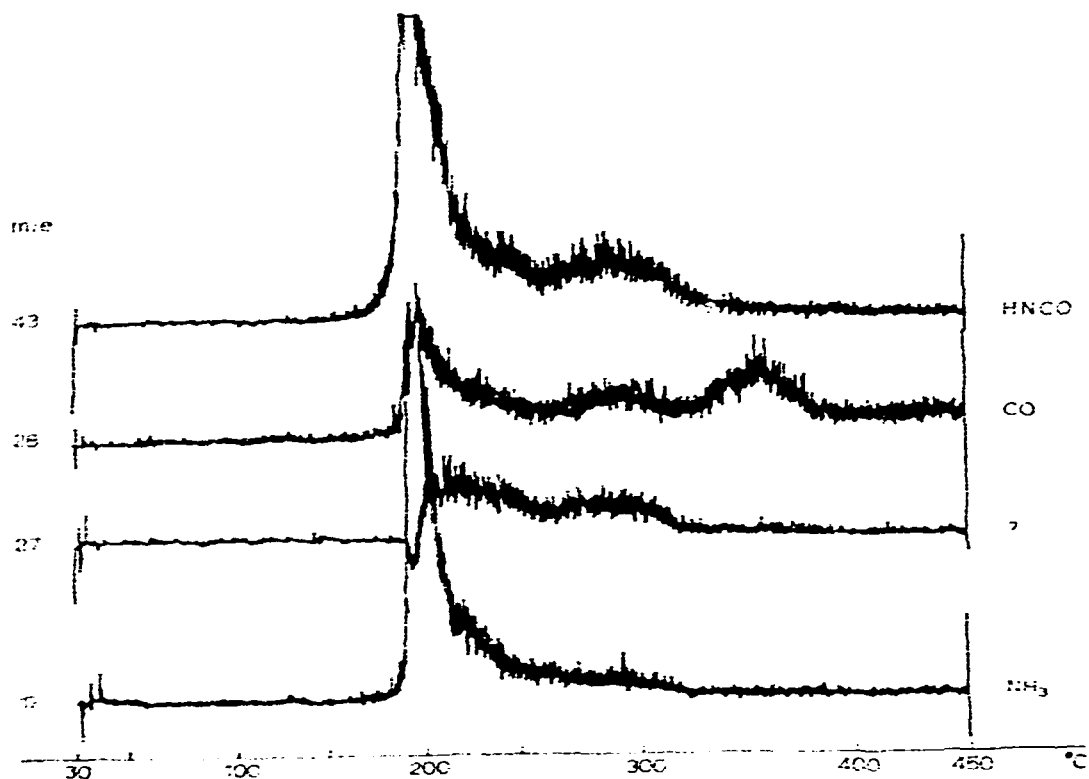


Fig. 12. Ion intensities versus temperature for biuret at  $10^{-5}$  torr.



urea to the dimer biuret and the trimer cyanuric acid. See Fig. 7. The differential thermogram (Fig. 8) of urea shows three decomposition ranges. The two higher ones are repeated in the thermogram of biuret (Fig. 9) and only the highest one remains for the decomposition of cyanuric acid (Fig. 10). The obvious conclusion would be to assume that urea forms biuret at approximately 175°C which is decomposed at 250°C to form cyanuric acid which in turn is stable to 375°C. However, the intensities of the mass peaks observed over the whole temperature range clearly show that these chemical reactions are not separate, but overlap to a very large degree (Figs. 11, 12 and 13). The final example deals with evaluation of fire retardant chemicals in polymer systems. The assumption we made is simple: To expect fire retardant properties the

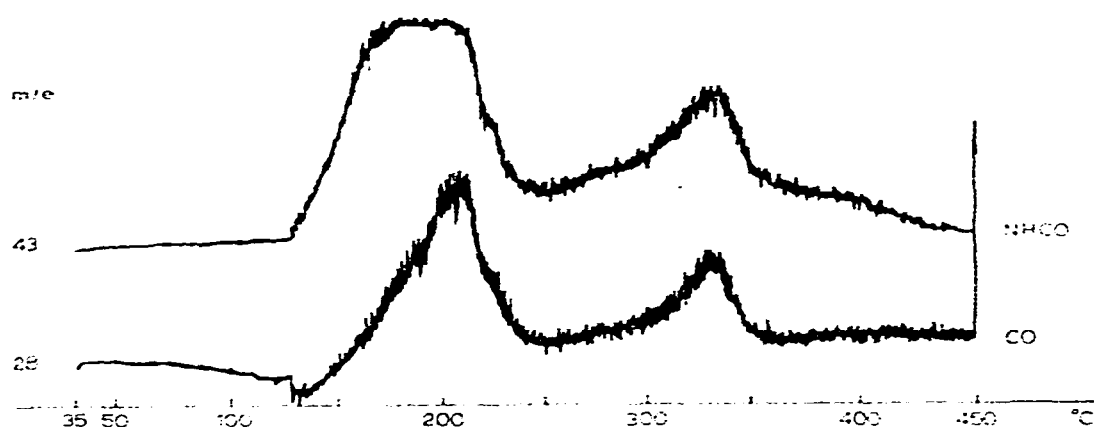


Fig. 13. Ion intensities versus temperature for cyanuric acid  $(\text{NHCO})_3$ .

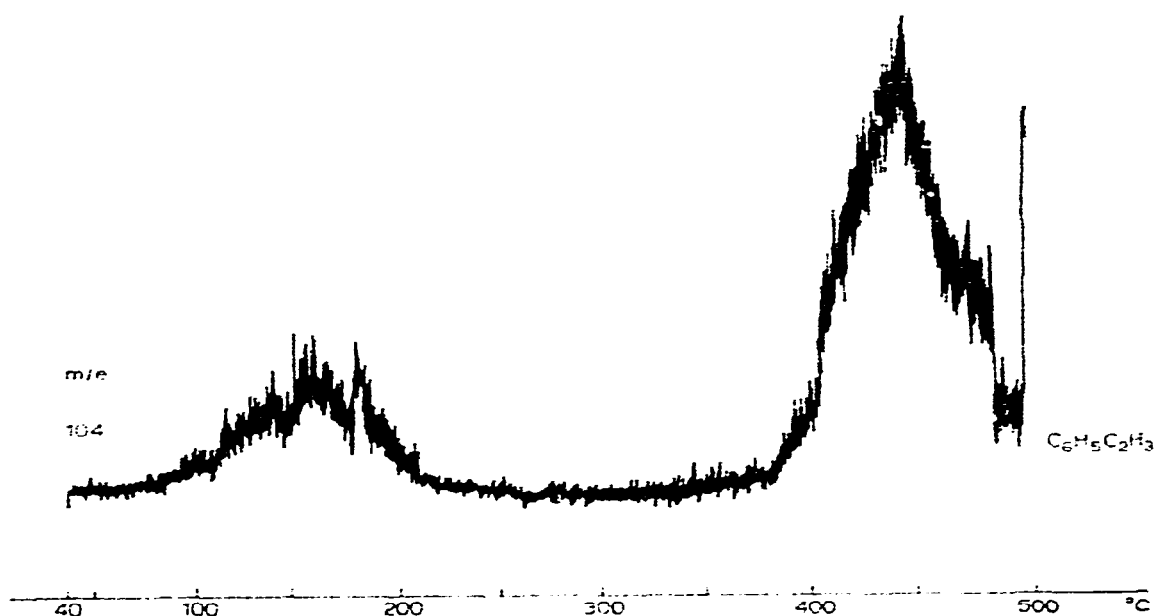


Fig. 14. Ion intensities versus temperature for polystyrene containing styrene.

fire retardant and polymer should decompose within the same temperature range. For example, polystyrene under our experimental conditions starts to decompose at approximately 400°C with release of styrene monomer as a potential fuel (Fig. 14). The brominated phenylether as shown in Fig. 15 starts to decompose at 200°C and

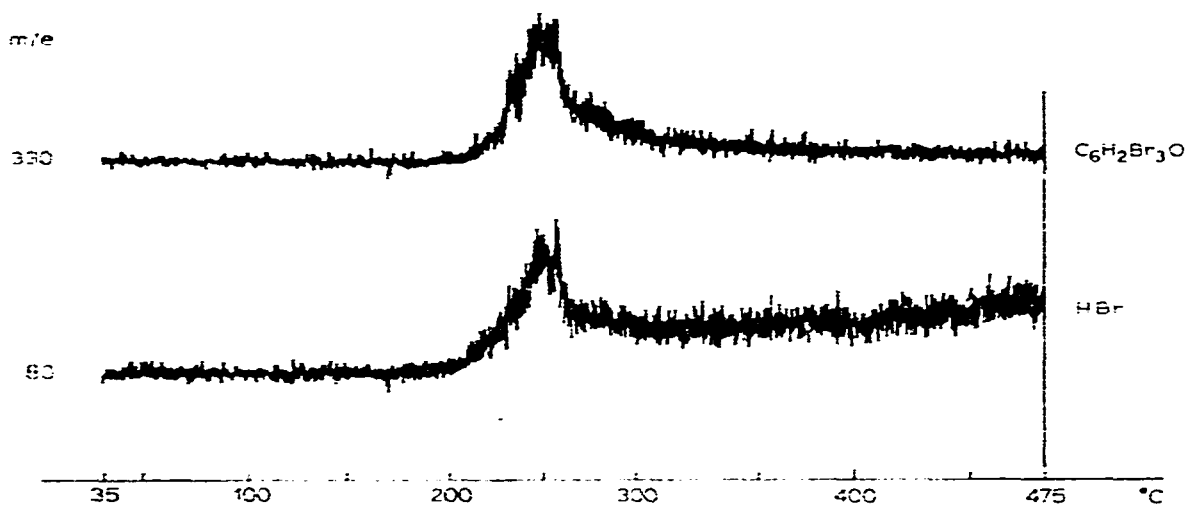


Fig. 15. Ion intensities versus temperature decomposition of B-8, an F.R. additive.

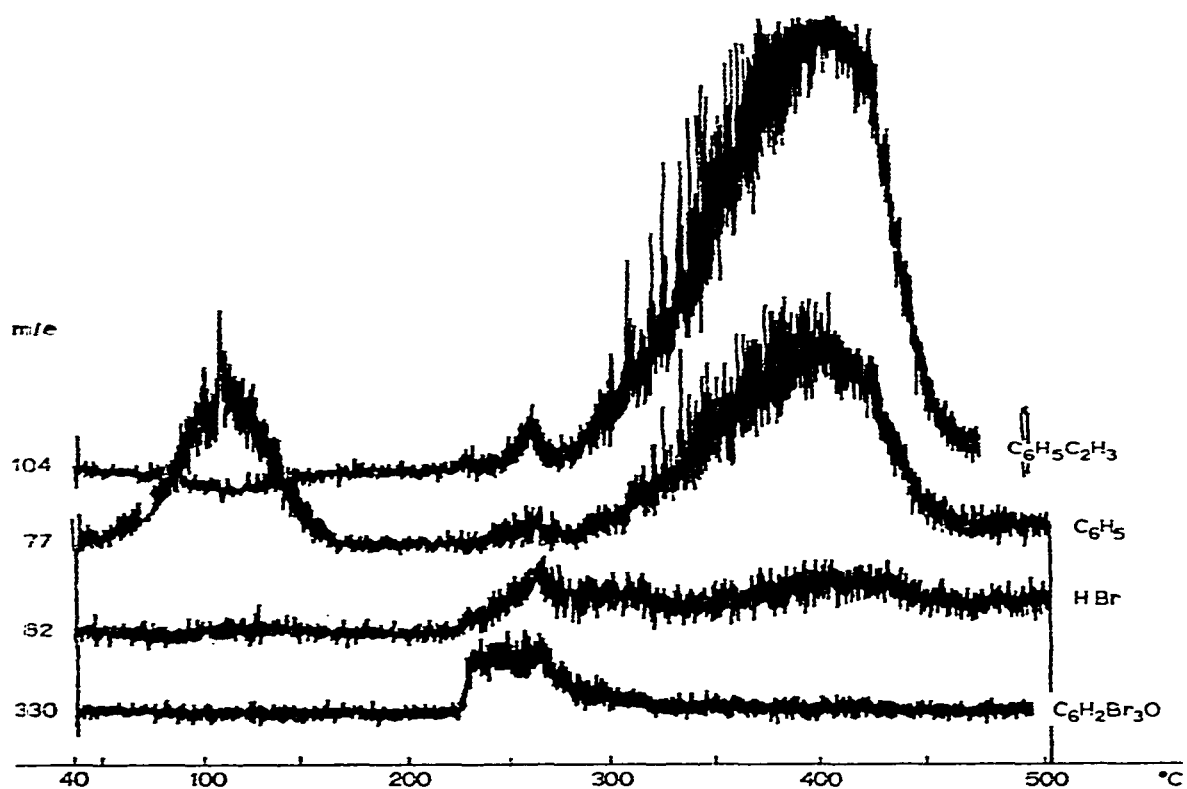


Fig. 16. Ion intensities versus temperature B-8 and polystyrene (benzene solvent).

if one assumes that the release of hydrogen bromide is connected with fire retardant properties this compound would be effective at the decomposition temperature of polystyrene. This is even more clearly demonstrated in Fig. 16 where this system has

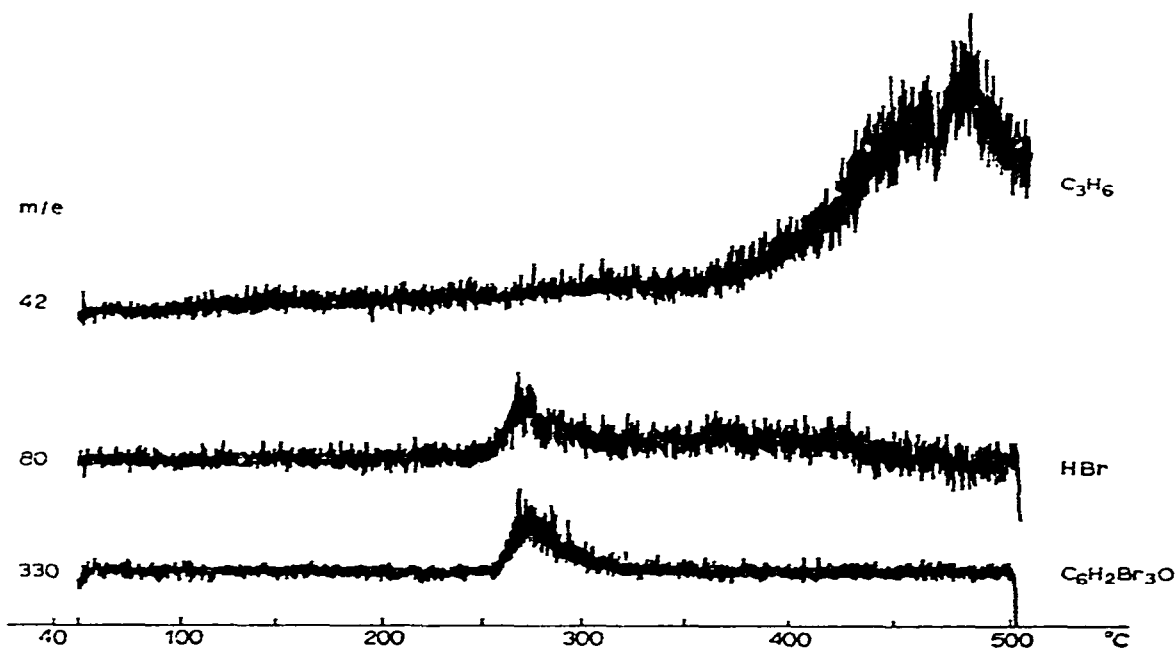


Fig. 17. Ion intensities versus temperature B-8 and polypropylene (approx. 50/50 w/w).

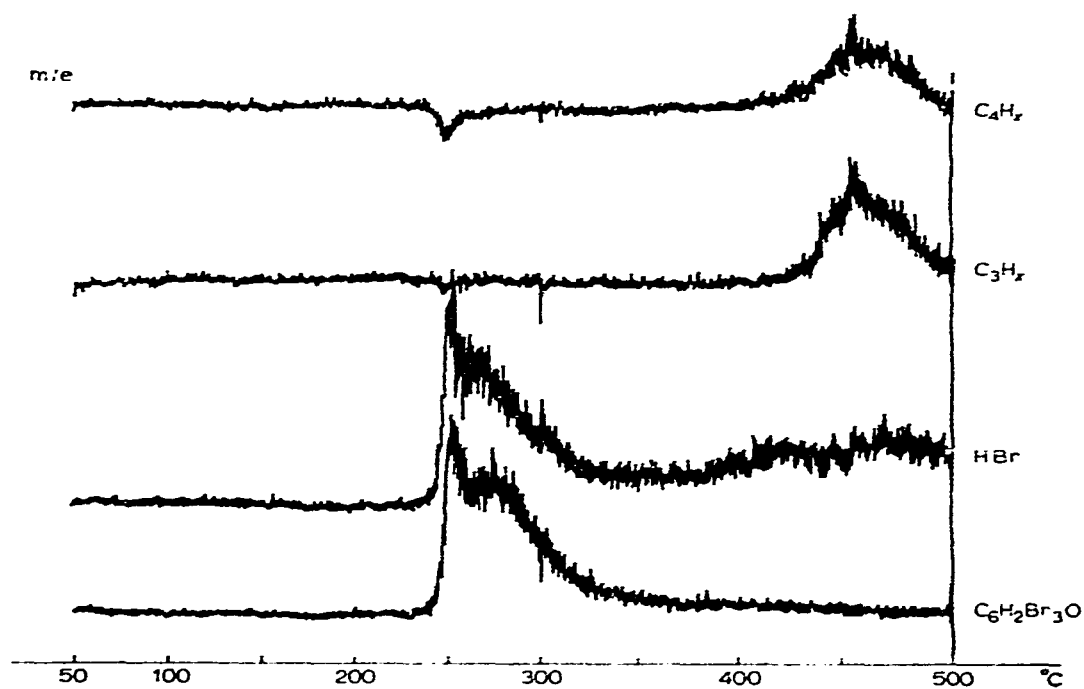


Fig. 18. Ion intensities versus temperature B-8 and polyethylene (approx. 50/50 w/w).

been combined. On the other hand (Fig. 17) one would expect the effect for polypropylene to be diminished and even more so (Fig. 18) in the case of polyethylene.

In conclusion, we hope to have demonstrated a powerful method available to solve a multitude of chemical problems. In the final table are listed problem areas where we have successfully used thermal mass analysis.

#### SOME AREAS OF APPLICATION

Study of thermally unstable materials

Polymer degradation studies

Dehydration reactions

Desorption studies

Curing of paints, adhesives, inorganic cements

Determination of purity

Entrapped gasses and solvents

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