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TG–GC–MS, TG–MS and TG–FTIR applications on polymers and waste products

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Abstract

A latex is studied using the off-line combination, TG–GC–MS. A mixture, $CuSO_4 \cdot 5H_2O$–cellulose, is studied using the on-line combination, TG–MS, and the amount of HCN in gases released by heating of a waste product is determined using the on-line combination of TG–FTIR, successive sampling, FIA and photometry. © 1997 Elsevier Science B.V.

Keywords: Latex; Copper sulphate; Cellulose; Waste product

1. Introduction

The variety of additives that are present in many materials requires the on-line and off-line combination of TG with gas-analysis techniques for the characterisation of the thermal behaviour and for the identification of the decomposition products.

This contribution shows three examples of evolved gas analysis. They are:

1. the off-line coupling between TG and GC–MS performed on a latex;
2. the on-line coupling, TG–MS, for the study of the degradation of $CuSO_4$ in the presence of cellulose; and
3. the on-line coupling, TG–FTIR, and the off-line use of FIA and photometry (via successive sampling of the gases coming from the TG) for the determination of the amount of HCN in the gases that are released during heating of an unknown waste product.

It will be shown that, by coupling of TG with appropriate techniques, an unambiguous characterisation can be obtained.

2. Experimental

All TG experiments are performed with a TA Instruments 2000-951. The on-line coupled MS is a VG Fisons Thermolab A Varian 3400 gas chromatograph coupled to a Finnigan TSQ 70 quadrupole mass spectrometer, is used for the off-line experiments.

The FTIR is a Bruker FTIR IFS 48 coupled on-line with the TG unit and operating with a resolution of $8\ cm^{-1}$.

The FIA (flow injection analyzer) is a Lachat Quickchem AE Analyser equipped with a photometer analyser.

3. Results

3.1. TG–GC–MS results of a latex

A latex composed of 80% NR (natural rubber) and 20% SBR (styrene butadiene rubber), is heated at

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20°C min^{-1} between room temperature and 600°C under a N_2 flow of 50 ml min^{-1}. At 600°C, N_2 is replaced by O_2 and the heating is continued at the same rate till 800°C to determine, in the same run, the ash content.

The inert working conditions of the TG equipment during heating in nitrogen have been checked with the copper oxalate test, as described elsewhere [1].

The evolved gases are collected in a cooled solution of dichloromethane. After the thermal experiment, the absorption solution is analysed using a GC–MS quadrupole spectrometer. After chromatographic separation, the individual components are identified by their mass spectra through interactive library search.

Fig. 1 shows that the latex degrades in inert atmosphere till a remaining weight of 7.5% at 600°C. Changing the dynamic purge gas from an inert atmosphere to an oxidative atmosphere causes only a small additional weight loss of 1.2% resulting in an inert filler and ash content of 6.3%. The use of GC–MS gives important additional information on the characterisation of the organic volatile compounds, as shown in Table 1.

From these results, it is clear that such a variety of gaseous products from heating a latex can only be identified using the combination of TG with a separation technique and a detection technique. If necessary, one can of course carry out successive trapping by changing the trapping absorbents at different temperatures or times (see example 3) to obtain temperature or time-resolved separation of the gases. The use of different suitable solvents (water, alcohols, CH_2Cl_2, etc.) offers additional possibilities. Absorption can also be done on a suitable solid (tenax, charcoal, chromosorb, etc.), followed by thermal desorption (TD), separation by GC and identification by MS, as illustrated elsewhere for the oxidative degradation of polystyrene [2].

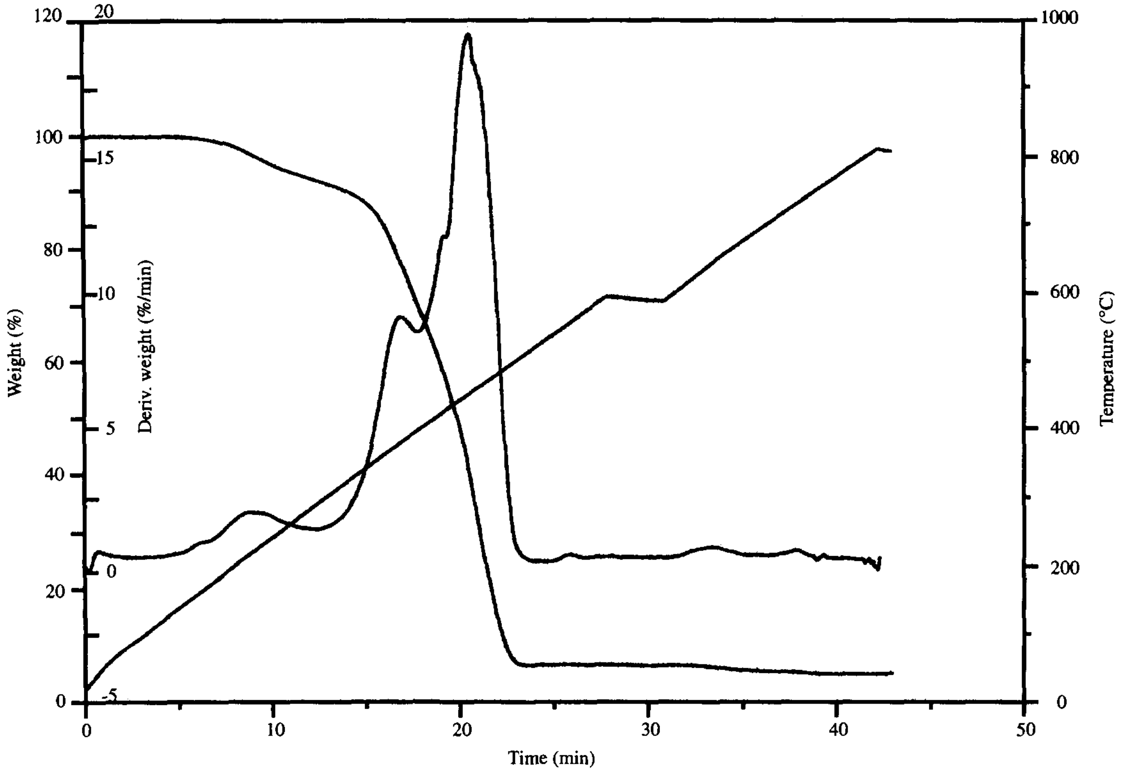

Fig. 1. TG–DTG plot of a latex in N_2 (till 600°C) and O_2 (from 600°C) at a heating rate of 20°C min^{-1}.

3.2. TG–MS results of the mixture, copper sulphate–cellulose

A mixture (1/1 weight) of $CuSO_4{\cdot}5H_2O$ and cellulose is heated in an He flow of 50 ml min^{-1} at a heating rate of 20°C min^{-1} from room temperature till 900°C.

The TG equipment is coupled to an MS to investigate the influence of cellulose on the degradation of copper sulphate by the on-line analysis of the gases evolved during heating of the mixture. The mass spectrometer is connected to the TG unit using a flexible, heated, silica-lined steel capillary. As TG proceeds at atmospheric pressure when MS must operate below 10^{-5} mbar, further pressure reduction was obtained by using a molecular leak (silicon carbide frit).

TG experiments on the pure cellulose have shown that, at a heating rate of 20°C min^{-1}, the degradation of cellulose takes place in the 250–400°C range with a maximum at 370°C. Figs. 2 and 3 show, respectively, the degradation of the mixture, $CuSO_4{\cdot}5H_2O$–cellulose, and the degradation of pure $CuSO_4{\cdot}5H_2O$. The identification of the degradation temperatures of the two compounds in the mixture is done by following

Table 1
Compounds absorbed in a dichloromethane solution during the TG experiment on a latex and identified by GC–MS

Dominance species
Alkyl-substituted benzenes
Traces
Xylene isomers
Styrene
Methylstyrene
Methyl(methylethenyl)styrene
Methylnaphtalene
Cyclohexylbenzene
Naphtalene compound
Diphenylpropane
Bis(*t*-Bu)phenol
Substituted styrene
Acetophenon compound
Aromatic amine

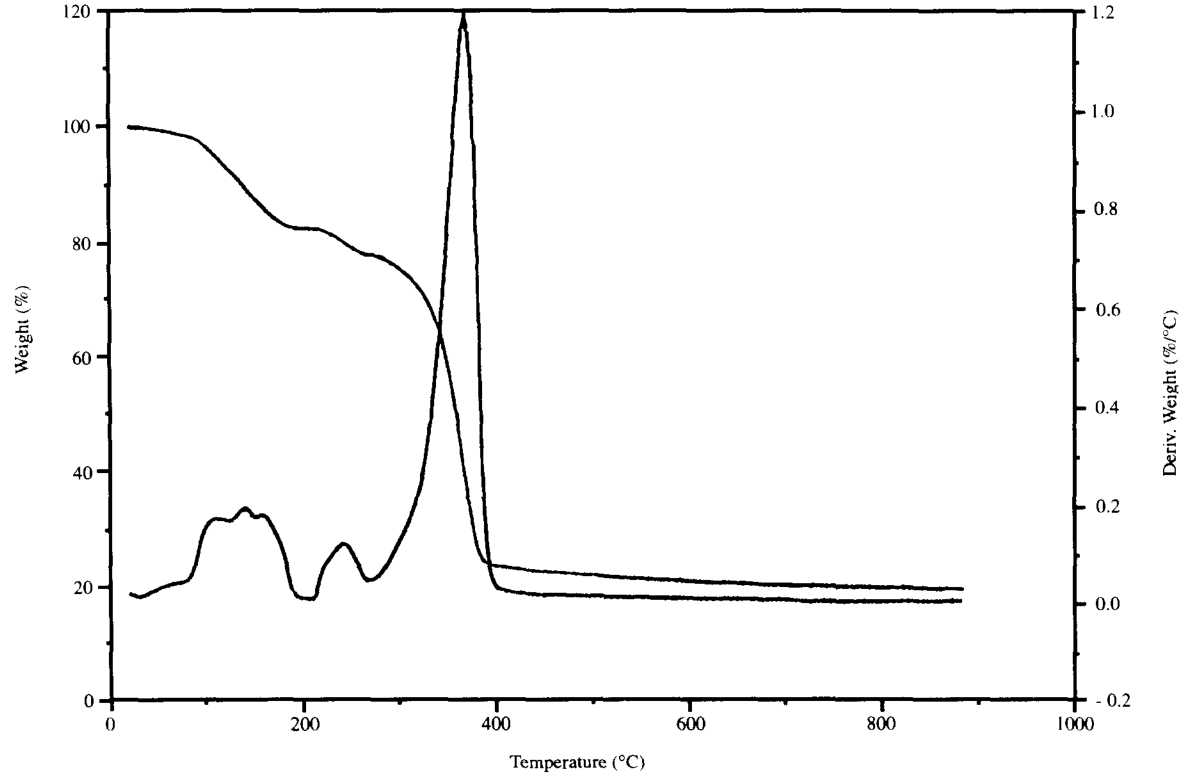

Fig. 2. TG–DTG plot of a 1/1-weight mixture of $CuSO_4{\cdot}5H_2O$–cellulose in He at a heating rate of 20°C min^{-1}.

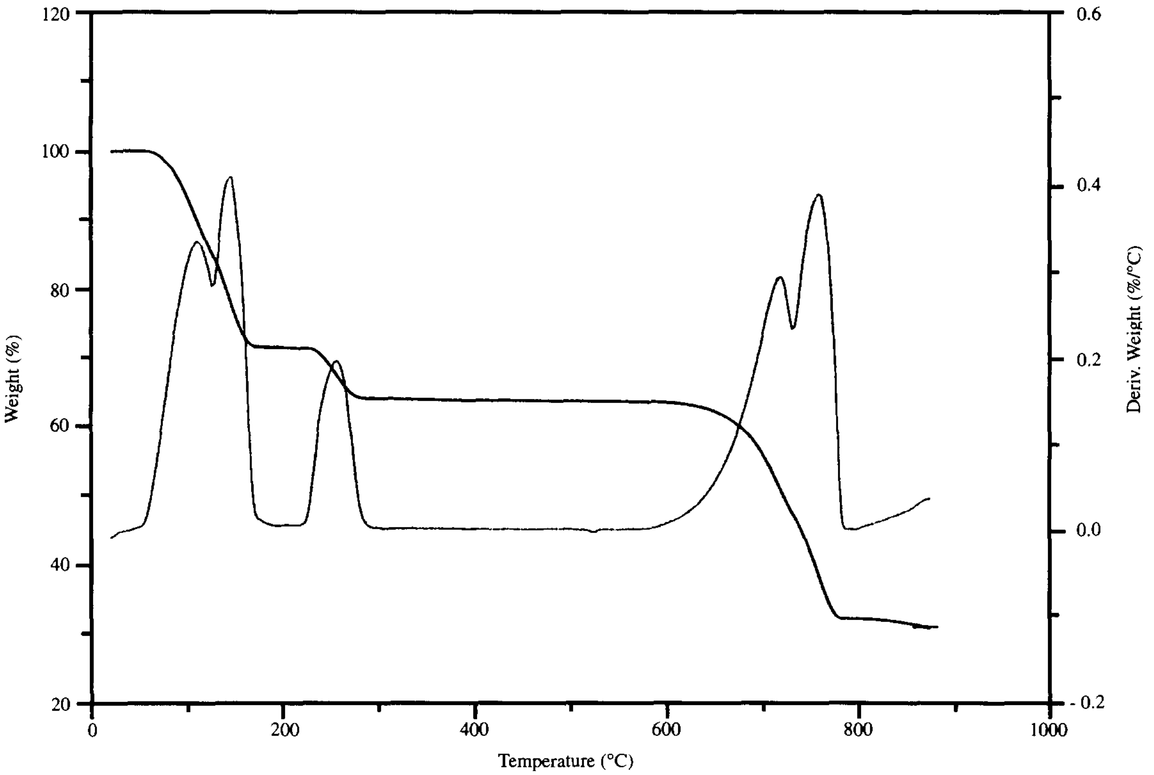

Fig. 3. TG–DTG plot of pure $CuSO_4{\cdot}5H_2O$ in He at a heating rate of 20°C min^{-1}.

typical degradation masses: m/e of 28 (CO) and 44 (CO_2) for cellulose, and 64 (SO_2^+), 48 (SO^+) and 32 (SO_2^{2+}) for $CuSO_4{\cdot}5H_2O$, as shown in Fig. 4. Typical ion-chromatograms of pure $CuSO_4{\cdot}5H_2O$ are given in Fig. 5.

From the unambiguous identification of the gaseous decomposition products as a function of the temperature, it is proven that the degradation of $CuSO_4{\cdot}5H_2O$ in the mixture takes place at a temperature that is 350°C lower than that in pure $CuSO_4{\cdot}5H_2O$.

This example clearly shows that mixing different components can drastically change the thermal stability due, in this case, to the reducing properties of the cellulose on the sulphate.

3.3. *TG–FTIR and TG–FIA–photometry results of a waste product*

In order to determine the presence of HCN in gases evolved during heating, a sample is heated in argon at different heating rates, as shown in Fig. 6. The sample is an organic waste product originating from the industry. The gaseous compounds are analysed by transmission FTIR. The outlet of the TG is connected to the FTIR by an interface that consists of a transfer-line and a gas-cell both heated up (200°C) to prevent condensation [3]. The FTIR spectrometer is used at such a speed so as to acquire four complete IR spectra within 1 s at a resolution of 8 cm^{-1}.

The total IR intensity measured with a liquid-nitrogen-cooled-MCT (Hg–Cd–Te, 600–4000 cm^{-1}) detector is given as a function of time or temperature in Fig. 7.

In Fig. 8, some typical FTIR spectra are given at different temperatures.

The results show that till 200°C only H_2O is detected. From 250°C, CO_2 is also evolved and from this temperature the detection of the CH-stretching vibration (2800–3000 cm^{-1}) shows the presence of hydrocarbons. The intensity of the CH absorption

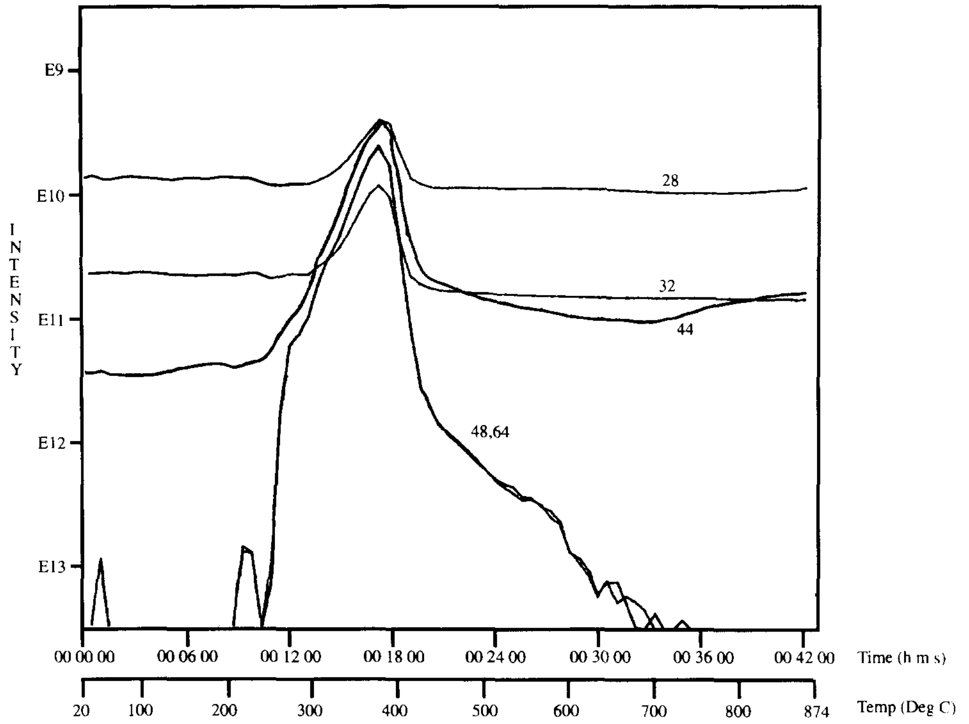

Fig. 4. MS results of a 1/1-weight mixture of $CuSO_4 \cdot 5H_2O$–cellulose during heating in He at a heating rate of 20°C min^{-1}.

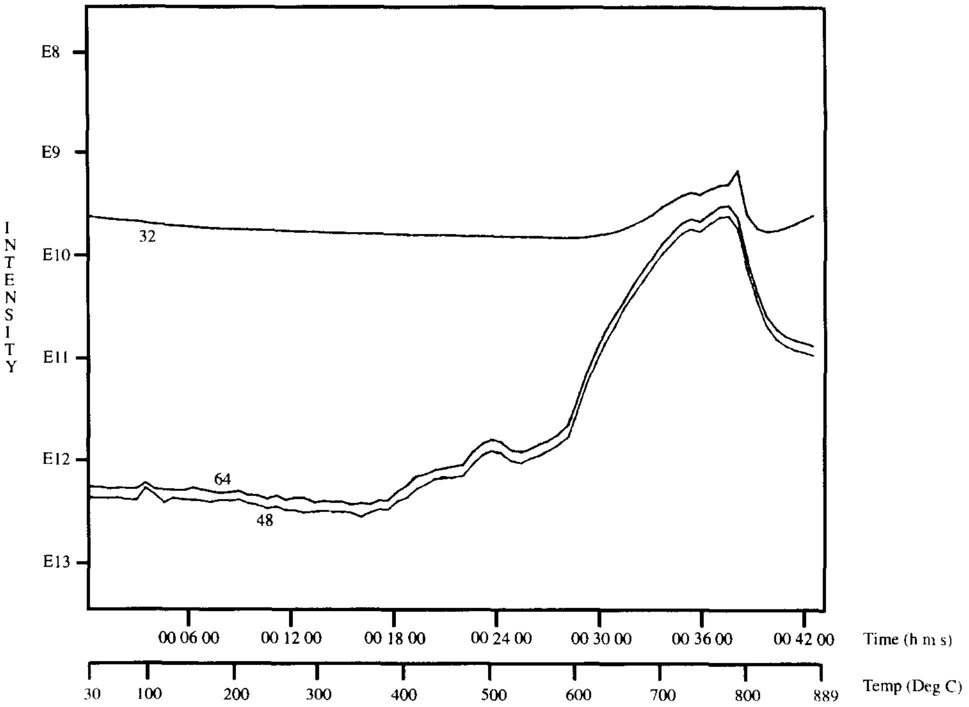

Fig. 5. MS results of pure $CuSO_4 \cdot 5H_2O$ during heating in He at a heating rate of 20°C min^{-1}.

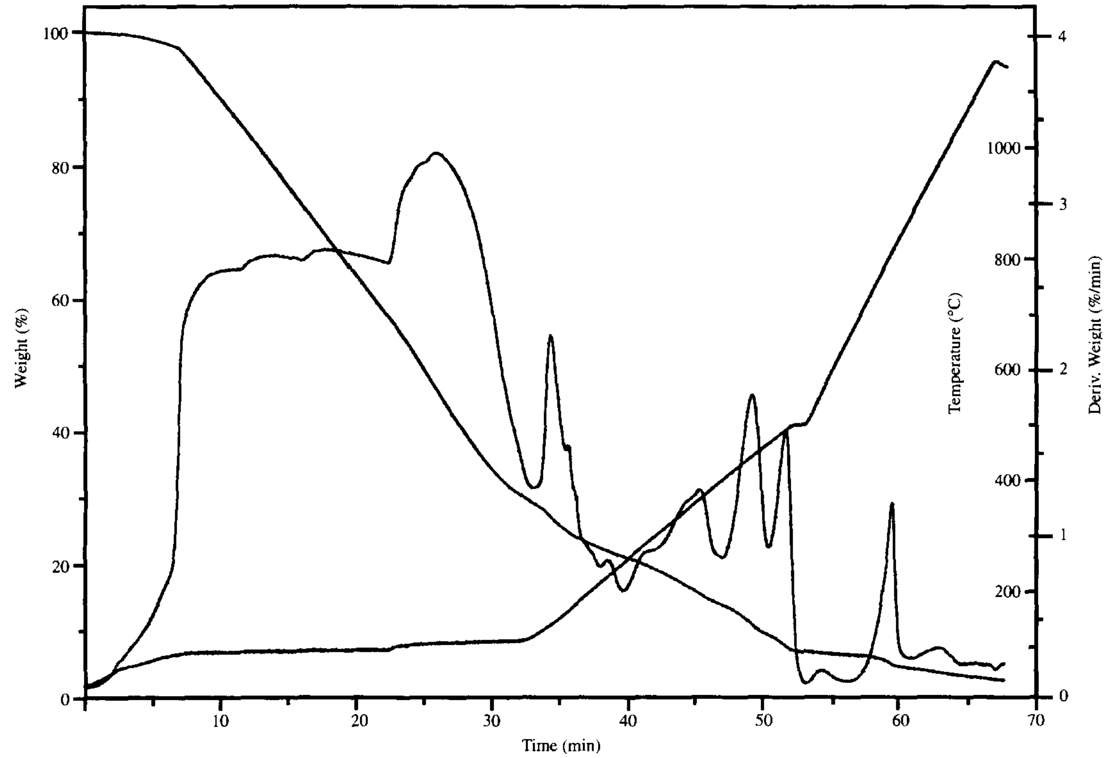

Fig. 6. TG–DTG plot of a waste product in Ar at different heating rates.

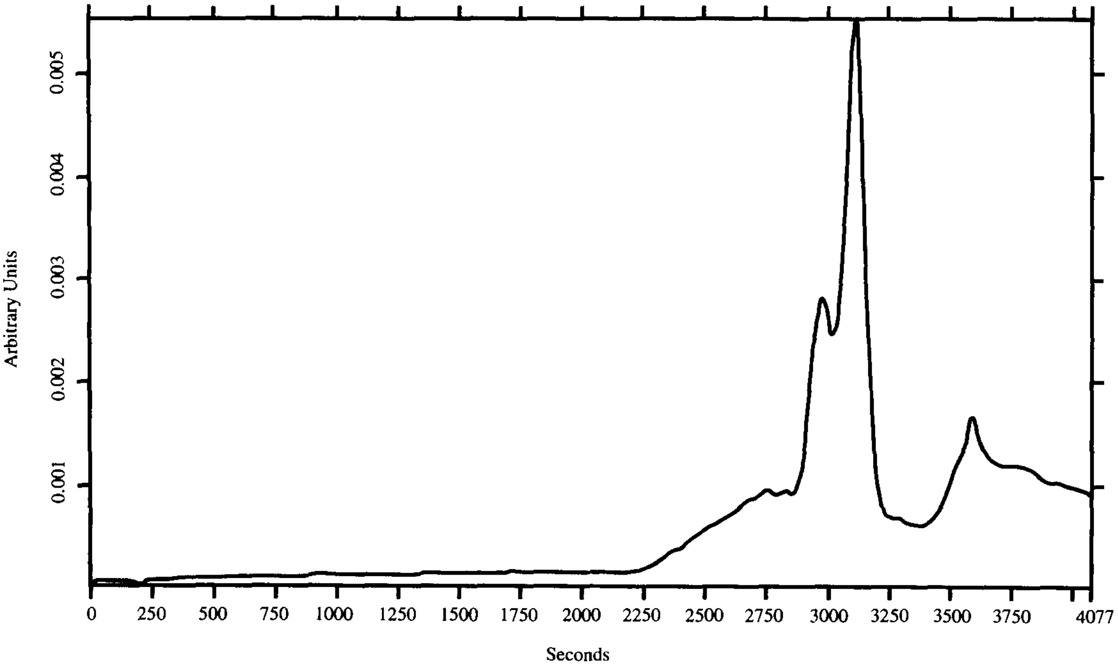

Fig. 7. Total (600–4000 cm^{-1}) FTIR spectrum versus time (or temperature) of gases released by heating of a waste product in Ar.

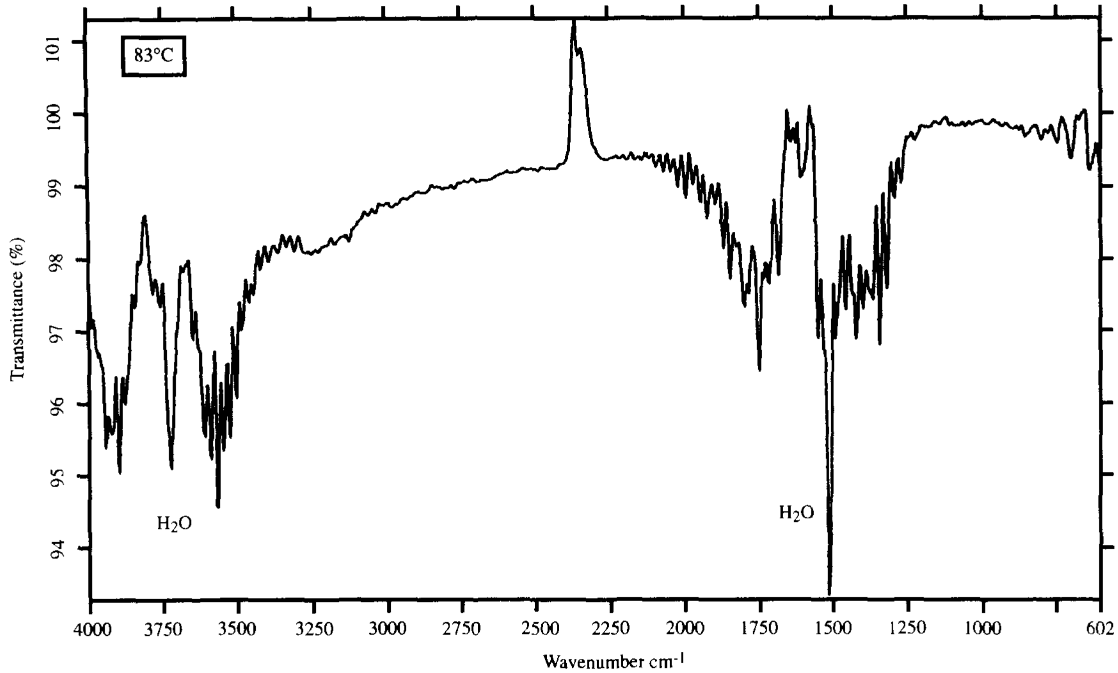

Fig. 8. FTIR spectrum of gases released by heating of a waste product in Ar at 83°C.

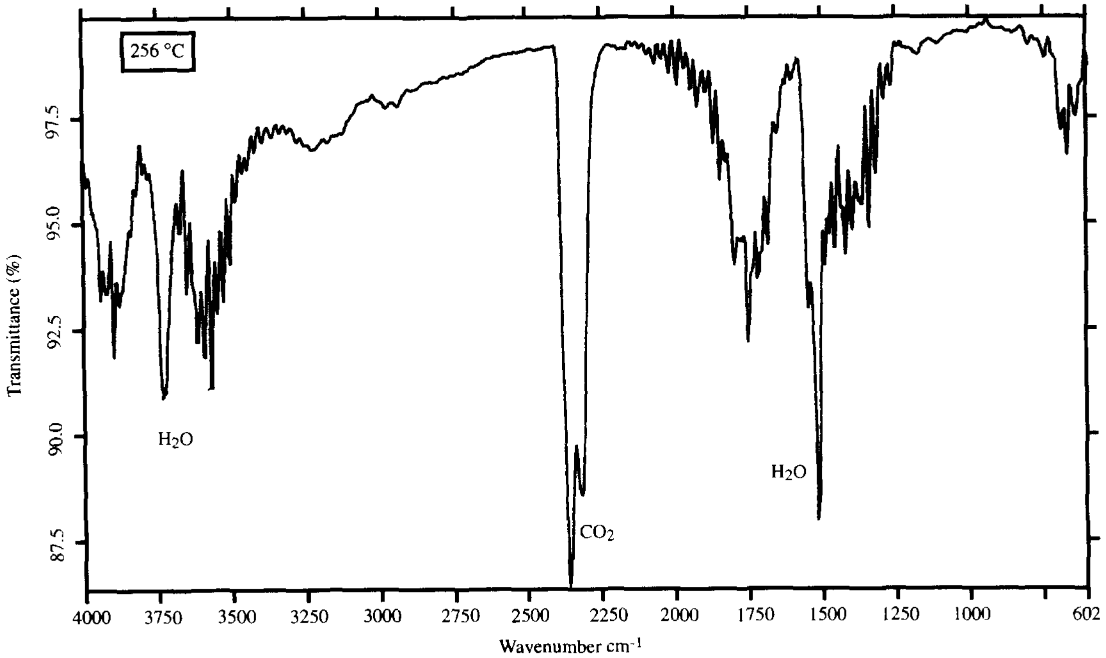

Fig. 9. FTIR spectrum of gases released by heating of a waste product in Ar at 256°C.

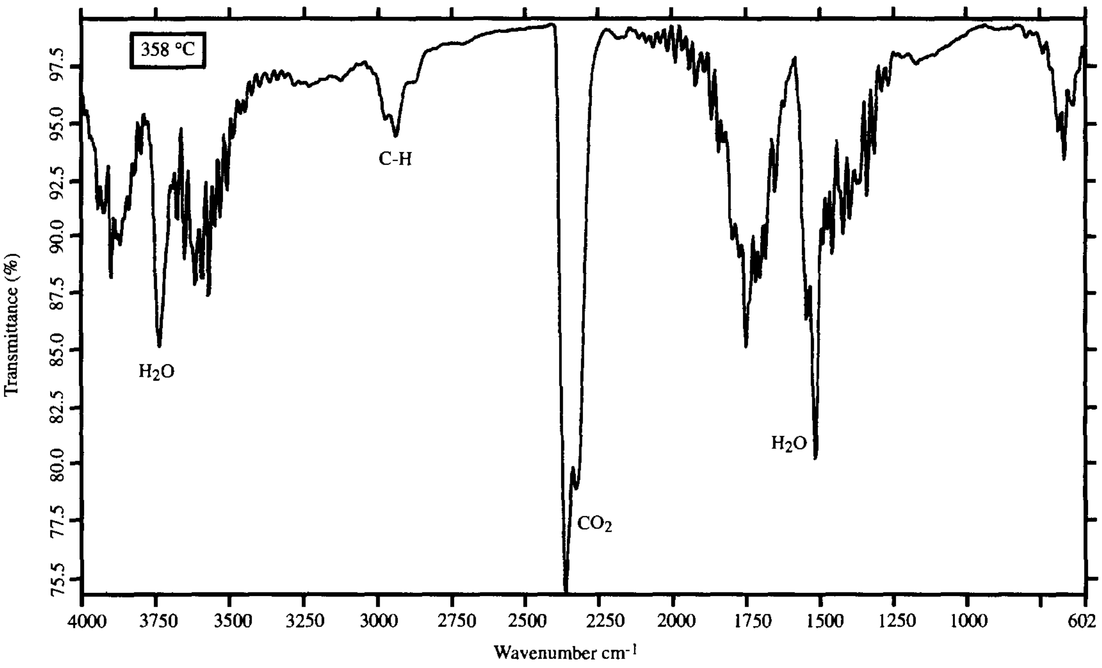

Fig. 10. FTIR spectrum of gases released by heating of a waste product in Ar at 358°C.

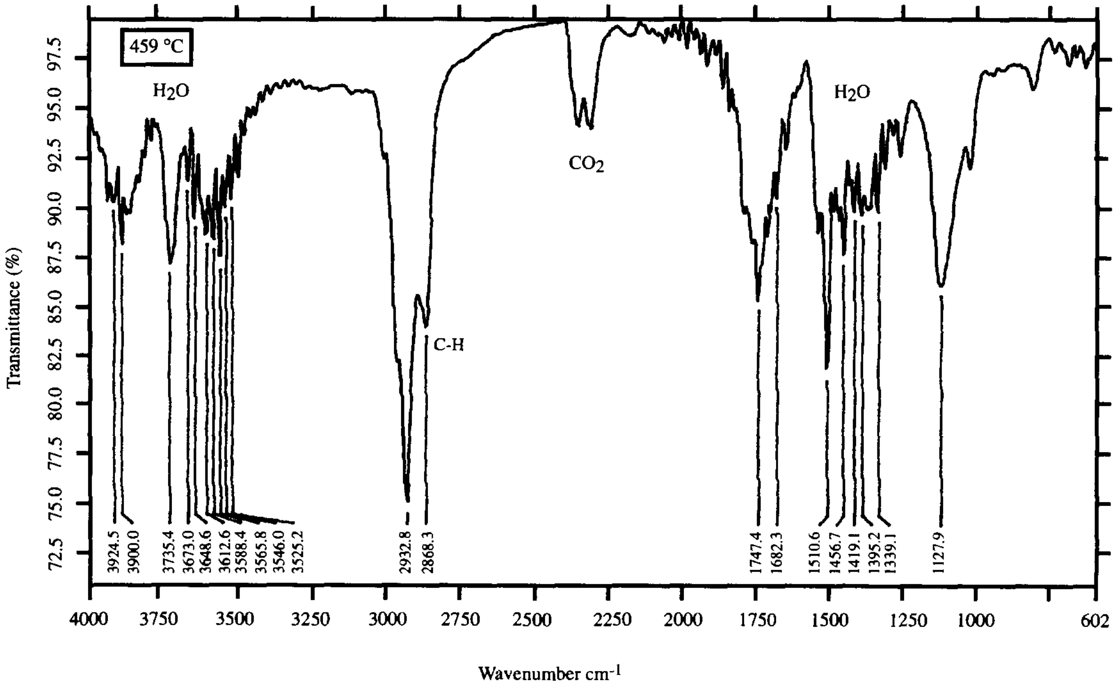

Fig. 11. FTIR spectrum of gases released by heating of a waste product in Ar at 459°C.

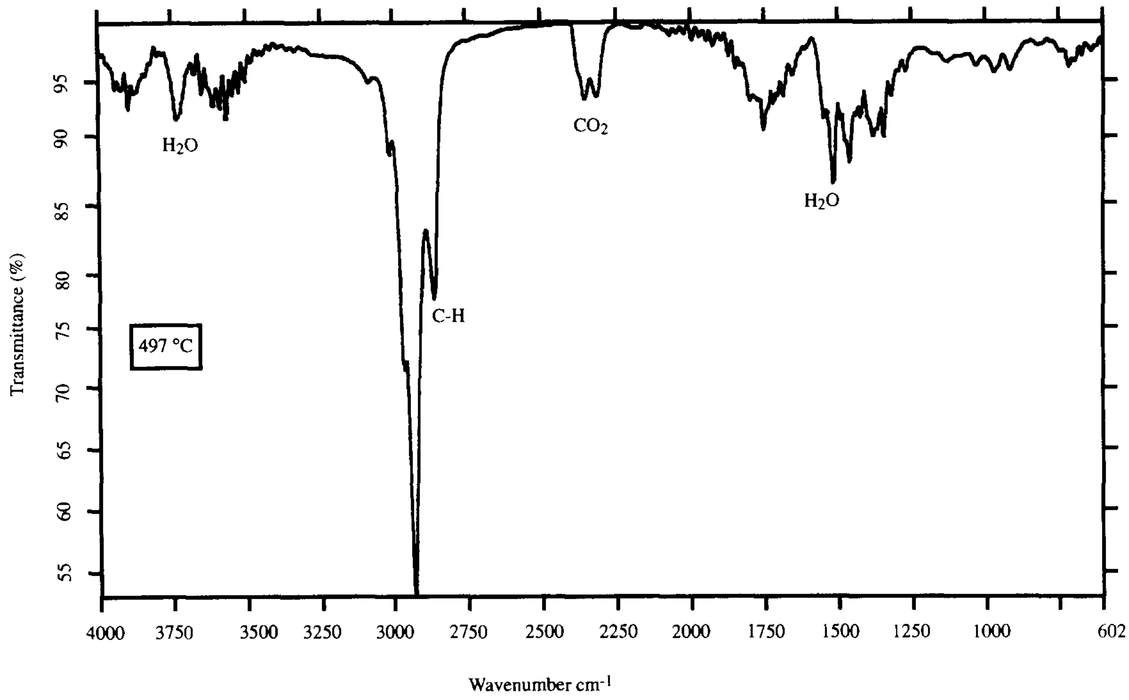

Fig. 12. FTIR spectrum of gases released by heating of a waste product in Ar at 497°C.

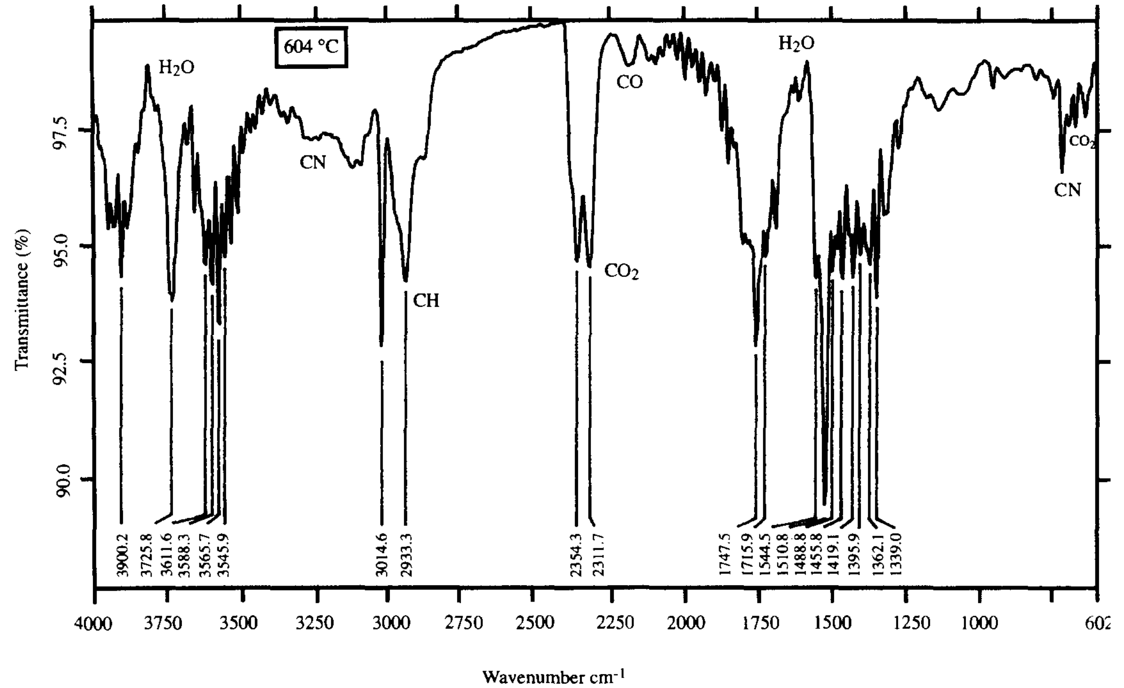

Fig. 13. FTIR spectrum of gases released by heating of a waste product in Ar at 604°C.

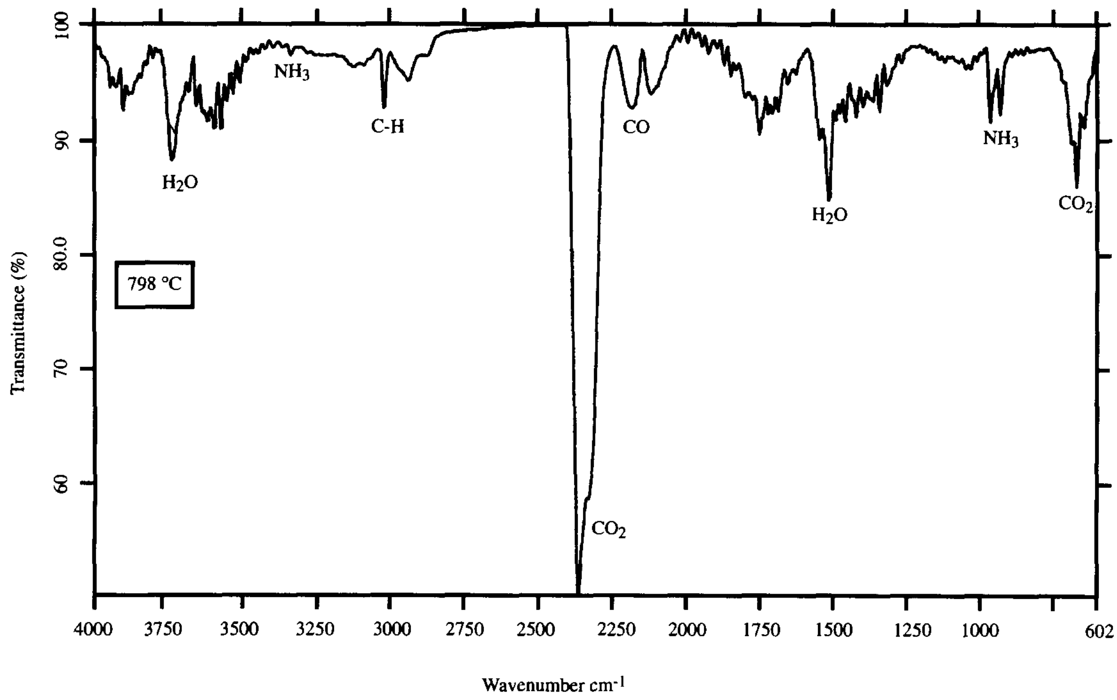

Fig. 14. FTIR spectrum of gases released by heating of a waste product in Ar at 798°C.

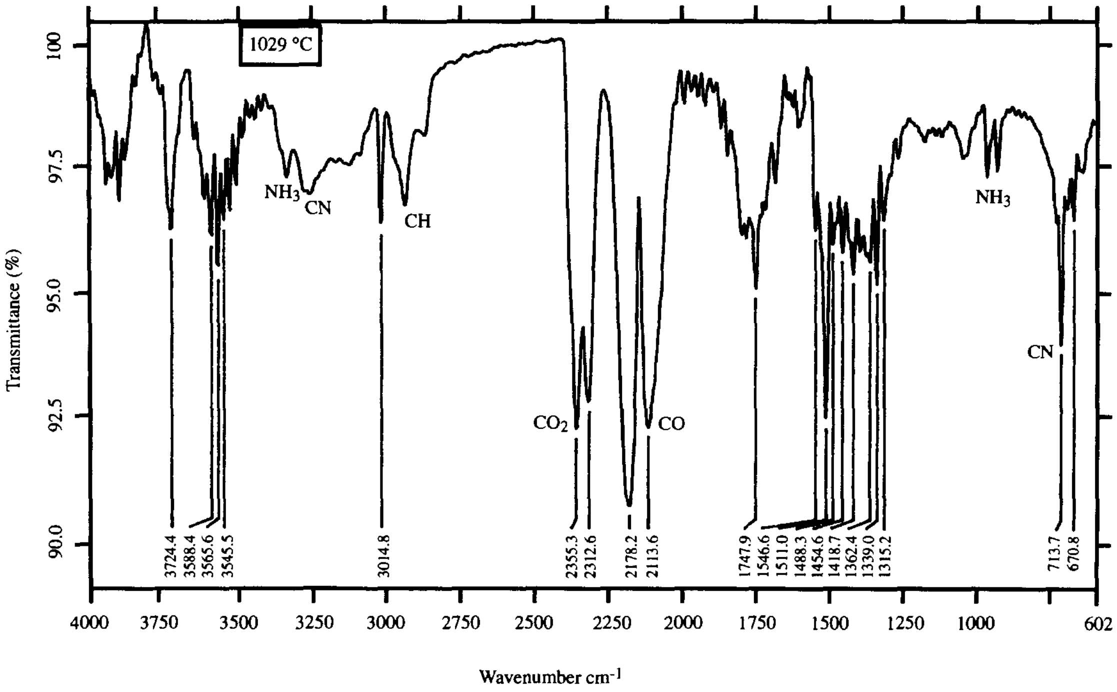

Fig. 15. FTIR spectrum of gases released by heating of a waste product in Ar at 1029°C.

increases as a function of temperature whereas the CO_2 bands decrease. Around 500°C (Fig. 12), the CH absorption band is the most important. From 600°C, again more CO_2 is detected. At a temperature of 800°C, characteristic bands of NH_3 (930, 964 and 3330 cm^{-1}) are detected. In Fig. 15, the presence of bands at 713 and 3260 cm^{-1} is an indication of the presence of HCN in the evolved gases.

In order to have an unambiguous qualitative and a semi-quantitative identification of the HCN, an additional experiment is carried out. A second TG experiment is performed on a 142 mg sample and the evolved gases are collected in a 1% NaOH solution. Successive collection is done at three different temperatures: 25–100°C, 100–500°C and 500–1150°C. The determination of CN^- is performed by photometry using a Lachat Quickchem AE flow-injection analyser (FIA). The total cyanide is converted to cyanogen chloride, CNCl, by reaction with chloramine-T at $pH < 8$. The CNCl then forms a red-blue dye by reacting with pyridine-barbituric acid reagent. The colour is read at 570 nm.

The results are less than 0.1 μg for the first solution, 15 μg for the second one and 66 μg for the third one indicating that indeed HCN is released at high temperatures but with absolute concentrations in the ppm level.

4. Conclusion

These examples of on-line combinations (TG–MS and TG–FTIR) and off-line combinations (TG–GC–MS and TG–FIA–photometry) are good examples of the possibilities of the combination of complementary analytical techniques for the study of different materials. These examples also illustrate that depending on the variety of the released gases, successive collection of samples at different temperatures or times in different solvents or on different absorbents offers additional possibilities for the combination of results obtained from thermal analysis with these other techniques.

Taking into account the broad gamut of additives that are present in many materials, it is only by the combination of the results from thermal analysis with other techniques (such as FTIR, AAS, ICP, IC, GC–MS, potentiometry, X-ray techniques, etc.) that a complete quantitative and qualitative information can be obtained. More applications can be found in an unlimited spectrum of materials going from polymers [2] to materials such as coal [4], clays [5], ferroelectric materials [6] and superconductors [7–9].

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