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Synergic chemical analysis – the coupling of TG with FTIR, MS and GC-MS

1. The determination of the gases released during the thermal oxidation of a printed circuit board

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Abstract

This contribution reports the coupling of TG with FTIR, MS and GC-MS (Synergic chemical analysis). During thermogravimetric analysis the gases evolved are analysed using 'real-time' FTIR and MS. Simultaneously the gases are collected on an absorbent trap (organic trap module, OTM) for subsequent analysis using GC-MS. As an example the technique has been used to identify the products evolved from a printed circuit board during thermal oxidation. The use of TG-FTIR-MS-OTM-GC-MS provided information that could not be available through single techniques alone. For example, it was possible to ascertain the temperature range over which bromophenol was released.

1. Introduction

Thermogravimetric analysis (TG) has become a common technique in the characterisation of materials. In polymers, loss of impurities or thermal degradation are observed as weight losses with respect to time or temperature. However, no chemical information about the gases evolved on heating can be obtained from TG alone. If the gaseous degradation products are simultaneously analysed using FTIR and mass spectroscopic techniques, evolved gas analysis (EGA), then it is possible to identify the compounds evolved and determine the temperature range over which they are released. There are numerous examples in the literature which reinforce the obvious advantages of TG-EGA [1–9] to identify degradation products. However, cognisance must be taken of two distinct disadvantages. Firstly, the presence of components at very low concentrations may be masked by higher concentration components and secondly the simultaneous evolution of more than one compound may make identification very difficult. However, by incorporating the separation capability of a gas chromatograph (GC) in the system, the components of a complex mixture can be separated. This can be achieved by trapping the gases evolved over the duration of the TG run and performing post-run analysis using gas chromatography-mass spectrometry (GC-MS) [10–12]. Once the identity of individual components is established the interpretation of real time results can be viewed with greater confidence.

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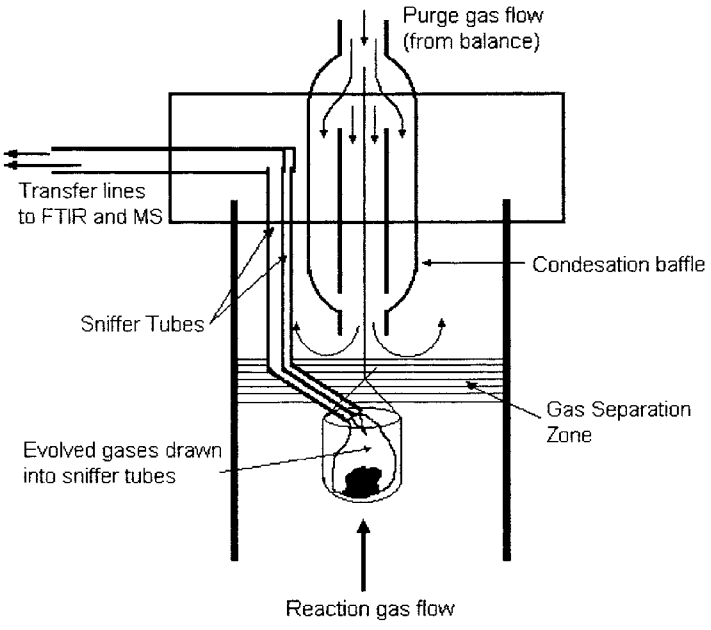

Fig. 1. The Sniffer interface.

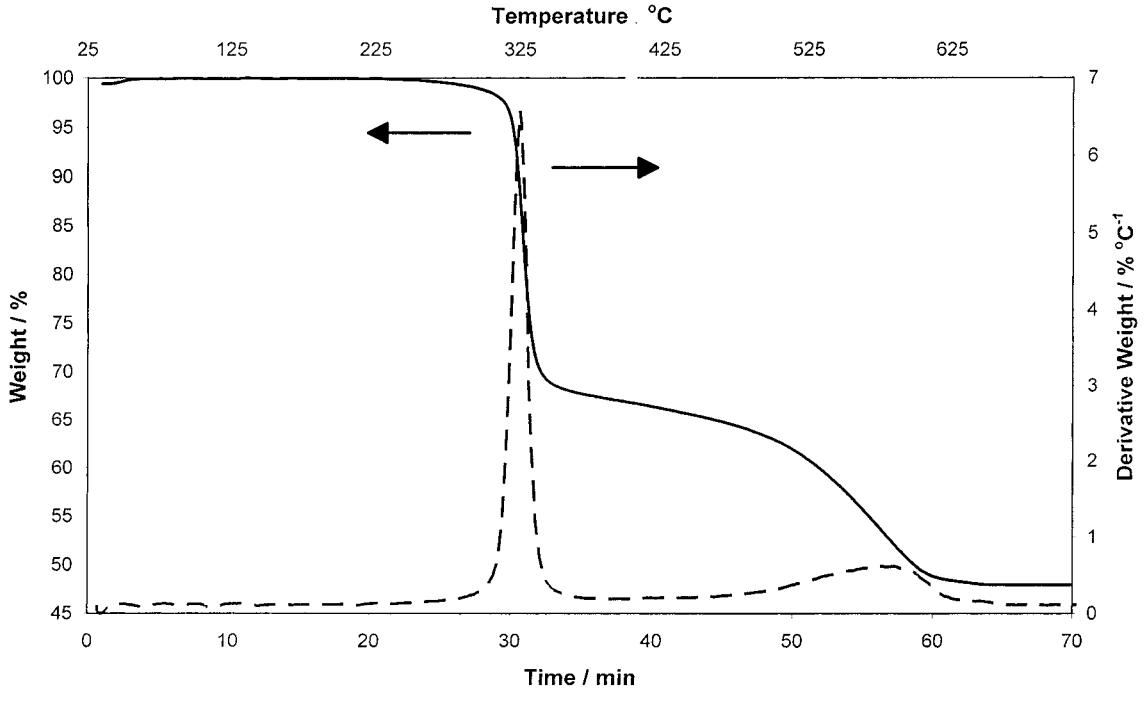

Fig. 2. Weight loss and derivative weight losses for the decomposition of PCB in air.

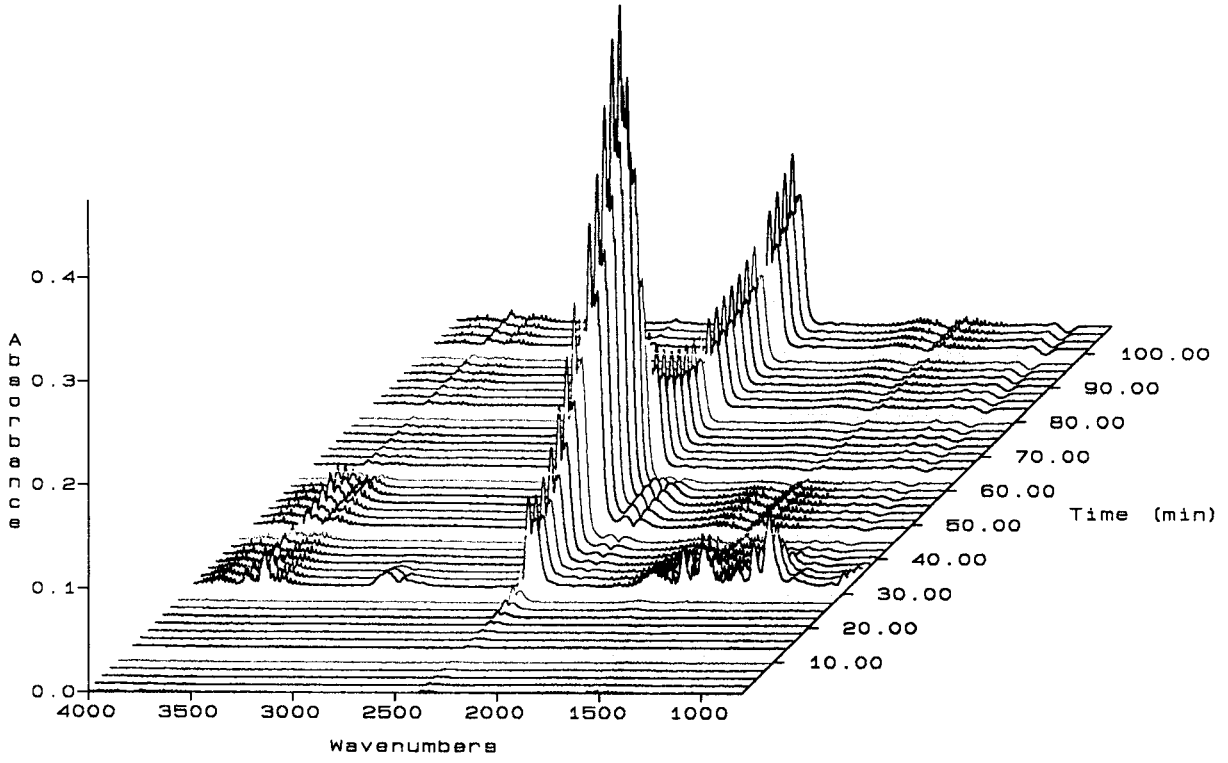

Fig. 3. The FTIR spectra of the gases evolved as the circuit board temperature was raised at 10°C min^{-1}.

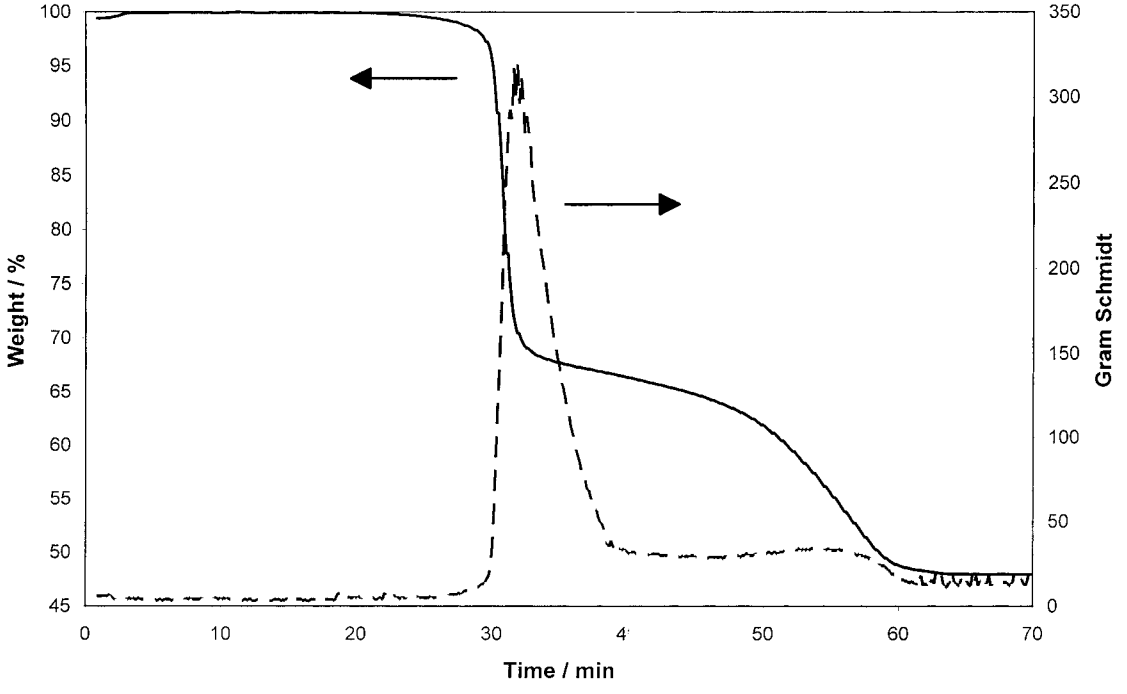

Fig. 4. Correlation of percentage weight loss with the total absorption observed in TG-FTIR.

In the current example the gases evolved during the thermal oxidation of a printed circuit board (PCB) have been identified using a TG-FTIR-MS-OTM-GC-MS, which offers the potential to record real time TG-FTIR, real time TG-MS and post run GC-MS from the same sample.

2. Experimental

Oxidation of a PCB was carried out using a Synergic chemical analysis system, supplied by Thermo Unicam, the heart of which is a Cahn TG-131 thermobalance fitted with two outlets which are connected to heated transfer lines. Samples of PCB (ca. 30 mg) were placed in the TG sample crucible and heated from 25° to 1100°C at a rate of 10°C min^{-1} under a flow of air (40 ml min^{-1}) at atmospheric pressure.

The evolved gases were transferred from the TG to the FTIR and MS via the Sniffer interface (Fig. 1). There are two Sniffer tubes, one each for MS and FTIR sampling respectively, which are constructed from a high temperature alloy and extend to the null flow region just above the sample cup. This arrangement enables the evolved gas to be sampled immediately and minimises any dilution effects [13]. Once sampled the gases entered the heated transfer lines the first of which went directly to a Unicam Automass system 2 quadrupole mass spectrometer. During 'real-time' TG-MS analysis the spectrometer scanned 4–500 amu every 1.5 s. A needle valve was used to restrict the flow of gases from the TG to the MS in order to maintain the integrity of the MS vacuum.

The second transfer line was connected to an infrared gas cell contained in a TG–IR interface (Mattson) which was linked to a Mattson Infinity series FTIR spectrometer. The outlet from the infrared gas cell flowed into a third transfer line which was connected to an absorbent trap (e.g. VOCARB 4000, Supelco) contained in an organic trap module (OTM, Cahn).

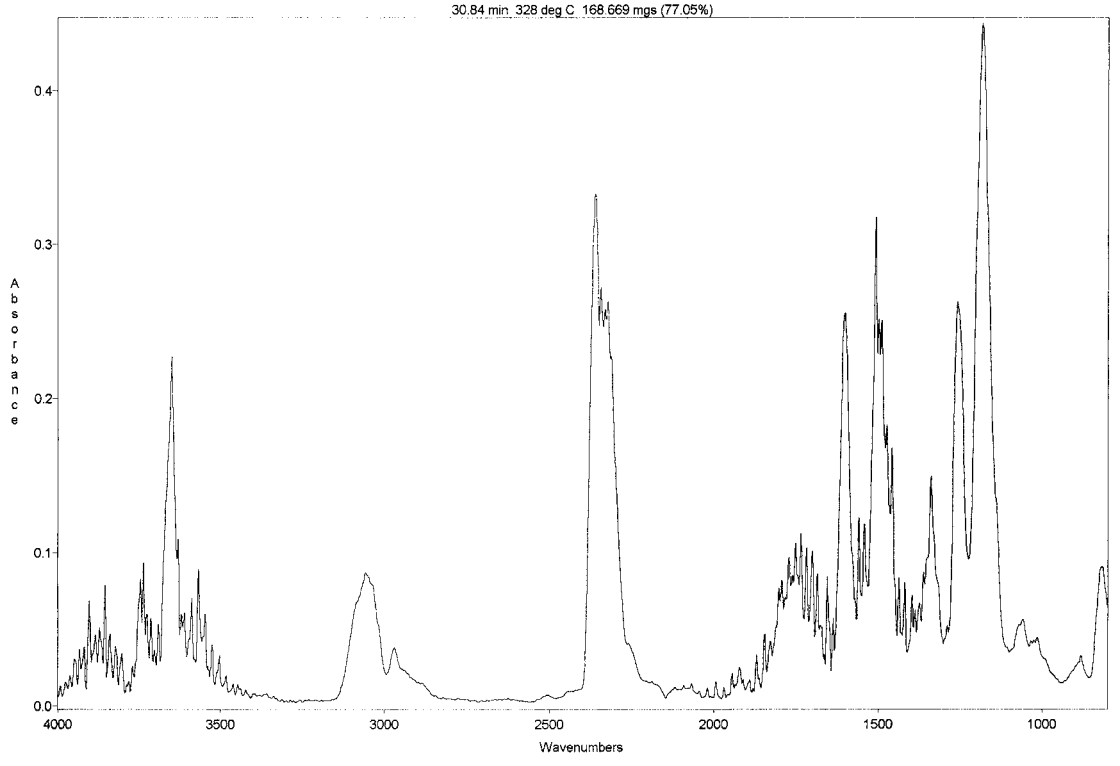

Fig. 5. Composite FTIR spectrum of the mixture of gases passing through the IR cell at 30.84 min (328°C).

The outlet of the OTM was connected, via a fourth transfer line, to the GC-MS (Automass System 2, Unicam).

Throughout the analyses, the gases released from the samples were collected on the absorbent trap. On completion of the analysis the contents of the trap were thermally desorbed onto the GC column (DB-1, 30 m × 0.25 mm i.d. ×0.25 μm d.f.). During thermal desorption the trap was heated to 250°C and helium passed through the absorbent bed for 4 min during which time the GC was held at 35°C while the contents of the trap were desorbed. The column was then heated at 5°C min^{-1} to 250°C and held at the upper temperature for 5 min. During the OTM-GC-MS analysis the MS scanned a mass range of 4–1000 amu every 1.5 s. On completion of the analyses the traps were baked at 300°C in an oxidising atmosphere for >3 h. After baking, a blank desorption run was used to confirm the cleanliness of the trap before further use.

The TG-FTIR transfer line was a rigid quartz tube maintained at 240°C. All other transfer lines were flexible, silica-lined, stainless steel tubing heated to 250°C. The length of the transfer lines was kept to a

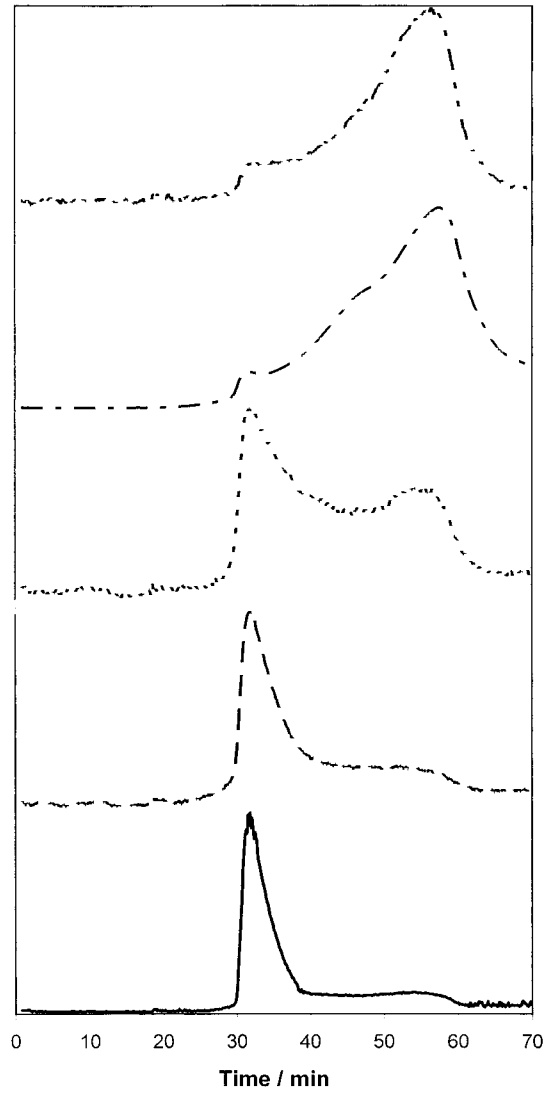

Fig. 6. Reconstructed TG-FTIR chromatograms for (from bottom to top) the total IR signal (4000–800 cm^{-1}); aromatic species (3150–3000 cm^{-1}); water (4000–3800 cm^{-1}); CO_2 (2500–2250 cm^{-1}); and CO (2250–2150 cm^{-1}).

Table 1
Volatile compounds evolved from the PCB, trapped using the OTM and subsequently desorbed and identified using GC-MS

Retention time/mm : ss	Compound
04 : 25	Acetic acid
04 : 55	Toluene
05 : 22	Dibromoethane
07 : 03	*o*-Xylene
07 : 10	Tribromomethane
07 : 38	*p*-Xylene
07 : 53	Dibromopropane
08 : 16	Methoxybenzene
08 : 34	Bromobenzene
08 : 45	Dibromopropane
09 : 42	Tribromoethane
10 : 38	Benzofuran
11 : 29–12 : 54	Phenol
13 : 24	Bromophenol
13 : 55	Methylphenol
14 : 21	Methylbenzofuran
14 : 32	Methylphenol
15 : 50	Bromomethylphenol
16 : 08	Ethylphenol
16 : 20	Dimethylphenol
16 : 27	Dibromobenzene
17 : 06	Dibromobenzene
18 : 46	Ethylmethylphenol
19 : 27	Propylphenol
19 : 35	Phthalic anhydride
21 : 09	Dibromophenol
21 : 48	Dibromophenol
23 : 45	Tribromobenzene
25 : 10	Dibenzofuran
30 : 11	Tetrabromobenzene

minimum. The TG–IR interface consisted of a gas cell (10 cm path length) that was heated to 250°C to prevent condensation on the KBr windows. The detector was a wide band mercury-cadmium-telluride (MCT) (4000–800 cm^{-1}) and 16 scans were acquired every 10 s at a spectral resolution of 4 cm^{-1}.

3. Results and discussion

3.1. TG-FTIR

Fig. 2 presents the weight loss and the associated derivative thermogram (DTG) of the PCB as a function of time and temperature during heating at 10°C min^{-1} in dry air. Fig. 3 shows how the FTIR spectrum of the evolved gases changed throughout the analysis while the total infrared absorbance profile is plotted against time in Fig. 4. Comparison of the DTG trace and the total infrared absorbance profile indicates that the positions of the absorbance maxima correlate with the weight losses observed in the TG trace, although there is a delay and some diffusional broadening as the evolved gases pass through the IR cell.

The main weight loss occurs between 280° and 380°C (26–36 min), the FTIR spectra obtained during this interval (Fig. 3) show the presence of a complex mixture containing H_2O (1500–1600 and 3400–4000 cm^{-1}), CO_2 (2250–2500 cm^{-1}), CO (2000–2250 cm^{-1}) and phenol (3700–3600, 3150–3000, 1650–1570, 1540–1440, 1380–1300, 1280–1230 and 1225–1100 cm^{-1}) which is detailed in the spectrum collected at 31 min (328°C) in Fig. 5. Infrared spectra obtained from subsequent weight losses (400–1100°C) indicate the presence of H_2O, CO_2 and CO. Fig. 6 illustrates how the evolution of aromatic species, water CO_2 and CO differed during the oxidation of the circuit board although it is not feasible to differentiate between different types of aromatic species.

3.2. TG-OTM-GC-MS

Additional information about the organic compounds evolved from the PCB during heating was

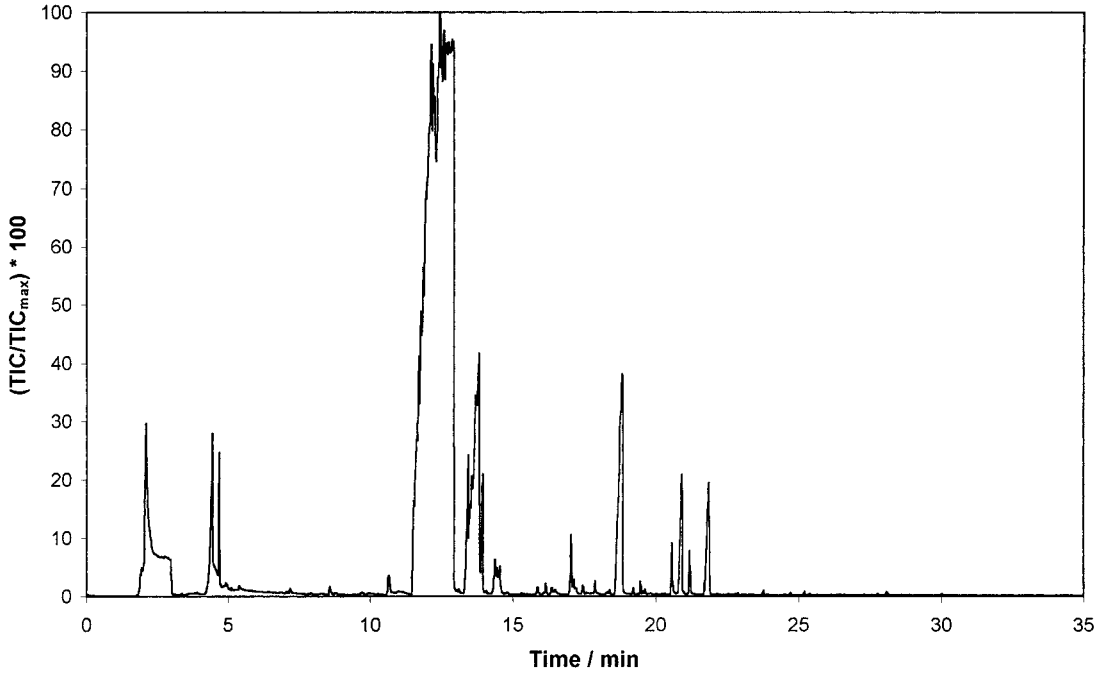

Fig. 7. TIC chromatogram for the complex mixture of compounds collected on the OTM during the oxidation of the circuit board and then subsequently desorbed.

obtained from the GC-MS analysis of the complex mixture of molecules collected on the OTM during the analysis. The total ion chromatogram is shown in Fig. 7 and numerous compounds including several brominated aliphatic and aromatic species (identified using the mass spectral database, Table 1), were found which could not be readily distinguished using only the 'real-time' TG-FTIR or TG-MS data.

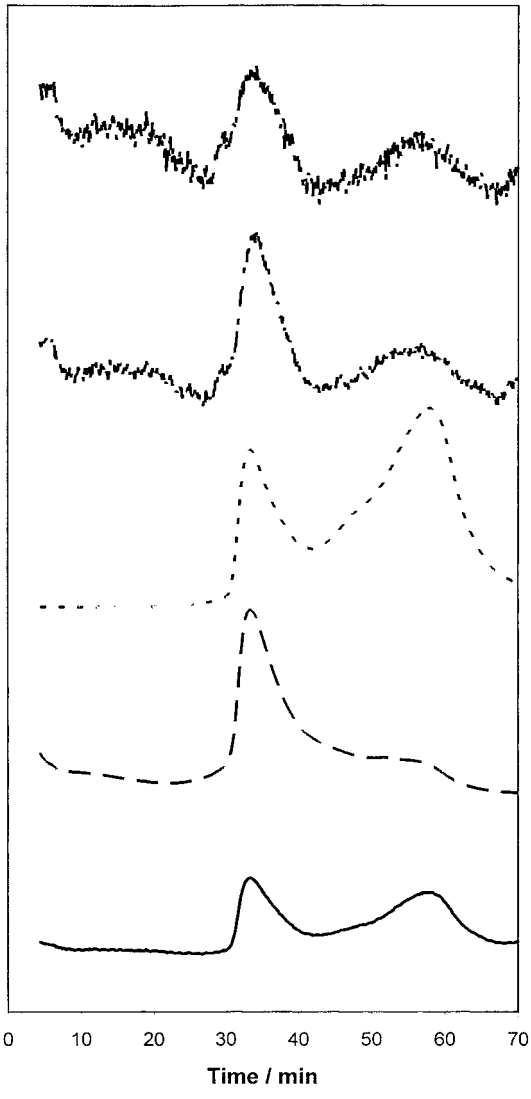

Fig. 8. Reconstructed specific ion chromatograms for (from bottom to top) the TIC; water (m/z = 18 amu); CO_2 (mz = 44 amu); phenol (m/z = 94 amu); bromophenol (m/z = 172 amu).

3.3. TG-MS

The total ion chromatogram, TIC, (Fig. 8) shows an increase in the MS output at 26 min, which corresponds to the first weight loss of the PCB. Characteristic ions can be used to obtain information about when particular compounds are evolved from the sample using the 'real-time' TG-MS data, e.g. 18 amu for H_2O and 94 amu for phenol (Fig. 8). The evolution profiles for water, carbon dioxide and phenol obtained from the 'real-time' TG-MS data were in good agreement with those from TG-FTIR (Fig. 6). However, the information derived from TG-OTM-GC-MS enabled the thermal evolution of bromophenol (m/z 172) to be extracted from the real time MS data. Clearly, the bromophenol evolved along with phenol. TG-FTIR could not have provided this information because the vapour phase spectra of phenol and bromophenol are not sufficiently different. Moreover, the identification of bromophenol from amongst the wealth of different ions in real time TG-MS data would have required considerable effort.

4. Conclusions

The PCB analysed started to degrade at 280°C to form a complex mixture of gaseous products. The use of the OTM-GC-MS facility in the Synergic chemical analysis system facilitated identification of a wide range of degradation products and permitted data regarding the evolution of specific compounds to be obtained. The use of TG-FTIR-MS-OTM-GC-MS provided information that single techniques alone would not be able to provide without considerably more knowledge of the sample.

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