

# The use of a simultaneous TGA/DSC/FT-IR system as a problem-solving tool

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Thermal analysis (TA) of complex samples has been greatly assisted by the coupling of Fourier transform-infrared spectroscopy (FT-IR) analysis to the TA experiment. Evolved gas analysis has been very successful in combined TGA/FT-IR experiments, whereas during a combined differential scanning calorimetry (DSC)/FT-IR experiment, the FT-IR analysis has generally been directed at the sample itself. By combining a simultaneous TGA/DSC instrument with FT-IR evolved gas analysis (STA/IR), we are now able to obtain three sets of complementary information on the same sample in one experiment. An STA/IR study of a sample of zinc stearate was made to demonstrate the operation of the instrument. This demonstrated that the sensitivity of the FT-IR analysis was greater than that of the TG analysis, as a small amount of water vapour was released during the sample melt, even though no weight loss was measured at the same time. Practical applications of this instrument combination include the detailed examination of various formulations of solder paste and an epoxy-based encapsulant. Solder pastes from three vendors were shown to contain different organic species, and to lose these organics at different rates under different atmospheric conditions, to give varying residual levels of organics. The encapsulant samples were shown to contain different, albeit very low, levels of an ester species, which may explain their different physical behaviour.

## 1. Introduction

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) are well established as routine analytical tools for the study of the thermal behaviour of materials. On their own, however, these techniques only provide physical data about a sample, although a skilled analyst can often deduce some chemical properties from these results. Fourier transform-infrared (FT-IR) spectroscopy, on the other hand, is able to obtain chemical information about a thermal process much more directly, and with a higher degree of confidence.

As an example, a material may show a DSC endotherm at a certain temperature which, as a single datum, is not very informative. Thermogravimetric analysis on the same sample may show a weight loss at the same temperature, thus indicating that the process is not just a simple melting, but involves the loss of some material. These two pieces of information still do not define the process, which could be loss of water of crystallinity, loss of a minor component, or even thermal degradation. By sweeping the gases evolved to an FT-IR for analysis, this problem can often be solved, because water, monomers, various additives, and decomposition products can usually be differentiated.

We have been active for some time in utilizing the power of spectroscopy to solve these important questions raised by thermal analysis experiments. In 1987 the first commercially available combined TGA/FT-IR instrument was discussed [1]. In this instrument, the gases evolved during a TGA experiment are swept through a heated transfer line to an FT-IR spectrometer, which is used to record continuously infrared spectra of these gases. A number of articles have been published to show the utility of this combined instrument, such as studies on a range of polymers [2], gunpowder [3], and amine-activated epoxies [4], and references therein. These articles have clearly demonstrated the potential for TGA/FT-IR as a general purpose analytical tool for solving problems involving weight loss as a function of temperature.

One particularly useful type of information to be gained from an evolved gas analysis (EGA) experiment, such as TGA/IR, is how fast the gases are evolved during the experiment. The level of total gases being evolved is observed by the evolved gas profile (EGP), which is a measure of how the total infrared absorbance changes as a function of time and temperature. By integrating selected regions of the infrared spectrum continuously during the experiment, the

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evolution of particular functional groups (e.g. hydrocarbon, carbonyl) may be monitored by their respective functional group profiles (FGPs). Sometimes it is possible to select carefully a FGP region to include only the response for a single evolved gas product, which then is termed a specific gas profile (SGP). Examples of common gases that can be individually monitored in this way are the oxides of nitrogen and oxygen, water, isocyanic acid (from urea), and hydrogen chloride. These profiles are monitored continuously during the TGA/IR experiment, and are able to provide a wealth of detailed information for the analyst. The total area of the SGP for a gaseous product can often be related directly to the amount of a particular component in the original sample. Examples of this type of situation include the measurement of nitrocellulose in gunpowder by monitoring the evolution of nitric oxide [3], and the calculation of activator/resin ratio in cured epoxy by measuring the release of *bis*-phenol A (resin), and a cyclic alkene, which was related to the diamine curing agent [4].

Samples being studied by DSC, on the other hand, may give heat-flow peaks that do not coincide with any weight loss. In order to study the causes for these peaks, it has been found useful to perform the DSC experiment in a hot cell under an infrared transmitting microscope [5, 6]. In this case, the infrared spectrum is obtained for the sample itself, rather than the evolved gases. The interesting observation was made [6] that some samples will show no DSC peak during a physical change, because the endothermic and exothermic processes involved cancel each other, but the infrared spectrum may show evidence for the change.

These two combinations of TGA and DSC with FT-IR do, however, require completely different experiments. A more effective way of obtaining TGA, DSC, and FT-IR data on the same sample is to perform simultaneous thermal analysis (STA) on one sample, with concurrent FT-IR evolved gas analysis. This allows for one experiment to be performed that can give the maximum amount of important information on a single sample, with the minimum amount of instrument and operator time. It also solves the persistent problem of using two different samples for the TGA and the DSC and getting slightly different results due to sample size and morphology.

This paper describes a combined STA/FT-IR system, and demonstrates the type of results to be expected using a test sample of zinc stearate. This sample was chosen because it degrades to give stearic acid, which can be used to demonstrate the ability of the transfer line to carry a relatively high boiling compound from the furnace to the spectrometer for analysis. It also shows different DSC and TGA curves, thus demonstrating the utility of STA. More important experiments were then performed on samples of a more practical nature. Results of studies on various samples of solder paste and encapsulant demonstrate the application of STA/FTIR to electronic assembly problems, where quick turn-around time is essential.

## 2. Experimental procedure

A Polymer Laboratories STA 625 simultaneous

TGA/DSC analyser was used for thermal analysis. A heated transfer line made of silica-lined stainless steel was inserted into the base of the furnace with only minor modifications to the STA. In order to obtain good gas transfer, the normal purge direction (up through the furnace) was reversed, this makes no apparent change to the observed data. A purge flow rate of 40 ml nitrogen per minute was passed through the furnace and transfer line.

FT-IR evolved gas analysis was performed by using a Bio-Rad FTS 40 spectrometer with attached interface for EGA. This interface bench has been described before [2]; it contains a heated gas cell, room-temperature deuterated triglycine sulphate (DTGS) detector, and controllers for both heated gas cell and transfer line. The temperatures of the cell and transfer line were maintained at about 230 and 220 °C, respectively. Infrared spectra were recorded continuously at 4 cm<sup>-1</sup> resolution, co-adding 8 interferograms per spectrum to give a temporal resolution of about 15 s.

The figures shown, which contain several IR or thermal curves together, have all been presented so that the various curves are plotted with the same y-axis scale. In the case of the FT-IR spectra, however, the upper spectra have been offset vertically for clarity. All spectral manipulations, such as spectral subtraction, are discussed in the text.

The spectra obtained for various evolved gases were used to identify the actual species being given off, by the method called spectral searching. In this technique, the spectra are compared by computer to entries in a library database, and the best matches are reported. The database used was a library of approximately 3500 spectra, originally generated for vapour phase samples by the US Environmental Protection Agency, and available from Bio-Rad, Sadtler Division, Philadelphia, PA. The spectrum of a sample vapour is compared to each library data entry in turn, and a value for the difference between the two is computed. This value is called the hit quality index; a value of 0.0 for the HQI indicates a perfect match, values from 0.2–0.6 indicate a good match, and values above 1.0 indicate little correlation. It should be noted that all results of spectral searching need to be displayed, and their accuracy verified by the operator.

The sample of zinc stearate (octadecanoic acid, zinc salt – technical grade) was obtained from Aldrich Chemical Company, Milwaukee, WI.

## 3. Results

### 3.1. Degradation of zinc stearate

A sample of zinc stearate (5.7 mg) was heated to 600 °C at 20 °C min<sup>-1</sup>. The DSC curve shown in Fig. 1 gave a sharp endotherm at 128 °C, corresponding to the melting point of the material. No weight loss was observed on the TG curve at this temperature, but the infrared spectrum recorded at the same time showed that a very small amount of water was released. Fig. 2 shows the 1700–1800 cm<sup>-1</sup> region of the spectrum, integrated as a function of time. This region is where the expected stearic acid carbonyl should appear, but is also sensitive to the presence of water vapour. A

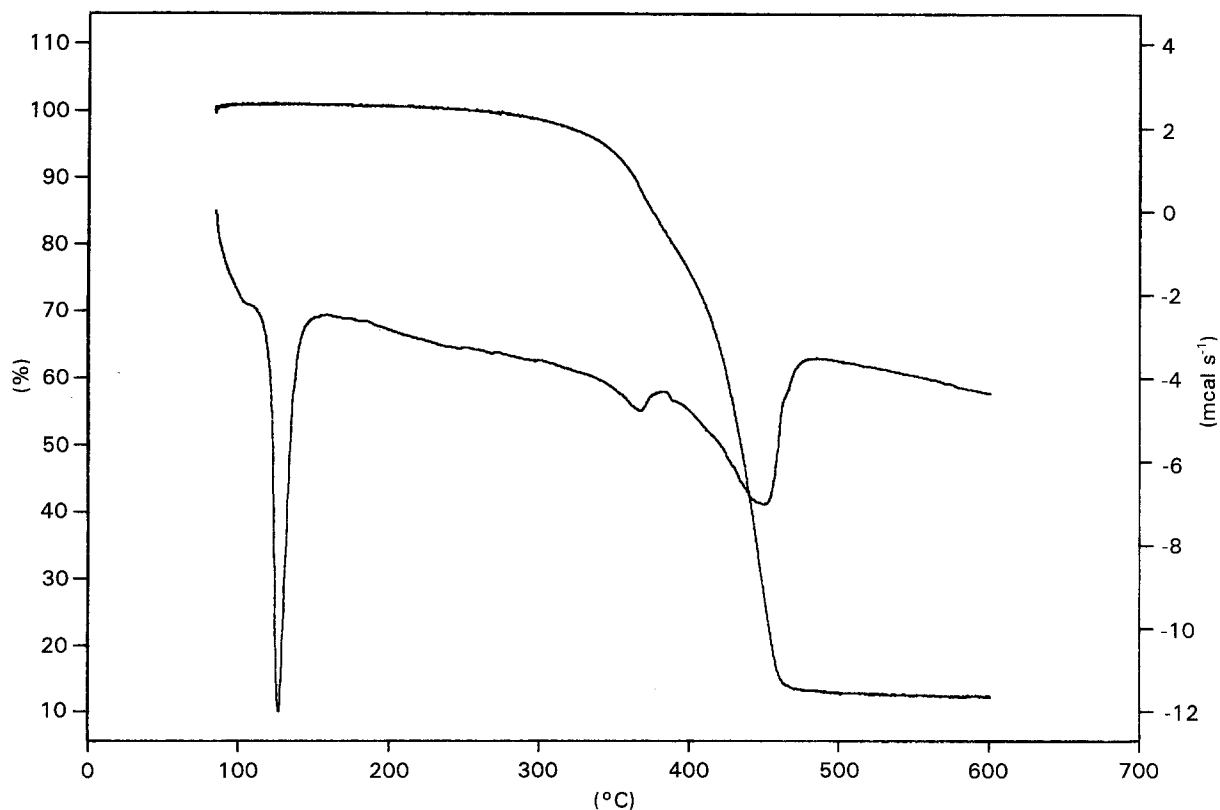


Figure 1 TG and DSC curves for zinc stearate heated at  $20^{\circ}\text{C min}^{-1}$  under a nitrogen atmosphere.

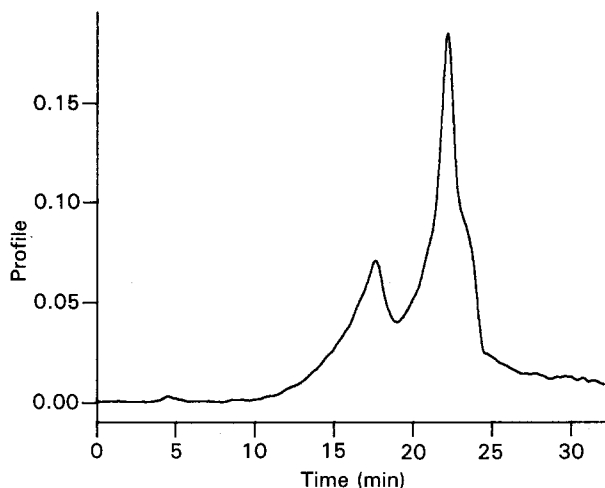


Figure 2  $1700\text{--}1800\text{ cm}^{-1}$  profile for zinc stearate as a function of time when heated at  $20^{\circ}\text{C min}^{-1}$ . This region integrates carbonyl responses.

very small peak can be seen at 4.5 min in Fig. 2, showing the release of water for less than a minute. The fact that the FT-IR can observe small amounts of material evolved, even though the TG curve detects no weight loss, is not unusual; the FT-IR is sensitive to a fraction of a microgram, whereas the STA is sensitive to 1  $\mu\text{g}$ .

Thermal decomposition of the zinc stearate is observed to commence gradually below  $300^{\circ}\text{C}$ , and takes place over a wide temperature range. The reason for this is not understood; furthermore, the derivative of the weight loss profile shows two peaks (at about  $380$  and  $440^{\circ}\text{C}$ ), rather than the one expected. The derivative curve is very similar to the infrared profile

shown in Fig. 2, except that it shows no peak corresponding to the water loss mentioned above.

The infrared spectra of the two major weight loss regions are shown together in Fig. 3; these two spectra are plotted on the same absorbance scale to show the relative amounts being evolved. The spectral regions around  $2350$  and  $670\text{ cm}^{-1}$  in both spectra can be ignored, they are due to a relatively small amount of carbon dioxide (which has a strong spectrum), this could arise from decarboxylation of the stearate or some oxidation taking place. The C-H stretching region of the spectrum ( $2800\text{--}3000\text{ cm}^{-1}$ ) shows the

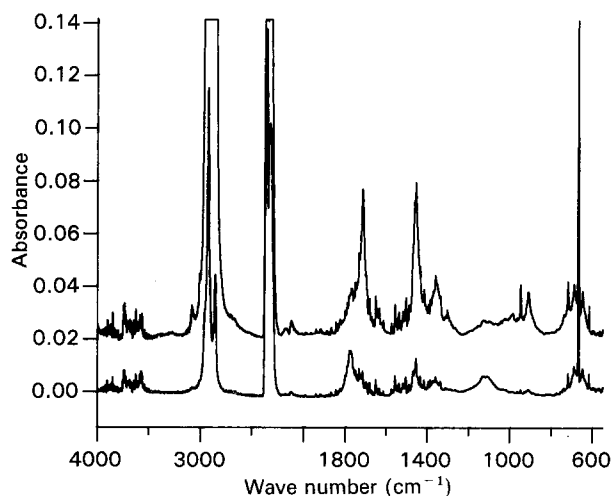


Figure 3 Infrared spectra of the gases evolved during the two major weight losses occurring when heating zinc stearate under nitrogen. This plot has a scale change at  $2000\text{ cm}^{-1}$ . Note the regions of the spectra at  $1780$  and  $1720\text{ cm}^{-1}$ , which are both assigned to stearic acid, in different states.

band shape typical of a long hydrocarbon chain, such as a stearate. Of particular interest is the carbonyl region of the spectrum, the same region being integrated in Fig. 2. The spectrum recorded at 380 °C shows a carbonyl maximum at 1777 cm<sup>-1</sup>, whereas the spectrum recorded at 440 °C shows a second, stronger peak at 1717 cm<sup>-1</sup>. Both spectra show a weak peak at 3575 cm<sup>-1</sup> that is due to the O–H stretching motion of the stearic acid in a non-hydrogen-bonded environment.

At first the presence of two carbonyl frequencies in these spectra was puzzling. The expected product, stearic acid, would be expected to show a band at about 1780 cm<sup>-1</sup> in the gaseous phase, and so the band at 1717 cm<sup>-1</sup> was initially considered to be due to a different type of functional group, such as an aldehyde or ketone. However, the behaviour of stearic acid in a TG experiment has been studied [7], and the second band at 1717 cm<sup>-1</sup> has been assigned to stearic acid in the condensed phase. This frequency is indeed the normal one to be expected for a carboxylic acid, because most acids are solids or liquids at room temperature, and are strongly hydrogen-bonded under normal conditions.

The observation of two carbonyl frequencies for stearic acid is important. It indicates that the gas transfer from the STA to the FT-IR is excellent, because the stearic acid is being observed in both gaseous and solid aerosol forms. Any flow restrictions or cold spots in the transfer line would be expected to give rise to a reduction in, or complete loss of, the amount of aerosol being delivered to the gas cell.

The spectra in Fig. 3 show the presence of some other minor components. In particular, a number of bands in the regions 3700–4000 and 1300–1800 cm<sup>-1</sup> can all be attributed to a small amount of water. In the higher temperature spectrum, new bands at 3015 and 949 cm<sup>-1</sup> can be assigned to methane and ethylene, respectively, and bands at 3085 and 910 cm<sup>-1</sup> appear similar to bands of 1-hexene, although it should be commented that the last compound is probably an “average” alkene that is observed. These compounds are all presumably due to some thermal decomposition of the stearic acid occurring at the rather high production temperature. A very weak pair of bands at about 2200 cm<sup>-1</sup> is to be expected, they arise from a trace of carbon monoxide, commonly found in the presence of carbon dioxide. Rather more interesting, however, is the appearance of a single sharp band at 2120 cm<sup>-1</sup>, which is tentatively assigned to zinc carbonyl.

The residual weight on the pan at 600 °C is about 12% of the original, which is close to the theoretical value of about 10% to be expected were pure zinc metal to be left on the pan.

### 3.2. Evaluation of different solder paste formulations

Tin/lead solder pastes are used in the assembly of printed circuit boards to provide solder joints that act as the mechanical and electrical interconnections between the board and components. A typical solder

paste formulation includes about 90% metal, mixed with organic binder, activator and solvent [8]. During the assembly operation, some of the organic materials burn off or vaporize, but a significant portion of the original weight of organics remains with the metal as a residue. Earlier research efforts had concentrated on effective cleaning processes; however, due to the industry attempts to eliminate chlorofluorocarbon (CFC) cleaning for environmental reasons, there is a significant interest in the use of no-clean solder pastes. Even though these no-clean pastes leave benign residues, if the amount of residue is not minimized, it can lead to aesthetic and testability problems. As part of our evaluation of no-clean solder pastes for our assembly process, STA/FT-IR was used to evaluate three commercial solder paste formulations. This type of work is essential in choosing a paste that will be compatible with our process profile, as well as in obtaining important information such as the solder composition, residual organics, rate of volatilization and a better understanding of the chemistry and thermal behaviour of the pastes.

DSC provides information on the melting temperature of the paste, which is an indirect way of checking the composition of the tin/lead alloy in the paste. Information on the amount and rate of evolution of volatiles and level of residual organics can be obtained using TGA. The details of the flux chemistry involved are generally proprietary to the manufacturer of the solder paste; however, information about the types of solvent, activator and binder may give clues to the basic characteristics of the pastes. It was considered that evolved gas analysis (EGA) during a combined TGA/DSC experiment would be able to give important information about these volatile components, at the same time as verifying the specifications set by the thermal characteristics of the sample.

Three no-clean solder pastes from different vendors (A, B and C) were evaluated by heating about 25 mg paste from 40 °C to 270 °C, at a ramp rate of 10 °C min<sup>-1</sup>, both in air and nitrogen. The first important datum obtained from the evaluation was the melting point of the solder pastes. The DSC data demonstrated that the pastes from the different vendors all have the same melting point at around 184.6 °C. The melting temperature of a solder reflects its composition; therefore, these results show that all the vendors have the eutectic tin/lead (63/37) solder composition.

The TGA data provided information on the evaporation rate of the solvent/vehicle systems and the amount of residues left after thermal treatment in air and nitrogen, as shown in Figs 4 and 5, respectively. In air, the rate of weight loss as a function of temperature is similar for the pastes from Vendors B and C, but slower for the paste from Vendor A. Under nitrogen atmosphere, all the pastes showed faster weight loss than in air; however, this effect was more pronounced for the paste from Vendor C. The comparison of Figs 4 and 5 reveals quickly that these different formulations vary in behaviour not only among themselves, but also alter their behaviour as a function of atmosphere. These results have important ramifications in the

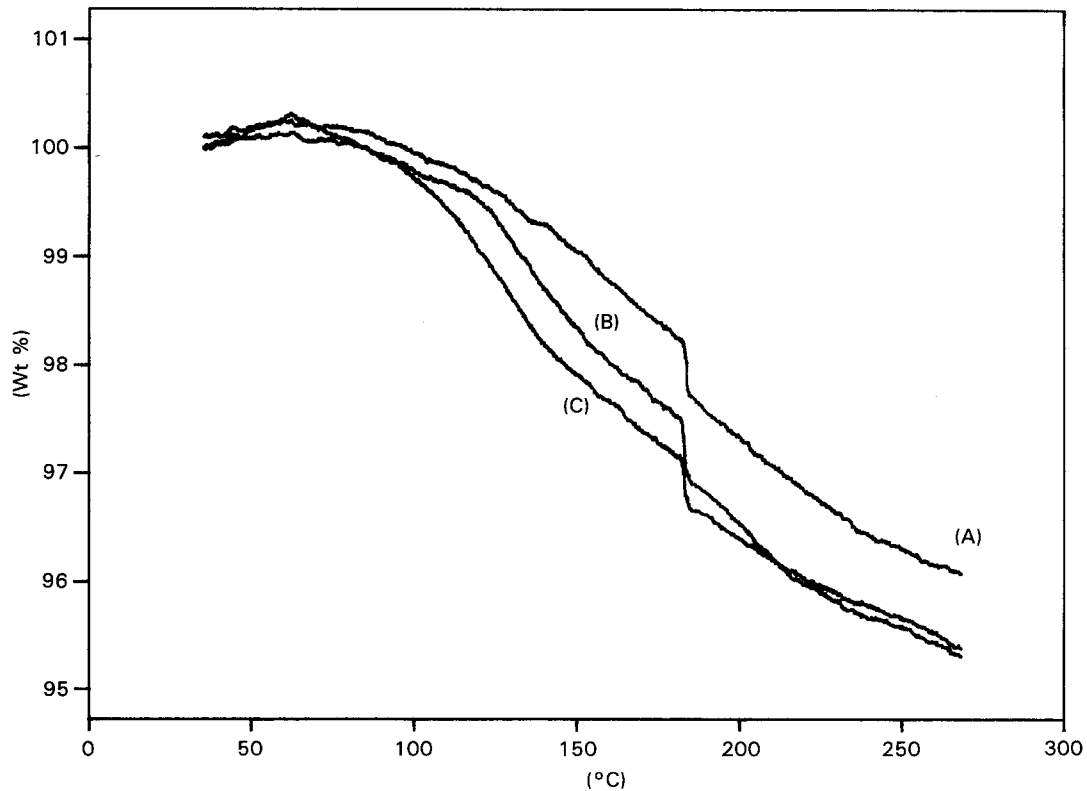


Figure 4 TGA curves of weight per cent versus temperature obtained by heating the three solder paste samples under dry air at  $10^{\circ}\text{C min}^{-1}$ .

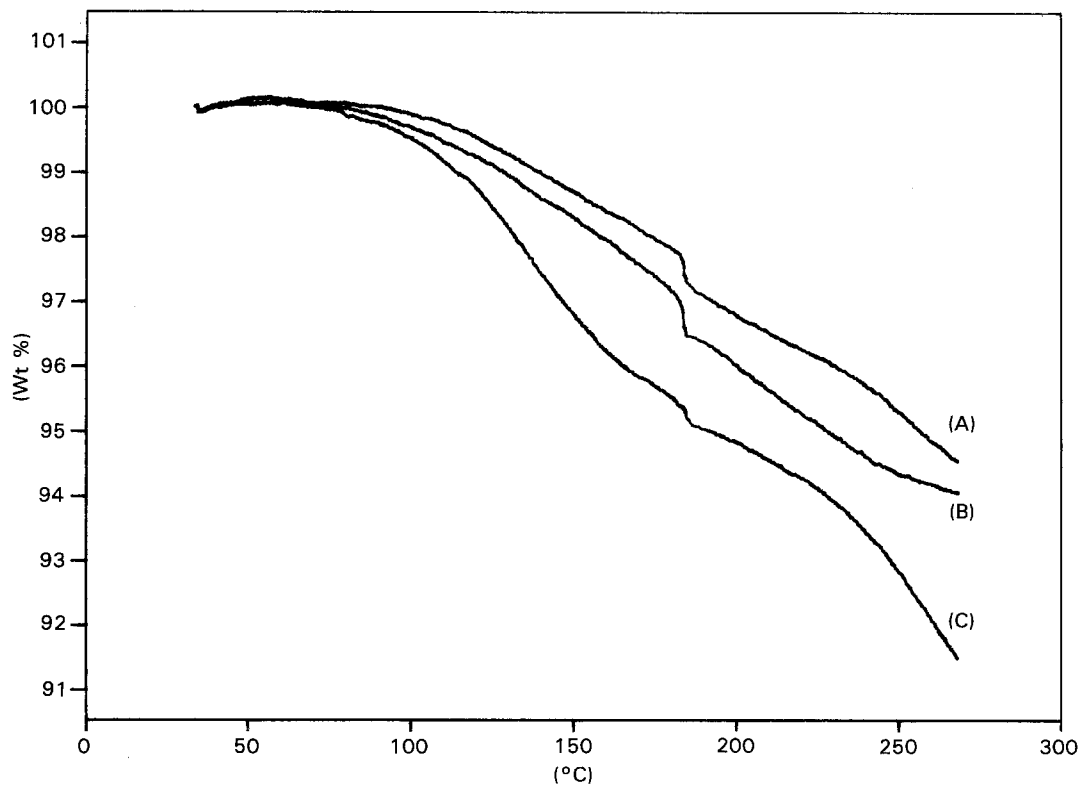


Figure 5 TGA curves of weight per cent versus temperature obtained by heating the three solder paste samples under nitrogen at  $10^{\circ}\text{C min}^{-1}$ .

choice of a preferred formulation. It is desirable to remove the maximum amount of organics during the assembly operation; however, rapid evaporation of the solvents can lead to a problem known as solder balling.

Table I shows the numerical data for the amount of residues left after thermal treatment (metal content is

90%) and the melting points of the different pastes. The pastes from Vendors C and B left about the same amount of residue, when heated under an air atmosphere, while Vendor A's paste left a higher amount of residue. Under a nitrogen atmosphere, there was a significant reduction in the amount of residue left behind in general, but the greatest reduction was in

TABLE I

Vendor	Melting temp. (°C)	Residue (%)	
		Air	N <sub>2</sub>
A	184.7	96.1	94.6
B	184.6	95.3	94.1
C	184.7	95.4	91.6

the paste from Vendor C. The general reduction in the amount of residue left behind in a nitrogen atmosphere has been observed by other authors for rosin-based flux [9]. Because the pastes being studied in our work are also rosin based, it can be assumed that the higher amount of residue under an oxygen atmosphere is due to an oxidation reaction leading to a non-volatile product (such as auto-oxidative polymerization reaction product, as suggested in [9]). The results listed in Table I show that the paste from Vendor C is the most sensitive to the gaseous environment; this may be due to the presence of a smaller amount of rosin or a different reaction mechanism under nitrogen. Inert atmosphere soldering is becoming more common in this industry, as more manufacturers discover similar effects.

During the heating of the pastes, the volatile components of the paste (solvent or reaction products) were analysed by FT-IR spectroscopy. The analysis consisted of examining and comparing the various types of evolved gas profiles (EGPs) available for the different samples, as well as the infrared spectra obtained during each experiment. The infrared spectra of the major gases evolved from the three solder paste formulations, under a nitrogen atmosphere, are shown together in Fig. 6. These spectra were recorded at 12 min into the various experiments, at temperatures about 130 °C. The observed spectra did not vary much during the evolutions, although their intensity did vary with temperature, which indicates that the formulations all included a single major organic component. It is clear from Fig. 6 that the gases evolving from each sample are different, although they are all

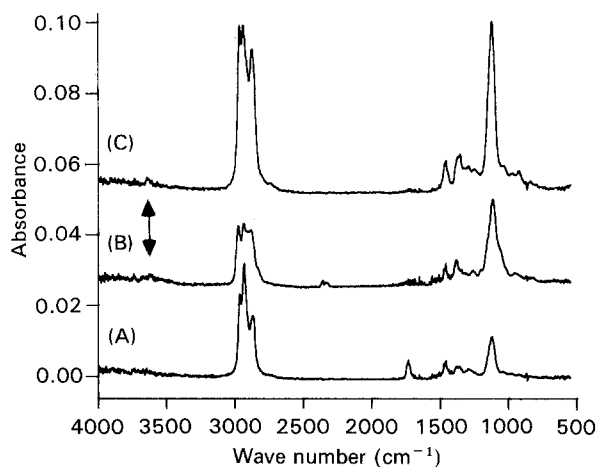


Figure 6 Infrared spectra of the gases evolved at about 130 °C from three different formulations of solder paste. A, B and C refer to the samples from Vendors A, B and C, respectively. The arrows point to the weak absorptions assigned to hydroxyl compounds.

ether-based materials (presumably solvents), as demonstrated by the common infrared absorption at about 1120 cm<sup>-1</sup>. The top two spectra show that the organic species in formulations B and C are similar substances, differing only in the hydrocarbon C–H stretching region of the spectra (3000–2800 cm<sup>-1</sup>). Note that these two spectra have essentially the same ether/hydrocarbon band intensity ratio, which indicates that the carbon number of the two solvents is similar, but that they probably differ by type of chain branching. In addition, both spectra show a very weak band near 3650 cm<sup>-1</sup>, which would indicate a hydroxyl (alcohol) group as well. This similarity may explain the identical behaviour of the two pastes observed in the TGA results in air. Each spectrum was searched against libraries of spectra of vapour phase compounds. Although the exact ether/alcohols were not to be identified from the library entries available, the closest matches for the organics evolved by samples B and C were, respectively, 1-butoxy-2-propanol and 1, 2-dibutoxy ethane.

The lowest spectrum of the three (A) in Fig. 6 is quite different from the top two in three ways. The ether band is still present, but is much weaker than the hydrocarbon band. The shape of the hydrocarbon C–H stretching region is characteristic of a longer hydrocarbon chain in this compound, which is in agreement with the higher intensity of this band. There is no evidence for an alcohol functionality, but instead an absorption can be seen at 1740 cm<sup>-1</sup>, which is typical of a carbonyl group, probably an ester or perhaps a ketone. However, careful examination of the series of spectra recorded during the heating of sample A revealed that the carbonyl species evolved somewhat earlier than the ether, and was thus due to a different compound. The tool of spectral subtraction was used to obtain spectra of the two individual species, although the spectrum of the carbonyl compound was very weak. Searching these spectra against the same library data base gave a good match for the solvent as di-hexyl ether (as shown in Fig. 7), and, allowing for the weakness of the carbonyl spectrum, gave an indication that acetone was the second material.

It should be mentioned also that a small amount of carbonyl compound was observed to be evolved in all of the experiments listed, except when the paste from Vendor C was heated under nitrogen. The actual species may not be the same in each experiment, because the material believed to be acetone evolved from sample A at a low temperature. The absence of this carbonyl peak when heating sample C under nitrogen suggests that there may be a different reaction mechanism which makes this paste more sensitive to the environment, as seen in the TG analysis. We will discuss the carbonyls evolving from samples B and C further below.

The study of the FGPs obtained for each sample was found to be very revealing. The evolution of the major ether species could be conveniently studied by using the 1000–1300 cm<sup>-1</sup> profiles obtained for each sample, as shown together in Fig. 8 for the samples heated under nitrogen. The infrared absorbance

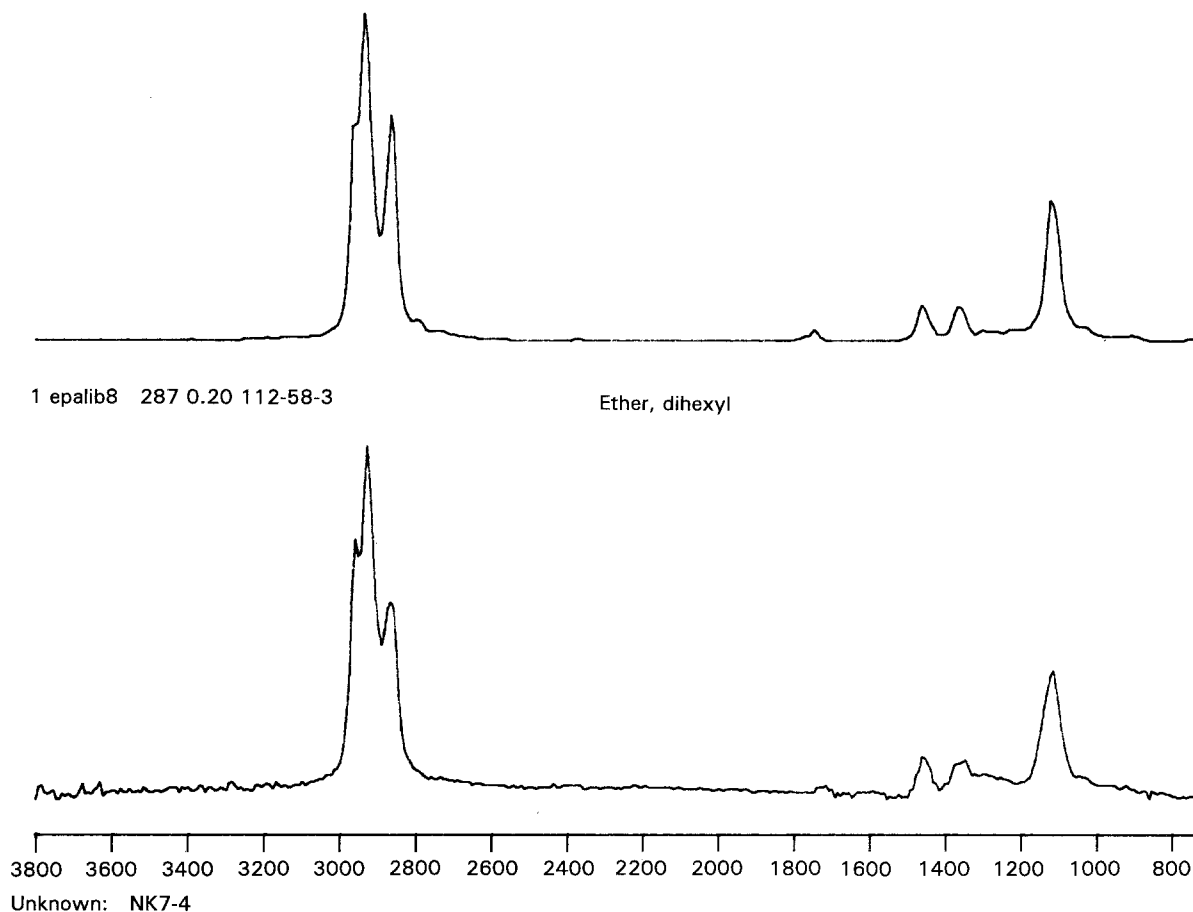


Figure 7 Results of the spectral search for the spectrum of the major gaseous component evolved from sample from Vendor A. The spectral contribution from the carbonyl compound seen in Fig. 6 has been subtracted prior to the search.

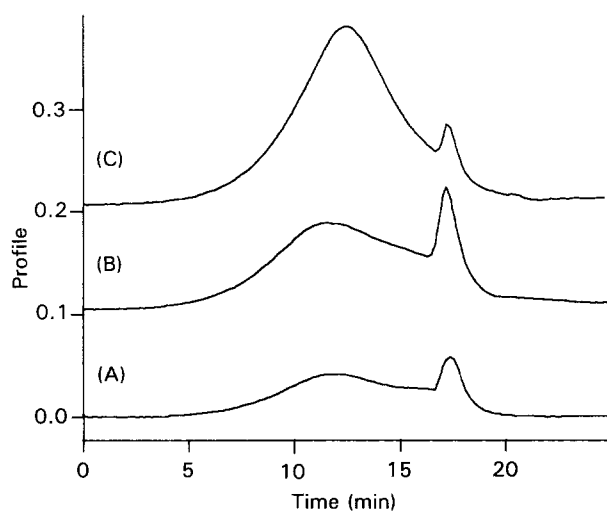


Figure 8 1000–1300  $\text{cm}^{-1}$  profile for gases evolving from solder paste formulations when heated under nitrogen.

shown by a functional group (such as an ether) varies from one molecule to another, because it is affected by the overall molecular structure. The gases evolved from the three samples are known to be different, and thus exhibit differing infrared molar absorptivities. Because of this, the relative integrated intensities of these three curves cannot be relied on to determine accurately the relative quantities of each material lost; this information should be taken from the TG data. Having said that, the relative ether absorptivities near

1100  $\text{cm}^{-1}$  for each sample in Fig. 6 do correlate loosely to the relative weight losses seen in Fig. 5 at 130 °C. The rate of evolution of solvent from the three samples increases in the order  $A < B < C$ . More importantly though, examination of Fig. 8 shows the evolution profile for solvent loss to differ subtly among the samples. Although each evolution is broad, and occurs over a 15 min (150 °C) span, they all show two major features. The first, major weight loss is very broad and peaks at about 130 °C, but a second, sharper loss coincides with the solder melt. What was surprising was the observation that the pastes from Vendors A and B liberated a fairly high proportion of the solvent at the melt, whereas that from Vendor C lost only a few per cent of the evolution during the melt. Close examination of the TG curves confirmed this result.

Further detailed information was gained from a study of the other FGP data available. For example, Fig. 9 shows the FGP for the region of the infrared spectrum between 1680 and 1780  $\text{cm}^{-1}$ , for the three pastes heated under both air (curves A1, B1, and C1), and under nitrogen. Absorptions in this region are normally ascribed to carbonyl compounds or water vapour. The paste from Vendor A showed two peaks at 9 and 17.3 min in these profiles (100 and 185 °C, respectively), and the paste from Vendor C also showed two peaks under air at 12 and 17.3 min (130 and 185 °C), but these peaks were absent when heated under nitrogen. The profiles for the sample from

Vendor B showed only one peak at 19 min (200 °C), with no sharp peak at the melting temperature. Note that this evolution from sample B is taking place after the major solvent loss has finished. The spectrum obtained for sample B at about 20 min was very surprising. Spectral search gave results that indicate that this material is a dialkyl ester of phthalic acid. Because most no-clean pastes have carboxylic acids as activators, the presence of an ester may be due to a reaction product from the activator or there may be a phthalic ester as part of the formulation. The usefulness of FT-IR evolved gas analysis is well demonstrated in Fig. 9, when comparing the 1680–1780  $\text{cm}^{-1}$  FGP for the same paste (Vendor C) in air and nitrogen. The profile obtained under nitrogen is much simpler, in that the two peaks at 130 and 185 °C seen under air are now absent. This indicates that both peaks are due to evolution of carbonyl compound, as evolution of water would still be expected to occur under nitrogen. These two carbonyl evolutions are probably due to oxidation, while the later peak observed in this region under nitrogen could be due to evolution of water, activator or reaction products. A detailed analysis of these FT-IR spectra would shed more light on the chemistry of the pastes. However, because of the uniqueness of these functional group profiles, differences observed for the pastes can be used as fingerprints for quality control.

As mentioned earlier, these are no-clean solder pastes, which means that the residues are benign and can be left on the board after processing. However, for aesthetics reasons and because of possible interference with electrical testing, the amount of residue needs to be minimized. These results so far point to Vendor C's solder paste as being the preferred material, as long as

no solderballing is experienced during reflow operation.

### 3.3. Study of the degradation of encapsulant samples

After assembly of several plastic-encapsulated components, it was found that certain batches were experiencing failures. In the electronic industry, epoxy-based encapsulants are used as cost-effective material to protect semiconductor devices. However, failures of plastic-packaged semiconductors have been traced to the properties of epoxy material such as water absorption, volatiles, ionic contaminants, thermal degradation and coefficient of thermal expansion [10, 11]. STA/FT-IR was used to determine if there are major differences in the encapsulants of the "good" and "bad" materials.

A study of two batches of encapsulant, denoted 9027 ("bad") and 9114 ("good"), were selected for study by STA/FT-IR. Because the production process involved the application of high temperature, a sample of batch 9027 that failed after going through an assembly process was also studied and labelled as 9027F. This would allow us to model the effect of the assembly process on the encapsulant material. The three samples were ground, and 21 mg each sample was heated up to 400 °C at 10 °C  $\text{min}^{-1}$ , under an air atmosphere. Samples 9027 and 9114 had 6.19% weight loss, while sample 9027f had 6.04% weight loss, but otherwise the weight loss profiles were essentially identical. Some variations in the sample behaviour was observed using DSC, however, as can be seen in Fig. 10. The DSC curve of sample 9027F showed a subtle difference from the other DSC curves at temperatures above 300 °C. Whether this difference was relevant was questionable, because the temperature is above that expected during processing. Each DSC curve shows the major maximum above 300 °C (oxidative decomposition), as well as a subtle inflection at about 240 °C, as shown in Fig. 10.

We were very interested to note the inflection in the DSC trace near 240 °C, because this temperature would be encountered during normal processing. Careful examination of the TGA data gave no indication of a weight loss occurring at this temperature, but the infrared spectra recorded at about 240 °C did reveal that a very small evolution of gas was occurring. The spectra of the gases evolved from the three samples are shown together in Fig. 11; note that these are very weak spectra having absorbances of about 1 mA unit. For clarity, a relatively strong band due to carbon dioxide near 2350  $\text{cm}^{-1}$  has been removed from these spectra. Rather surprisingly, the spectra for samples 9027 and 9027F are the same, even though sample 9027F had gone through the assembly process. In all three spectra, a pair of bands at 1260 and 1100  $\text{cm}^{-1}$  are observed; these bands are easily assigned to the evolution of a poly(dimethyl siloxane). Such a material is commonly found on the surface of materials as a mould release agent. Note that this type of material has a strong infrared spectrum, so these bands are due to a very low level of mould release. The

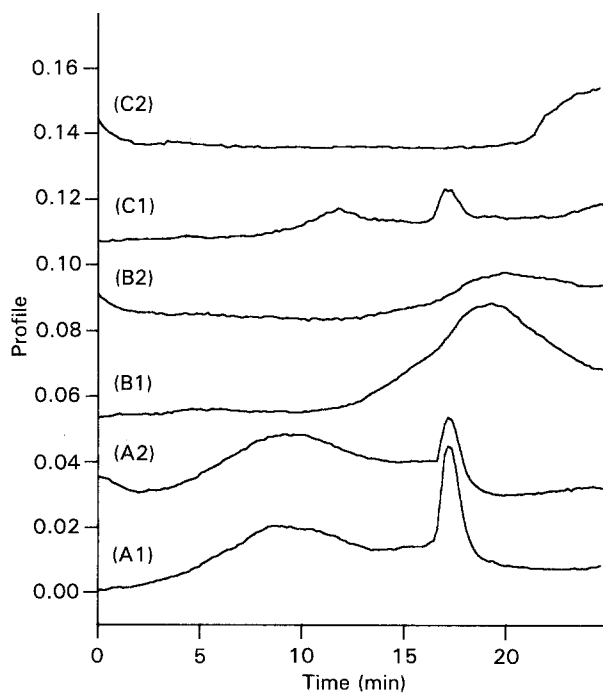


Figure 9 1680–1780  $\text{cm}^{-1}$  profiles obtained by heating the three solder paste samples under air, curves A1, B1 and C1, and also under nitrogen, A2, B2 and C2.



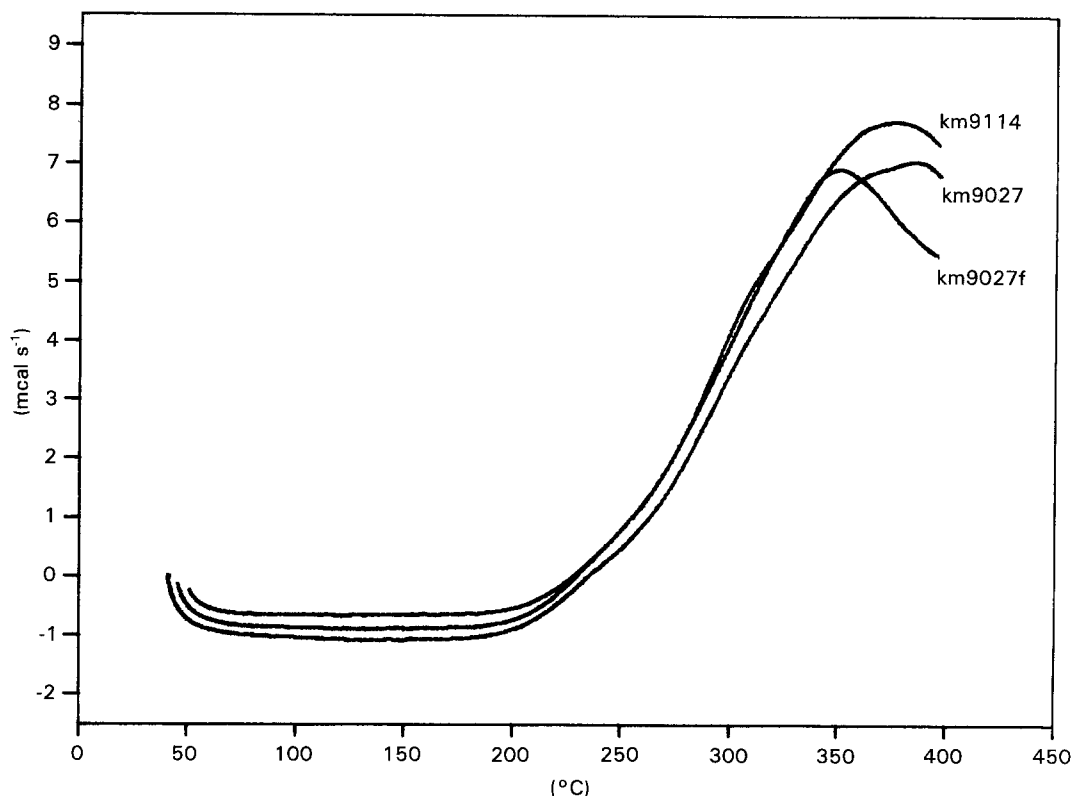


Figure 10 DSC curves for three samples of encapsulating material, heated at  $10^{\circ}\text{C min}^{-1}$  under air.

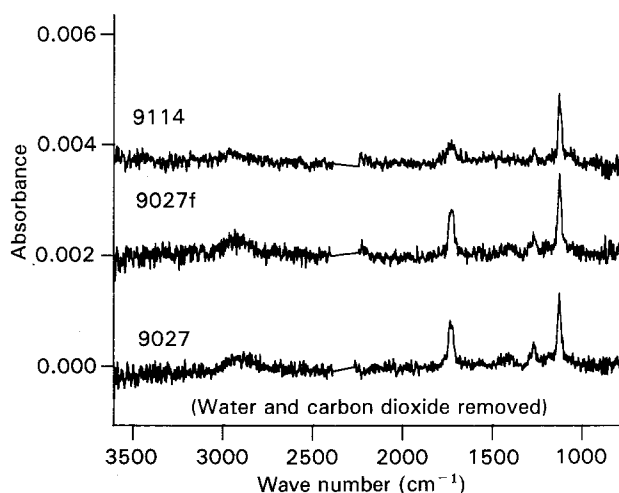


Figure 11 Infrared spectra obtained for the gases evolved from the encapsulant samples at about  $240^{\circ}\text{C}$ . The spectral bands due to water vapour and carbon dioxide have been subtracted for clarity.

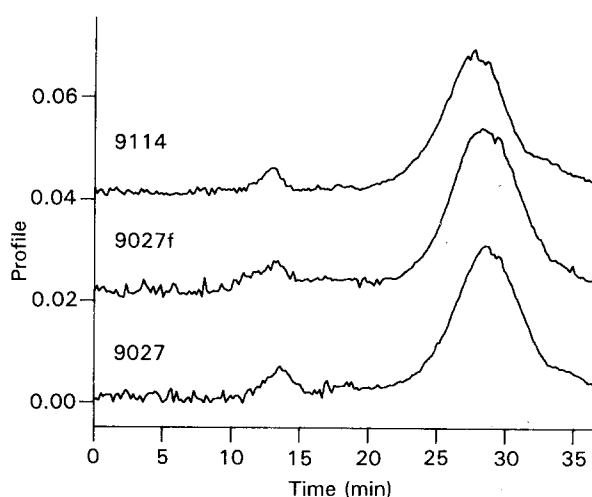


Figure 12  $1000\text{--}1300\text{ cm}^{-1}$  profile for the three samples of encapsulating material when heated under air.

functional group profiles (FGPs) for the  $1000\text{--}1300\text{ cm}^{-1}$  region (shown in Fig. 12) also show the evolution of silicone from all three samples at about 14 min. The intensities of the spectral bands are the same for all samples, as are the intensity and shapes of the profiles, demonstrating that all formulations contain the same amount of mould release, or that it is at least released from inside the bulk at the same rate.

Another very weak spectral feature can be seen in the three spectra shown in Fig. 11, at about  $1740\text{ cm}^{-1}$ . This band is assigned to an ester species, along with the broad feature at around  $2900\text{ cm}^{-1}$ , and it is interesting to note that sample 9114 (a good batch) appears to contain a lower level of this mater-

ial. The  $1680\text{--}1780\text{ cm}^{-1}$  profile was found to be sensitive enough to be useful in monitoring the ester component in a routine fashion. The source of this carbonyl compound is not yet known; it may be present as a processing aid, or as a by-product of the epoxy polymerization reaction.

The higher temperature evolutions from the samples were also studied, and were found to be essentially the same from all three samples. The spectra of the volatiles from sample 9027f are shown in Fig. 13. The original spectrum is the lower plot, and the upper plot is the same spectrum after subtraction of bands due to water vapour. In addition to water, bands due to carbon dioxide ( $2350\text{ cm}^{-1}$ ) and carbon monoxide ( $2150\text{ cm}^{-1}$ ) are clearly to be seen. These two oxides of

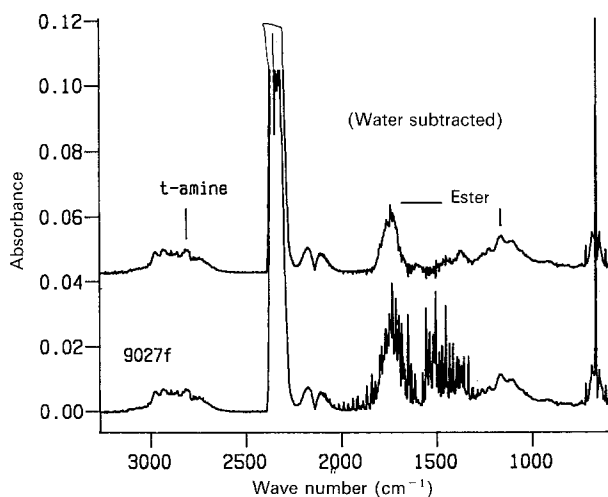


Figure 13 Spectrum of gases evolved from sample 9027f at about 350 °C when heated under air. The bottom spectrum is the original data, the top one is the same spectrum after subtraction of the contribution due to water vapour.

carbon are commonly seen together in EGA experiments, as carbon monoxide is unstable and disproportionates to give carbon deposit and carbon dioxide.

More interesting are the absorbances to be seen at about 2800 and 1740  $\text{cm}^{-1}$ , which are assigned to a tertiary amine and a carbonyl, respectively. The release of these two components was found to be coincident in all three samples, which means that either they arise from loss of a single, multifunctional component, or that they are two components released simultaneously (perhaps as breakdown products). The probable components to be expected in a typical epoxy encapsulant formulation are listed in Table II. We have already mentioned the presence of a poly(dimethyl siloxane) mould release agent at lower temperature, and now postulate that the tertiary amine and carbonyl functionalities released at the higher temperatures are due to loss of the catalyst, which is typically an amine compound. Catalyst systems based on a tertiary amine and an anhydride are common [12], the function of the amine is to activate the carbonyl so that it can react with epoxy. If this is so, then we believe that the catalyst being used is different from the cycloaliphatic diamine catalyst used in other epoxy formulations we have studied [4], because that material was released as an alkene, with ammonia being evolved at a slightly higher temperature.

Further failure analysis of the part showed that the actual failure was due to cratering (peeling off of the wire bond from the silicon substrate). This type of failure is believed to be due to formation of silicon nodules which during bonding can cause the die to

TABLE II Probable components in encapsulant formulations

Epoxy resin
Catalyst
Silica filler
Carbon black
Flame retardant
Mould release agent

crack [13, 14]. Moisture or other volatiles from any source will just show the hidden problem (die-bonding defect) by causing an electrical failure. It is postulated that the difference in the amount of the carbonyl and presence of moisture may be the reasons why the "bad" batch shows the defect.

#### 4. Conclusions

The experiments described demonstrate that STA/FT-IR has great potential as an analytical technique. It retains the important features of the combined TGA/FT-IR instrument, and adds the further dimension of DSC information as well, without adding any compromise. The observed spectra for the stearic acid produced by the decomposition of zinc stearate indicate that excellent gas transfer is being effected, because the stearic acid being produced is being swept over as both gas and aerosol. The detection of low levels of unexpected materials (ethylene and what is probably zinc carbonyl) demonstrate the common observation that the evolved gases often contain some surprises. Finally, the detection of the samples melting point by DSC and the simultaneous FT-IR detection of water vapour demonstrate the additional power of this three-way simultaneous STA/FT-IR analysis, especially as the TG curve showed no weight loss at that temperature.

The application of the DSC/TGA/FT-IR to practical problems has also been demonstrated. A study of solder paste formulations revealed very clearly that the three different vendors supplied samples with markedly different characteristics. Although the DSC showed that the solder was identical, FT-IR analysis showed that each formulation used a different organic solvent, and the TGA indicated a different level of residue on heating. What was particularly informative was the observation that the sample from Vendor C performed markedly differently in air than in nitrogen.

In the case of the encapsulant samples, the results obtained were much more subtle in that the differences found between a good and bad batch were very small. TGA results were essentially identical for the samples, and the DSC curves only varied at temperatures above concern. The FT-IR spectra did show a difference in the level of one component, which was found to be at a lower level in a good sample than in the bad one. It may be that evolved gas analysis may be the best way to perform quality control tests on these critical samples, because the more routine, single DSC and TGA tests were inconclusive.

To summarize, the advantages of using this type of combined instrument include:

1. obtaining three sets of complementary information on the same sample in one experiment, thereby eliminating experimental and sampling variables encountered when running samples on the individual instruments. This leads to more reproducible results and better interpretation;
2. minimizing instrument and operator time, thereby providing quick turn-around time and higher productivity;

3. providing thermal and spectroscopic fingerprints that give important chemical and physical information, and that, once characterized, can also be used for quality control.

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