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The thermogravimetric analyser - coupled - Fourier transform infrared/mass spectrometry technique

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Abstract

A thermogravimetric analyser was coupled to a Fourier transform infrared and a mass spectrometer in parallel to form a TGA - coupled - FTIR/MS system. This has been optimised to enable quantitative determination of the volatiles released from samples under investigation. The system itself and the modifications necessary to perform quantitative determinations are described in this contribution.

Calibration experiments indicate that the present system is able to determine quantiatively polar and non-polar components with boiling points up to about 250°C. For polymer research, the TGA - coupled - FTIR/MS system is especially suited to determine residual solvent, residual monomer and the released components in the earliest stage of a thermal degradation process.

Keywords: Simultaneous TGA/FTIR/MS; TG; TGA; TGA/FTIR coupling; TGA/MS coupling

1. Introduction

The relatively simple equipment needed for thermogravimetric analysis (TGA) and its high degree of automation has made this technique very popular. In polymer research in particular, it is often used to study the thermal stability of polymeric systems under practical conditions.

These systems often show complex TGA mass/temperature curves in which multiple decomposition products correspond with the weight change observed. TGA has thus

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proven to be an excellent quantitative technique, but it is less suitable for specification. This drawback can be eliminated if the components which are causing the mass loss detected are analysed simultaneously, the so-called evolved gas analysis (EGA). Several TGA–EGA systems are described in the literature, analysing the evolved gases by different techniques, i.e. thermal conductivity, cold-trapping followed by GC, mass spectrometry (MS) and infrared (FTIR). MS and FTIR have proven to be the most powerful techniques [1, 2].

User-friendly combinations of TGA/MS and TGA/FTIR with the essential reliable coupling of the various system components, became commerically available from different manufacturers in 1987/1988. Both systems have their own strong points. The MS technique is very sensitive and determines both polar and non-polar components, but is mainly qualitative. The FTIR technique, detecting only components with changing dipole moments, is better suited for quantitative determinations. The FTIR equipment, normally used to measure gas-phase spectra, can also be used in the diffused reflectance mode. This offers an additional possibility in the investigation of a thermally treated sample, i.e. a TGA residue.

However, the results of one single detection technique are often not sufficiently unambiguous to identify a certain component. A TGA coupled with both FTIR and MS (in parallel) should be a much stronger combination. In 1990, however, such a combination was not commercially available from one single manufacturer.

The need for a quantitatively working TGA - coupled - FTIR/MS system was felt strongly in our laboratory: mainly to study the first stage(s) of polymer degradation processes, but also to determine small amounts of residual solvent and/or residual monomer(s) in polymeric systems. A Perkin-Elmer TGA - coupled - FTIR system was purchased in 1990. This system was adapted to allow quantitative determinations. Such a quantitative TGA - coupled - FTIR sytem was described in the same year by Mittleman [3]. A Balzers MS was subsequently purchased and coupled, using the method described by Dufour and Raemaeckers [4], in parallel with the TGA - coupled - FTIR, resulting in a TGA - coupled - FTIR/MS system. The results of the first measurements made clear that further system adaptations were necessary to perform the desired quantitative measurements. The TGA/FTIR coupling, the TGA/MS coupling, the system modifications, and some typical calibration results are reported in this contribution.

2. Experimental

2.1. The TGA–FTIR coupling

The original Perkin-Elmer 'vertical furnace' TGA is shown in Fig. 1A. The glass ball-joint coupling offers the opportunity to move the furnace tube downwards (hydraulically) in order to put a sample into the sample pan. The helium purge gas flow (60 ml min^{-1}) is simple and shown in Fig. 1A.

The glass ball part of the ball-joint was replaced by Perkin-Elmer to mount a stainless steel capillary lined with a PTFE (teflon) tube, see Fig. 1B. The evolved TGA

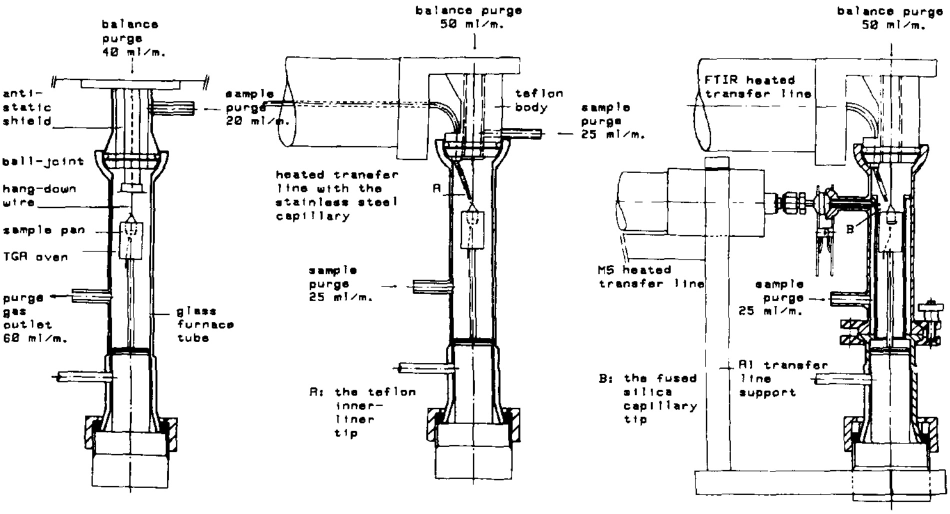

Fig. 1. A. The Perkin-Elmer vertical furnace TGA 7 system. B. The TGA 7 with a flexible, heated TGA-FTIR transfer line. C. The TGA 7 with flexible, heated TGA-FTIR and TGA-MS transfer lines.

gases are sampled just above the sample pan and pass down the heated PTFE line to a 5 cm long, single-pass heated FTIR gas cell. The increased helium purge gas flow now enters the TGA furnace via three different entrances, see Fig. 1B. This whole gas flow (100 ml min^{-1}) leaves the system via the heated capillary/FTIR gas cell.

The use of a PTFE inner-liner (inner diameter 1.15 mm) allows simple, rapid replacement upon fouling. The total volume of the transfer line and gas cell is about 5.8 ml (gas cell, 4.8 ml). This results in a TGA-FTIR transfer time of about 3.5 s. The temperature of the transfer line and the gas cell are continuously variable between 20 and 230°C. The heated gas cell is fitted with spring-loaded KBr windows to maintain a gas seal at all operating temperatures.

2.2. The TGA-GTIR/MS coupling

The TGA - coupled - FTIR furnace tube was modified by Balzers according to the ideas of Dufour and Raemaeckers [4] to connect with the MS heated transfer line, see Fig. 1C. The MS interchangeable capillary tip is shifted as close as possible to the TGA sample pan. This tip forms the end of a fused silica capillary (inner diameter 0.25 mm) which is connected with the MS and can be heated up to 400°C. The FTIR capillary tip/TGA sample pan distance remains constant when the furnace tube moves downwards to open the system for the sample loading procedure. The MS capillary, however, is connected with the moving part of the furnace tube. Hence, the MS capillary tip must be positioned in such a way that this tip does not hit the TGA sample pan during the downward movement of the vertical TGA furnace.

The total gas purge rate was maintained at 100 ml min^{-1}: a balance purge of 50 ml min^{-1}, a sample purge of 25 ml min^{-1}, and an MS capillary purge of 25 ml min^{-1}. The helium for the MS capillary purge flows between the fused silica capillary and its stainless steel support line from the MS into the TGA. This heated gas stream has to keep the MS capillary tip warm enough to avoid condensation at this critical spot. About 5 ml min^{-1} of the total purge gas flow leaves the system via the MS capillary; the remaining 95 ml min^{-1} purge gas leaves via the FTIR capillary.

The TGA-coupled-FTIR/MS system is drawn schematically in Fig. 2. The Perkin-Elmer 1760-X FTIR is a single-beam improved Michelson interferrometer with a multicoated KBr beamsplitter giving a wavelength range from 370 to 7200 cm^{-1}. The heated FTIR gas cell and a second DTGS IR detector are mounted on an auxilary bench next to the 1760-X FTIR. The primary sample compartment has been left available for 'non-TGA' work, i.e. in our case diffuse reflectance measurements. The TGA–FTIR interface is operated using the screen pages on the 1720-VDU spectroscopy terminal. The Balzers QMG-420-180H MS is a quadrupole analyser with a 1–512 a.m.u. mass range. The system uses a crossbeam ion source with two filaments; the analysis chamber/gas-inlet system operates continuously at 100°C.

The whole system is controlled by three independent computers during an experiment. The TGA is controlled by the PE-7700 computer using its TAS-7 software. The FTIR spectra measured by the 1760-X FTIR are stored in the 1720-VDU spectroscopy terminal. The MS spectra measured are stored in the Tandon 386SX20 computer. The only 'hardware' connection between these three systems is a unit which triggers the 1720-VDU terminal and the Tandon 386SX20 computer to start at the same time with measuring and storing IR and MS spectra. This start can be software-controlled from

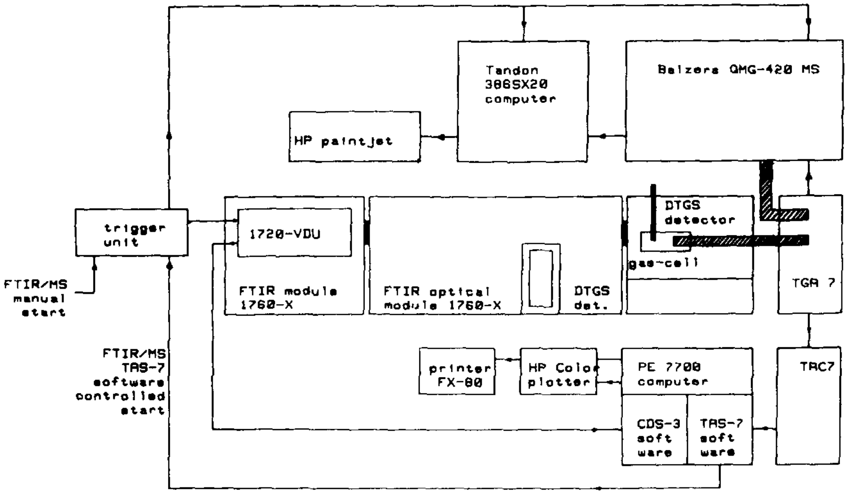

Fig. 2. Schematic diagram of the TGA - coupled - FTIR/MS system.

the TAS-7 software or manual.

2.3. *Modification of the heated FTIR gas cell*

Prevention of any purge gas leakage is of prime importance in order to perform quantitative experiments. Therefore, each experiment has to be begin and end with a measurement of the total purge gas flow. These checks initially indicated that purge gas losses occurred and increased as a function of time, despite tightening all joints on a regular base. The heated gas cell proved to be the weakest point of the system. Creep of the PTFE (teflon) inner gas-cell body caused a slowly increasing purge gas loss each time after tightening and heating. In addition, the thread of the aluminium gas-cell in- and outlet pipe holder (mounted in the aluminium gas-cell body) became worse after each joint-tightening operation.

The teflon inner gas-cell body was replaced by one of polyimide (Vespel). The two (silicone rubber) capillary sealing rings were substituted by two teflon ones, see Fig. 3.

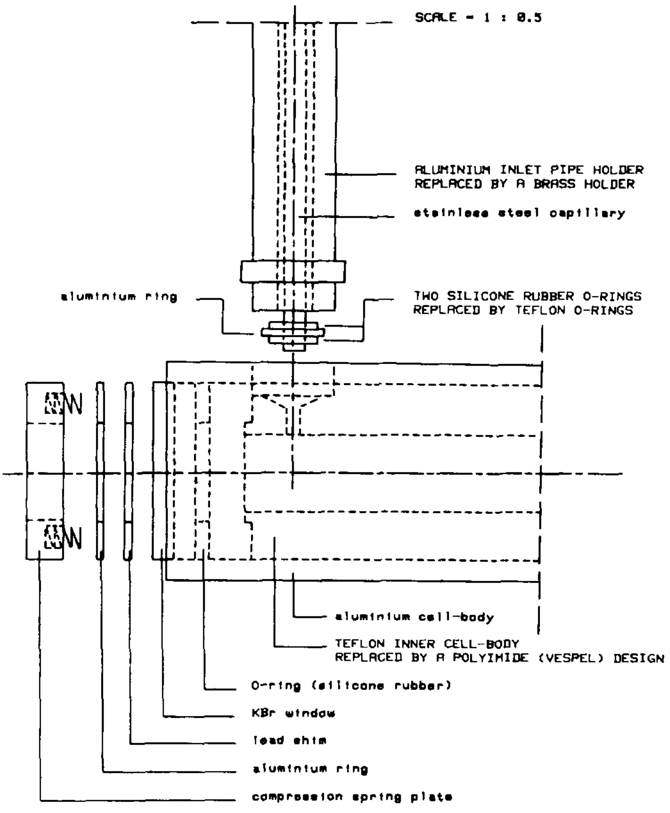

Fig. 3. A (partly) exploded view of the inner assembly of the heated gas cell.

Finally, the aluminium in- and outlet pipe holders were replaced by two new brass holders supported by an extra consolidation strap. These measures proved to be sufficient to prevent any detectable purge gas leakage: (Perkin Elmer has recently also modified its FTIR gas cell; the teflon inner gas-cell body is replaced by one of polyether–etherketone (PEEK)).

2.4. The tempertures of the heated capillary tips

Condensation effects at the opening of the teflon FTIR capillary and in the glass MS interchangeable capillary tip during the first experiments indicated that the temperature in both capillary tips was lower than that in the heated part of the capillaries. Thin thermocouples were mounted on these tips to measure the actual temperatures during an experiment. The measured FTIR/MS capillary tip temperatures at different TGA furnace temperatures are collected in Table 1. It was expected that the lengthened, non-heated FTIR capillary tip would be slightly too low in temperature, but the even lower MS capillary tip temperatures were really disappointing. The heating capacity of the helium sample purge via the MS heated transfer line proved insufficient to compensate for the heat losses in the non-heated end-part of the MS capillary.

An additional external heating source was used to solve this problem. Two Osram Xenophot HLX64 (15 V, 150 W) IR heaters mounted on moveable support arms were used to heat the MS capillary tip; a third one was used to heat the FTIR capillary tip. The three heaters are controlled by one Eurotherm 808 controller with the measuring and alarm thermocouples mounted near the small ball-joint of the MS heated transfer line/TGA furnace coupling, see Fig. 1C. The measurement of the FTIR/MS capillary tip temperatures was repeated using only these extra heating sources (without the TGA furnace) and the results are collected in Table 2. This shows that capillary tip temperatures after this modification can be brought in line with the TGA furnace temperature (and hence the sample temperature), up to about 210/215°C.

2.5. Checking the MS capillary tip location

Only 5% of the total purge gas flow leaves the TGA furnace tube via the MS inlet capillary. The tip of the MS heated capillary must be located in such a way that the MS

Table 1

The FTIR/MS capillary tip temperatures as a function of the TGA furnace temperature (FTIR/MS heated transfer lines at 200°C)

TGA furnace temperature/°C	FTIR capillary tip temperature/°C	MS capillary tip temperature/°C
50	61	40
100	74	55
150	92	73
200	106	92

Table 2
The FTIR/MS capillary tip temperatures as a function of the external heaters controlling temperatures (FTIR/MS heated transfer lines at 200°C)

IR heaters control temperature/°C	FTIR capillary tip temperature/°C	MS capillary tip temperature/°C
50	73	52
100	113	105
150	163	159
200	215	212

sample intake is representative of the evolved gas mixture. The only way to check this aspect is to compare the shape of the DTGA curve (TGA mass/time first derivative) with that of the MS concentration/time curve for a single component. A resin sample containing a certain amount of residual xylene proved to be a suitable calibration material for this purpose.

About 16 mg of this sample was heated in the TGA from 30 to 250°C at a rate of 5°C $\min^{-1}$. The xylene was driven out of the highly viscous resin matrix in at least four discrete steps resulting in a sharp-peaked DTGA curve, see Fig. 4. The $m/z = 106$ (xylene) concentration/time curve measured by the MS is shown in Fig. 4B. The similarity between the curves was encouraging; the four main peaks of the DTGA curve

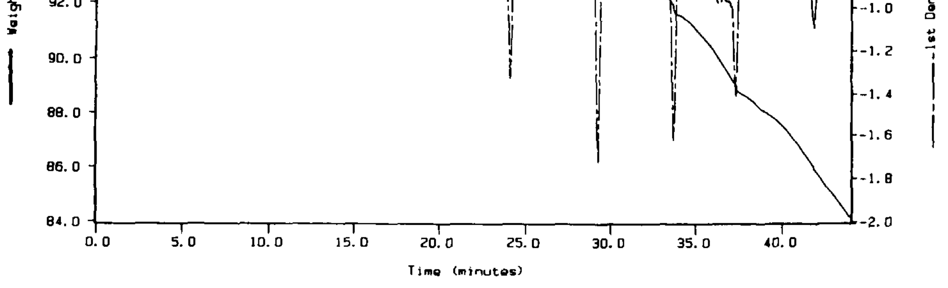

Fig. 4. A. The release of xylene from resin sample M7 as measured by TGA (mass loss) and DTGA (mass loss rate).

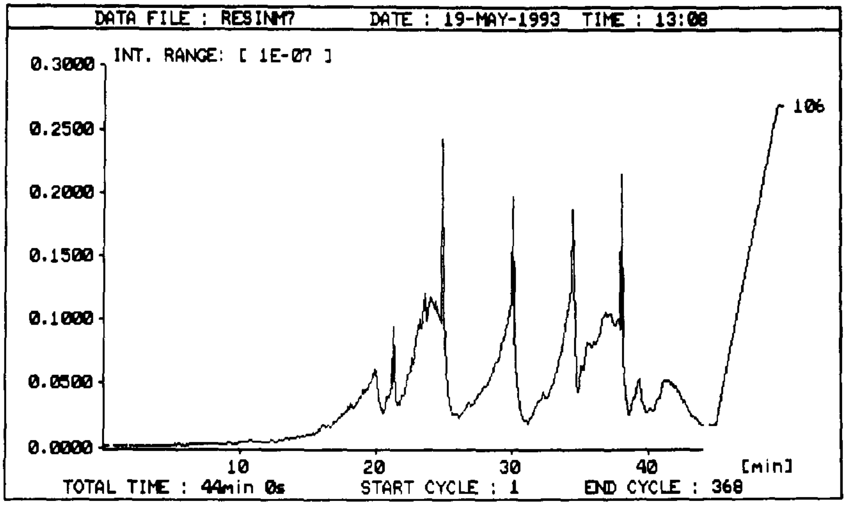

Fig. 4. B. The release of xylene from resin sample M7 as measured by the MS.

appeared about one minute later in the MS concentration/time curve. These results confirmed the proper location of the MS heated capillary tip.

3. Single-component calibration

The linear relation between the IR absorption and the sample concentration makes it possible to calibrate the TGA-coupled - FTIR system for the determination of the total amount of components released during a TGA experiment. The improved FTIR capillary tip temperature (up to 215°C) prompted us to attempt the quantitative determination of components with boiling points clearly higher than 200°C.

The relation between the MS Secondary Electron Multiplier (SEM) detector current measured per *m*/*z* value and the concentration of a mass component in a sample depends mainly on the SEM detector voltage and characteristics, the MS inlet pressure and the MS heated transfer line temperature. Also the polarity of the measured component versus the polarity of the heated capillaries (FTIR, telfon, apolar; MS, fused silica, slightly polar) might play an important role. Given this number of variables, quantitative MS component determinations are more complicated than quantitative FTIR component determinations, but they might be possible if at least a part of the calibration curve is linear.

The limitations for a quantitative determination of components (both by FTIR and MS), mainly set by the maximum capillary tip temperatures, were investigated by measuring calibration curves with the following pure components: *n*-tetradecane (boiling point 252.5°C, apolar); benzoic acid (boiling point 249.0°C, polar); glycerol, (boiling point 290.0°C, polar).

Five *n*-tetradecane samples with sample weights of between 1 and 8 mg were heated from 30 up to 200°C (rate 5°C min^{-1}) in the TGA using only the three external IR heaters. The TGA mass/time curve in Fig. 5 shows that the *n*-tetradecane sample completely evaporated during these experiments. No traces of condensed product were visible in either capillary tip. Fig. 6A shows an FTIR gas-phase spectrum with a strong CH_2 vibration at a wavelength of 2933 cm^{-1} measured during these experiments. The absorption intensity of this vibration is plotted as a function of the experiment time, i.e. the temperature, in Fig. 6B. The shape of this FTIR intensity/time curve agrees with the TGA first-derivative curve, see Fig. 5.

Subsequently, the FTIR intensity/time curves determined in this way were integrated. These integral values plotted as a function of the TGA sample weights resulted in a TGA-coupled-FTIR calibration curve for *n*-tetradecane.

Fig. 7A shows an MS spectrum of *n*-tetradecane measured during these experiments. It is a typical 'linear alkane' spectrum with the highest m/z value of 198 from the molecular ion of *n*-tetradecane and a fragment-spectrum with m/z values differing by one CH_2 group and an abundance maximum around the C3 and C4 fragments [5]. The intensity of fragment $m/z = 57$ is plotted as a function of the (experiment) time in Fig. 7B. The shape of this MS intensity/time curve also agrees with the TGA first-derivative curve, see Fig. 5. The MS intensity/time curves determined in this way were subsequently integrated. These integral values plotted as a function of the TGA sample weights resulted in a TGA-coupled-MS calibration curve for *n*-tetradecane.

Calibration curves for (polar) benzic acid were measured in the same way without any problem. Glycerol was measured without any problem for the TGA - coupled - FTIR system; however, the strongly polar vapour was not able to pass the tip region of

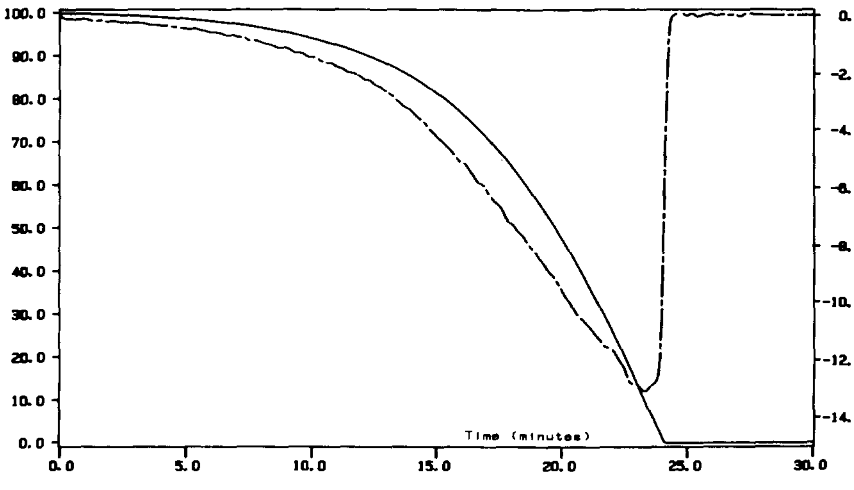

Fig. 5. The evaporation of *n*-tetradecane as measured by TGA (mass loss) and DTGA (mass loss rate).

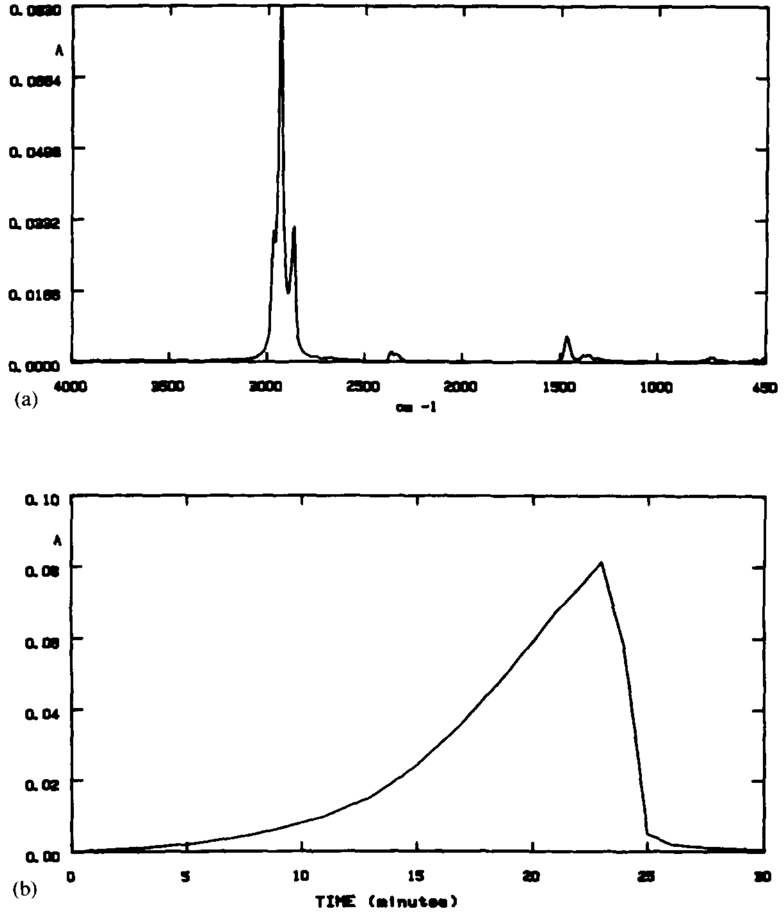

Fig. 6. A. The FTIR spectrum of *n*-tetradecane vapour. B. The intensity of the CH_2 vibration absorption of *n*-tetradecane vapour as a function of the measuring time.

the MS inlet capillary. The three FTIR calibration curves thus measured are shown in Fig. 8A. These curves for 'high' boiling point components proved to be linear over the whole concentration range investigated, with only small deviations from zero for a sample concentration of zero. A series of TGA-coupled-FTIR calibration curves measured on 'low' boiling point components, see Fig. 9, confirmed the linear behaviour of the systems. These results agree with the experimental results reported by Mittleman [3] for CO_2, SO_2 and NH_3.

Fig. 8B shows the two MS calibration curves measured for *n*-tetradecane and benzoic acid. Both curves show a linear region for the lower concentrations only. These lower concentrations, however, cover our area of interest. The MS calibration curve for

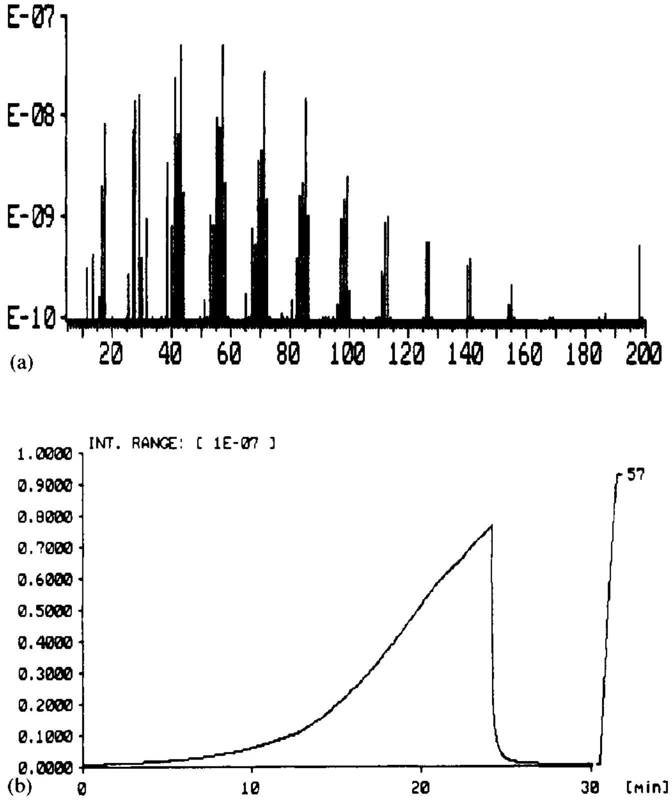

Fig. 7. A. The MS spectrum of *n*-tetradecane vapour. B. The intensity of *n*-tetradecane vapour MS fragment $m/z = 57$ as a function of the measuring time.

water, see Fig. 10, shows that this linearity also holds for 'low' boiling point components. Hence, a careful TGA sample size choice makes quantitative determinations possible, with both the FTIR and MS, for non-polar and polar components with boiling points up to about 250°C.

4. Detection sensitivity/limits

The detection sensitivity of the released components is determined by the TGA variables, sample weight, heating rate, purge gas rate, and specific variables for the FTIR technique and the MS technique as such. In our experiments sample weights between 5 and 50 mg, and heating rates between 0.1 and 10°C min^{-1} are used as experimental variables. The purge gas rate, however, is kept constant. A purge gas rate of 100 ml min^{-1} proved to be a good compromise between an acceptable FTIR

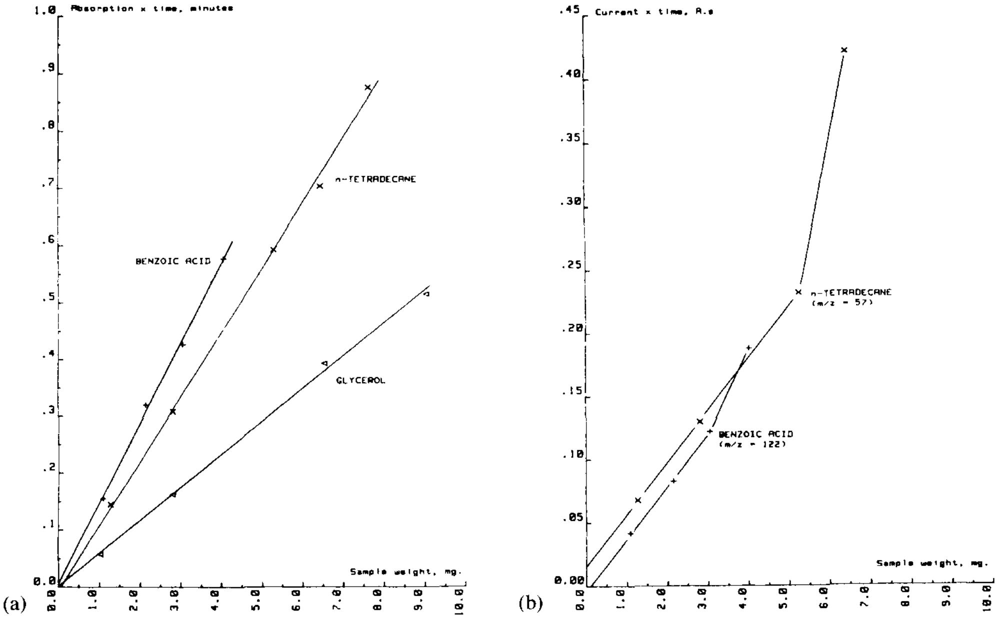

Fig. 8. A. TGA - coupled - FTIR calibration curves. B. TGA - coupled - MS calibration curves.

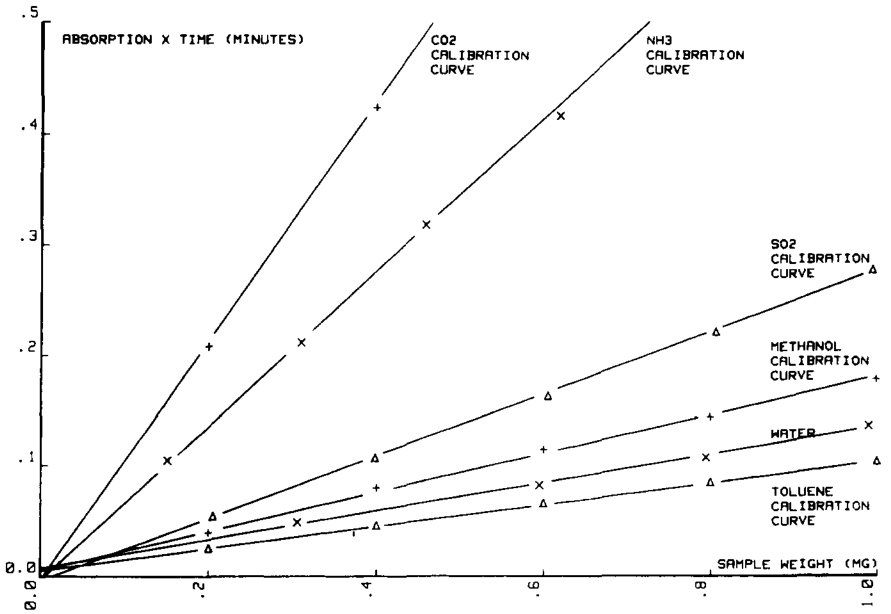

Fig. 9. TGA - coupled - FTIR calibration curves for 'low boiling point' components.

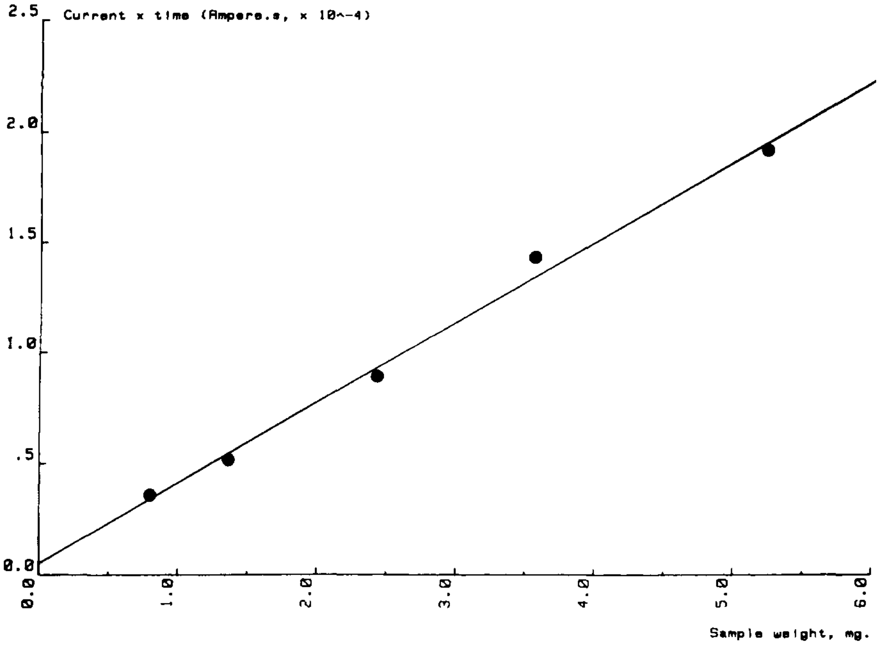

Fig. 10. The TGA - coupled - MS calibration curve for water.

sensitivity and a sufficiently short TGA/FTIR transfer time (and, hence, gave less chance of heated capillary fouling effects). The FTIR detection limit for systems with relatively strong single-component absorption bands, measured under optimised TGA conditions in terms of sample weight and heating rate, proved to be about 50 mg m^{-3}.

Small amounts of reaction water (1–3 mg) released from a thermally treated polymeric system over a time period of about 10 h could not be measured with the FTIR technique. A quantitative water determination was possible, however, by using the more sensitive MS technique. The MS detection limit for water proved to be about 4 mg m^{-3} during these experiments.

5. Conclusions

System optimisation in combination with a proper calibration procedure has resulted in a TGA - coupled - FTIR/MS system capable of performing quantitative component determinations with both FTIR and MS.

Calibration experiments show that the present system is capable of determining quantitatively polar and non-polar purge gas components with boiling points up to about 250°C. This makes the TGA - coupled - FTIR/MS system especially suited for identification and determination of residual solvent, residual monomer and other components released during the earliest stage of a polymer thermal degradation process.

For systems studied thus far, FTIR detection limits of 50 mg m^{-3} and MS detection limits of 4 mg m^{-3} have been observed.

Acknowledgement

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