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CHARACTERISATION AND ANALYSIS OF MICRO-CONTAMINANTS IN INDUSTRIAL POLYMERS

Application of TP-SIP-MS scanning electron microscopy and SEM X-ray microanalysis

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Abstract

Analysis of very small particles can present problems. This paper describes the application of temperature programmed solid insertion probe mass spectrometry (TP-SIP-MS), scanning electron microscopy and SEM X-ray microanalysis to the identification of foreign particles present in an industrial product. The relative advantages and limitations of the techniques are discussed. It is shown that TP-SIP-MS is a powerful tool for such work and complements the use of more conventional microanalytical methods.

Keywords: polymers, TP-SIP-MS, scanning electron microscopy, X-ray

Introduction

High technology industries rely on increasingly sophisticated analytical techniques for quality assurance and trouble-shooting. For instance, many areas of industrial activity, ranging from the manufacture of foodstuffs to the production of complex materials, require the analysis of contaminants which are often present as very small particles.

In some cases SEM, combined with an X-ray microanalysis, can give useful information on the composition of small particles. However, as the technique relies on analysis of X-rays emitted from the sample, it only provides information on the elemental composition and, furthermore, has severe limitations when applied to elements of low relative atomic mass such as nitrogen, carbon, oxygen and hydrogen. Unfortunately, therefore, it is not useful for the vast majority of organic compounds.

An alternative method is simultaneous thermogravimetry-evolved gas analysis (TG-EGA) [1, 2], a technique which has been applied to the study of polymers [3–5]. However, it does not have the sensitivity to deal with very small

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samples (<100 μg) or with materials which produce relatively involatile materials on heating. A variation of this approach, which is invaluable for all materials which have a measurable vapour pressure, or produce gaseous decomposition products, at temperatures up to 1000°C, is to use temperature programmed solid insertion probe mass spectrometry (TP-SIP-MS). The technique is equally applicable to most organic materials, where it provides a positive identification, and to inorganic substances and large organic molecules, which it characterises via the gas-phase products of their thermal decomposition. The technique is, therefore, a form of evolved gas analysis (EGA). TP-SIP-MS has been described previously [6] and its application to polymer characterisation has been discussed [7–9].

This paper describes the use of TP-SIP-MS in solving a problem which arose during the manufacture of a new material and compares results with the information provided by SEM and X-ray microanalysis. Despite stringent quality control, one batch of a complex composite material was found to contain a few very small particles (approximately 0.1 to 0.5 mm in diameter) of a foreign material which caused the product to fail during subsequent processing. It was vitally important that the identity of the foreign particles was determined, so that their source could be located and eliminated. It was possible that one of the constituents of the final product was responsible, either by not being incorporated correctly, or by being contaminated with an unrelated substance.

Experimental

Materials

The material which is the subject of this study is a heavily modified polyethylene which is fabricated into tubing. It contains a plasticiser and other modifiers including antimony oxide, alumino-silicates, decabromodiphenyl oxide, magnesium oxide, polyester, titanium dioxide, ethylene vinyl acetate, low-density polyethylene, zinc stearate and Irganox MD 1024 (benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-2-[3-[3,5-bis(1,1-dimethylethyl)-4-hydroxy phenyl]-1-oxopropyl]hydrazide), a commercial anti-oxidant. Irganox MD 1024 has a relative molar mass of 552 and a melt with decomposition above 210°C.

The TP-SIP-MS equipment

The TP-SIP-MS system has been described in detail elsewhere [6]. In essence, the SIP consists of a micro-furnace attached to a water-cooled tube which enters the mass spectrometer via a double airlock (Fig. 1). The sample is contained in a small Pyrex tube of 20 mm length and 1 mm internal diameter. The length of this tube is such that it enters the source of the mass spectrometer when the probe is in place, thus ensuring a very high sensitivity, as all of the gas evolved is transferred directly to the MS source. The base of the furnace block contains a K-type thermocouple which is used to measure both the sample temperature and provide the signal for the temperature controller. An essential feature of the technique is the temperature programming, which must be both linear and accurate if the results are to be reproducible and meaningful. The relatively simple temperature programmer supplied with the SIP did not meet these requirements and we used, therefore, an advanced temperature programmer, a Eurotherm 818P, which is capable of multi-stage ramping and self-tuning. The latter feature is important as the thermal characteristics of the SIP are very different from those of a normal furnace and it requires careful optimisation of the proportional, integral and derivative (PID) parameters to work successfully. In addition, because of the very low thermal mass of the SIP, it was necessary to step-down the voltage supplied to the furnace by the controller.

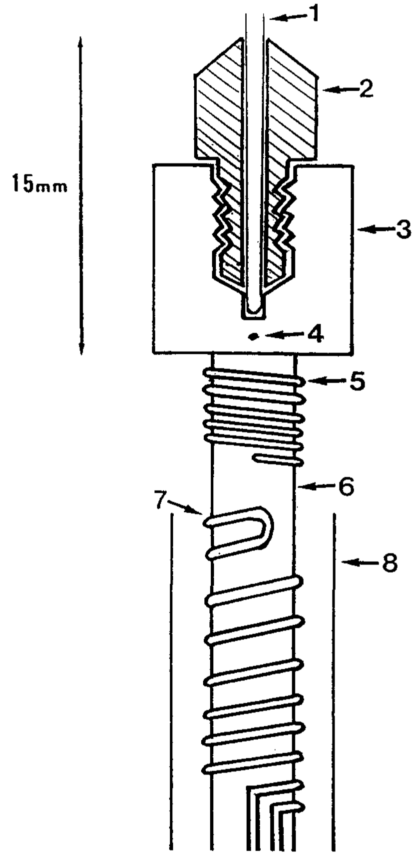


Fig. 1 Diagram of the solid insertion probe (SIP). 1 Sample tube; 2 Sample chuck; 3 Probe head; 4 Thermocouple position; 5 Heating coil; 6 Stainless steel shaft; 7 Water cooling coil; 8 Stainless steel outer sheath

The mass spectrometer, a VG Micromass 12F, has useful mass/charge range (m/z) = 12–600 and a resolution (10% valley) of approximately 2000. It is capable of scanning at a rate of 0.3 s per mass decade and has a sensitivity level in the femptogramme range.

The computer system controlling the mass spectrometer is produced by MS Services. Based on an ultra fast custom-designed 32 bit RISC chip set, it gives all of the usual facilities. For this type of work, the most useful features are background subtraction, multi-channel selected ion monitoring, both on and off-line, and very sophisticated data processing and display options. It provides three types of information which can be displayed simultaneously, if necessary. The main output is the total ion current (TIC), which is the instantaneous summation of all masses during one mass scan and represents the total amount of material evolved as a function of time. In terms of more conventional techniques its appearance is analogous to a derivative thermogravimetry (DTG) or differential scanning calorimetry (DSC) trace. In addition, the current mass spectrum at any point during the run can be shown in a second window on the VDU. If there is prior information on the system being studied, it is possible to show also selected evolved gas profiles, which represent the evolution of individual species in real time, i.e. as the run is taking place. These are formed by plotting the appropriate m/z values as a function of time. Naturally, each m/z value selected should represent only one of the possible evolved species. In cases where it is not possible to choose the m/z values beforehand, examination of the mass spectra after the run has been completed, will enable appropriate selections to be made. The software will then perform the necessary construction of the desired evolved gas profiles from the accumulated mass spectra. The ability to deconvolute the TIC trace into its component parts, either the individual mass spectra or the reconstructed evolved gas profiles, is the key to the success of the technique.

Once the sample, typically a few microgrammes, has been loaded into the MS, the instrument is set to perform repetitive mass scans, usually at a rate of one decade per second for the duration of the run, and the heating rate is set at a predetermined level, e.g. 20 deg·min^{-1}. The scan rate is chosen, together with the heating rate and temperature range, to give between 500 to 1000 mass scans per run, giving the TIC trace a reasonable level of resolution.

TP-SIP-MS is useful because it provides an enormous amount of information. Not only does the TIC trace give a characteristic evolved gas profile for each compound in a mixture of materials, but the mass spectra associated with each TIC peak give a positive identification of that component as it is vaporised. Alternatively, if the material decomposes, the mass spectra give extremely detailed fingerprints of the products which can be used to identify the material.

The SEM work and X-ray microanalysis were carried out using standard Jeol instrumentation.

Results

SEM

Figure 2 shows the end of a split in the tube, with the offending particle which caused the failure, labelled (A). A back-scattered image of the same region (Fig. 3) reveals different structural details and, the different relative atomic masses, an indication of a non-uniform distribution of an element of high relative atomic mass. Figure 4, again a back scattered image, but now of the wall of the tube, shows the uneven elemental distribution in more detail. It is clear from the micrographs that the foreign particle has a crystalline appearance, unlike the rest of the components in the tube. A brief examination of the particle under a low power optical microscope showed the particle to be light blue and confirmed its crystalline appearance.

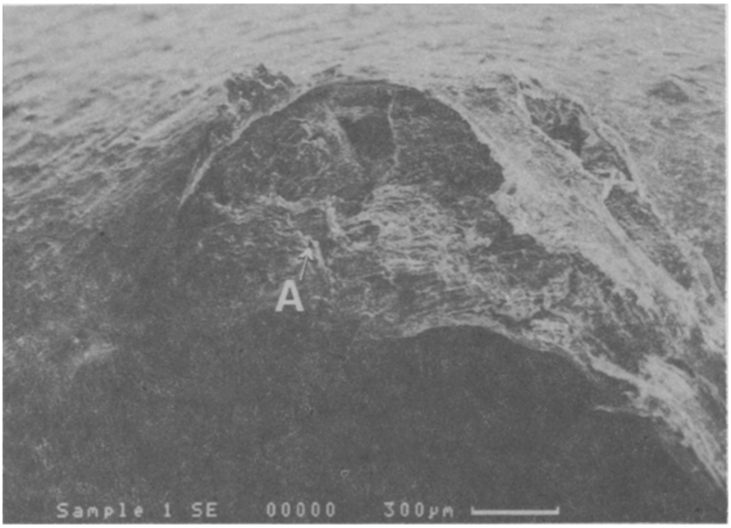


Fig. 2 SEM Micrograph of tube showing the foreign particle

X-ray microanalysis

The emitted X-ray spectrum (Fig. 5) of one of the bright spots, labelled (B) in Fig. 4, indicates that these are rich in bromine. Figure 6 is an X-ray spectrum of the 'background' of Fig. 4, which is the surface of the tubing, and so gives the elemental composition of the pipe material. It indicates the presence

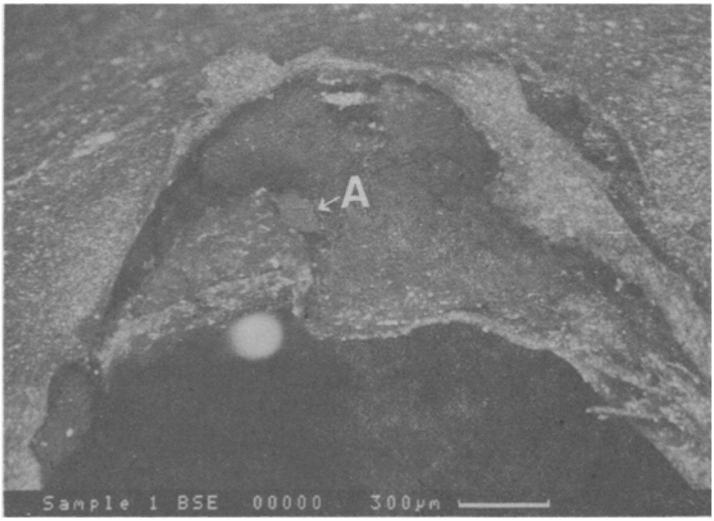


Fig. 3 SEM (Backscattered) micrograph of the tube and foreign particle

of relatively small amounts of sulphur and antimony as well as a some bromine, which could be present beneath the surface and hence not revealed in the SEM images. The X-ray analysis is, of course, not confined to the surface, but samples the composition from a depth of up to 500 μm. Figure 7 is the X-ray spectrum of the foreign particle and indicates that it contains no elements with a relative atomic mass above oxygen. The very small peaks shown are attributed to X-rays emanating from the materials beneath the crystal.

The X-ray microanalysis shows conclusively that the foreign particle is not one of the inorganic components of the product and, in addition, it does not contain bromine. Furthermore, the X-ray analysis reveals the absence of all elements of relative atomic mass above that of carbon. The rather obvious conclusion is, therefore, that the foreign particle is organic in nature. Even although this evidence is negative it is, nevertheless, useful as it eliminates many possibilities and shows that the TP-SIP-MS analysis is essential.

TP-SIP-MS

The organic components of the product were then analysed using TP-SIP-MS. In all cases, for each sample shown, a mass spectrum is provided for every peak in the TIC curve. Figure 8(i) is the TIC curve obtained for a sample of the finished product. It was taken from a section of the pipe shown in Fig. 4. Figures 8(ii–iv) are the mass spectra taken from the three TIC peaks.

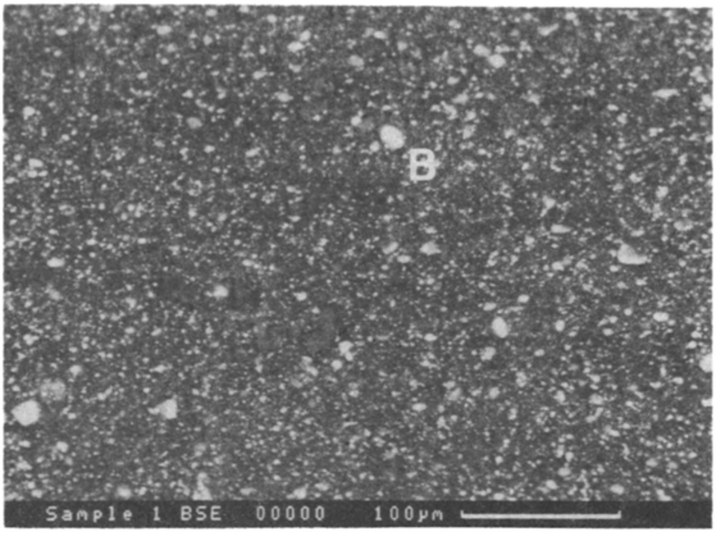


Fig. 4 SEM (Backscattered) micrograph of the tube wall showing uneven elemental distribution

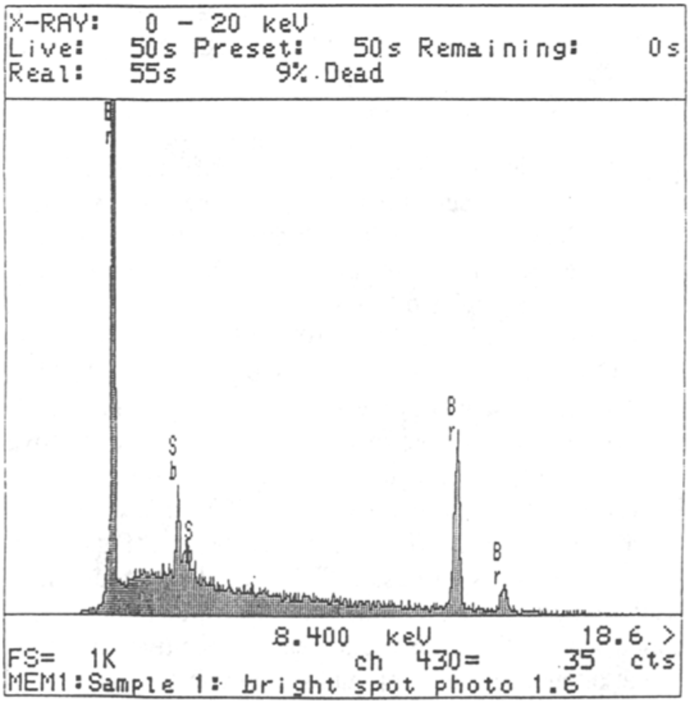


Fig. 5 Emitted X-ray spectrum of a selected region of the tube wall

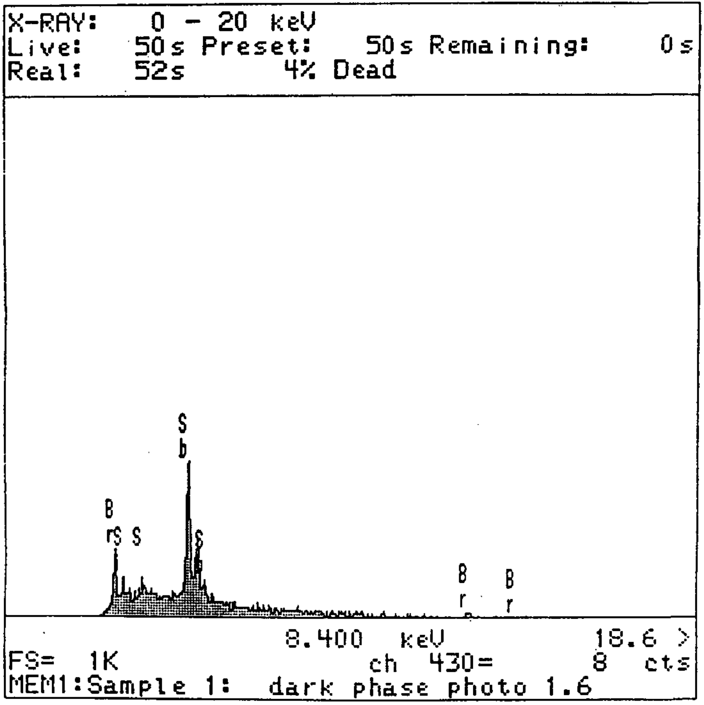
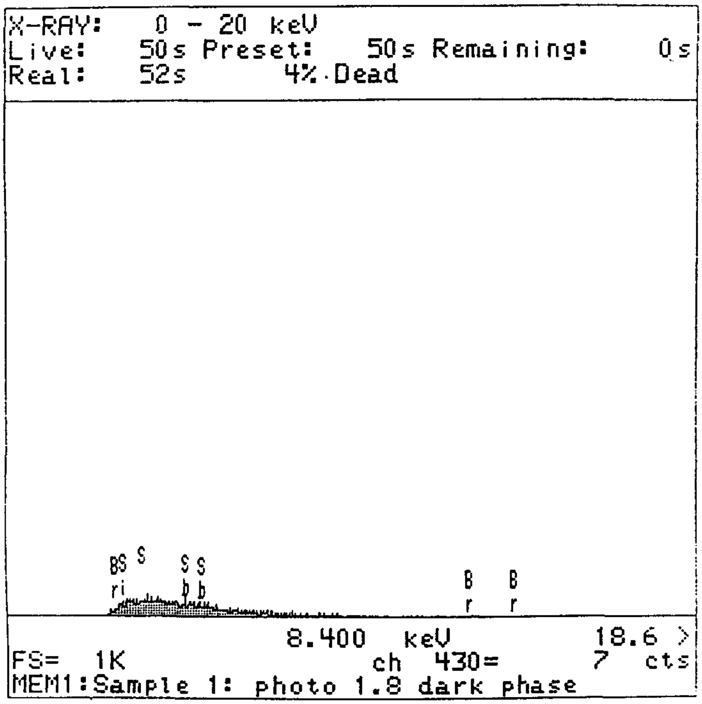


Fig. 6 Emitted X-ray spectrum of the tube wall

By contrast, the foreign particle gave a very different TIC trace, which is shown in Fig. 9(i), with the accompanying mass spectrum in Fig. 9(ii). Comparison of the TIC trace of the particle with those of the various components in the final product suggested that one of these could be the unknown particle. The TIC curve and the associated mass spectrum for this material, Irganox MD 1024, are shown in Figs 10(i–ii). Although the mass spectra associated with the TIC traces of the particle and Irganox MD 1024 could not be identified from the MS library, they were clearly very similar. Furthermore, the mass fragments of both mass spectra were consistent with the structure of Irganox MD 1024 (Fig. 11) and this provided the final confirmation of the identity of the unknown particle. In comparing the TIC traces, it should be noted that the time scale used in Fig. 8(i) is not the same as in Figs 9(i) and 10(i).

It is not possible, of course, to use a TIC trace alone to identify a totally unknown material. However, by studying the mass spectra from which the TIC curve is obtained it is usually feasible to reach a positive conclusion. In many cases, where one or more pure compounds are evolved, they can be identified using the MS library. However, if the mass spectra of the material(s) are not recorded in the library, it is possible to identify them by comparing their MS spec-



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X-RAY:    0 - 20 keV
Live:    50s Preset:    50s Remaining:    0s
Real:    52s        4% Dead
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Fig. 7 Emitted X-ray spectrum of the foreign particle

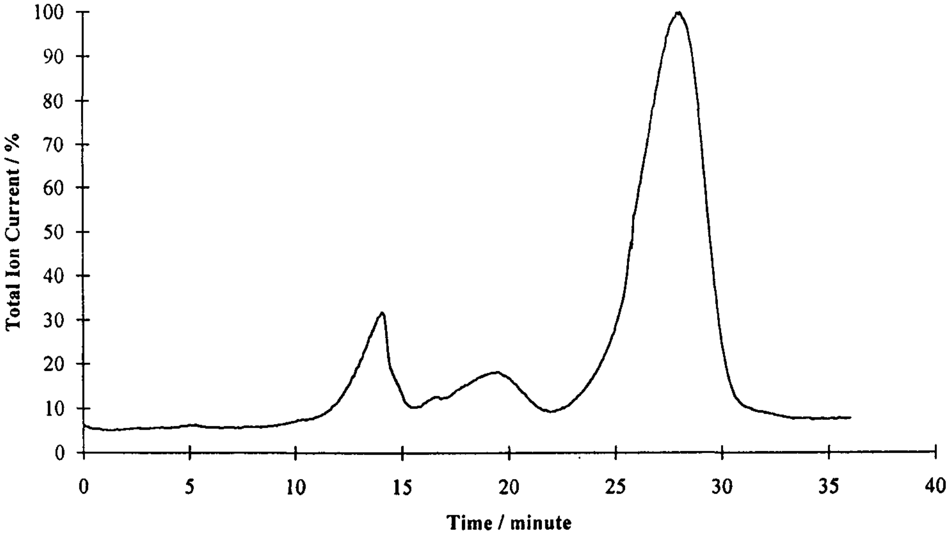

Fig. 8(i) TIC curve produced by TP-SIP-MS analysis of the tube showing three peaks

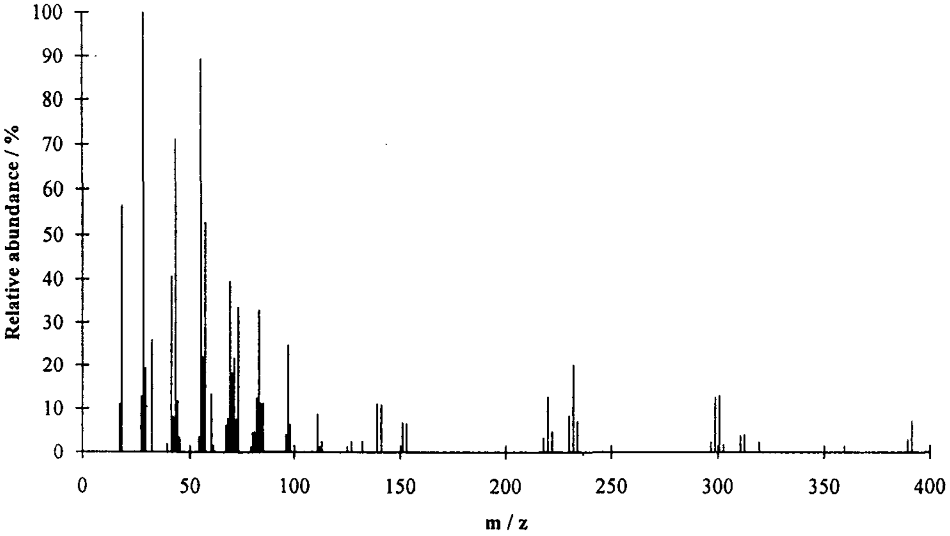

Fig. 8(ii) Mass spectrum from the first TIC peak of the tube

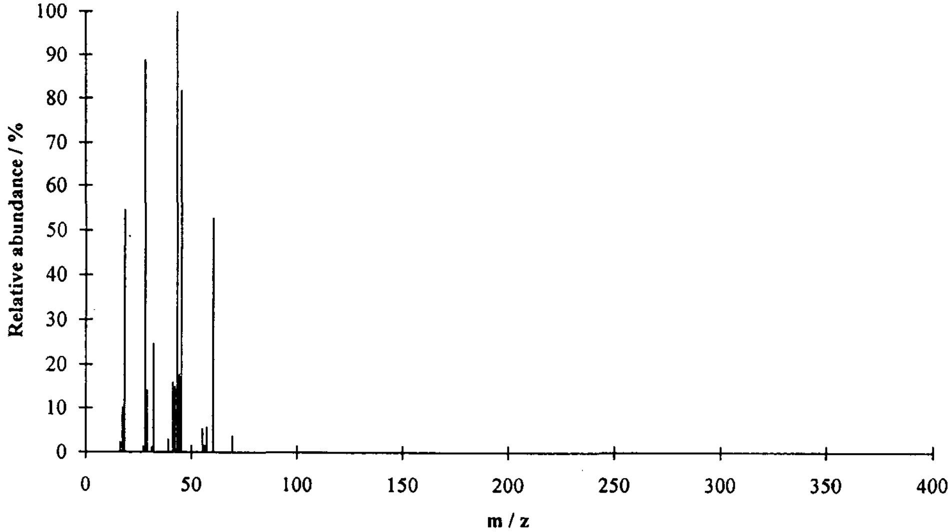

Fig. 8(iii) Mass spectrum from the second TIC peak of the tube

tra with those of known materials. This approach is only of value if the range of possible compounds is limited, but in many real industrial problems this conditions is frequently met.

Even if the materials detected in the gas phase are decomposition products, the TIC curve and its associated mass spectra can be used to identify the parent compound(s) by using them as a fingerprint. This is often the case with polymeric materials, where supporting information can be gained by seeking the mass fragments which would be expected for the thermal breakdown of the polymer. For example, PVC produces characteristic *m/z* peaks at 35 and 37 which are due to the evolution of HCl.

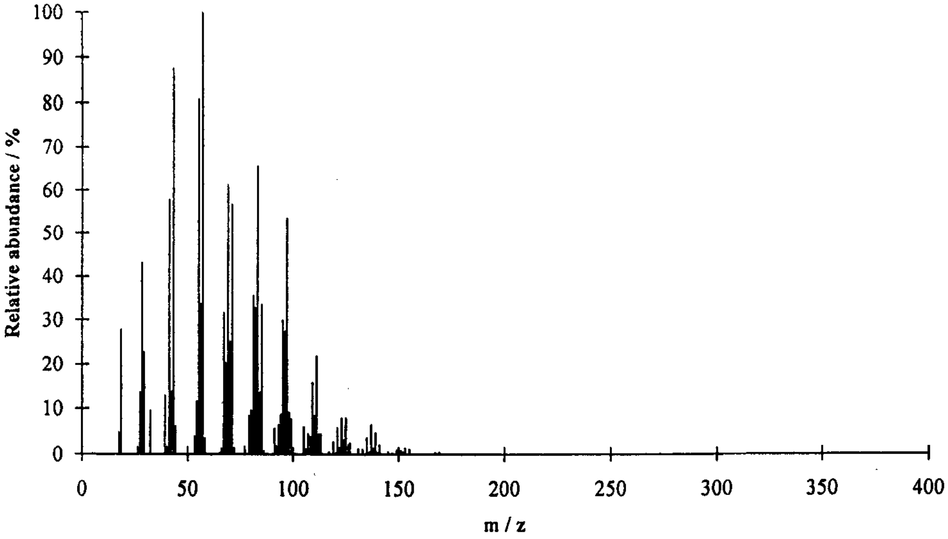

Fig. 8(iv) Mass spectrum from the third TIC peak of the tube

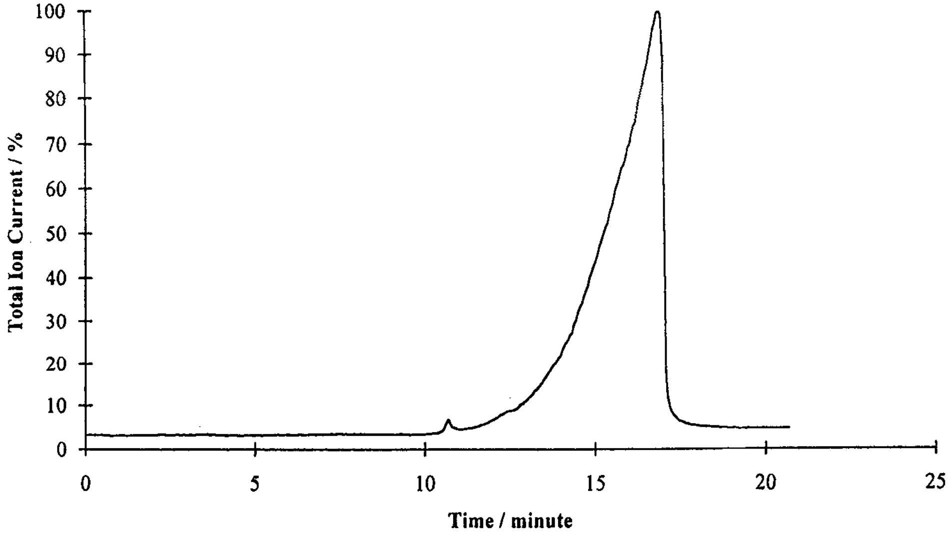

Fig. 9(i) TIC curve produced by TP-SIP-MS analysis of the foreign particle

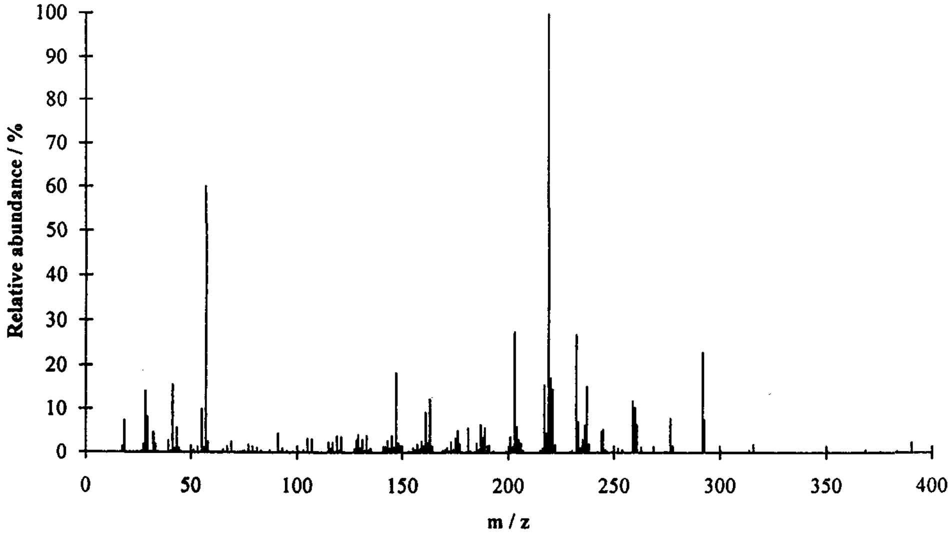

Fig. 9(ii) Mass spectrum produced by TP-SIP-MS analysis of the foreign particle

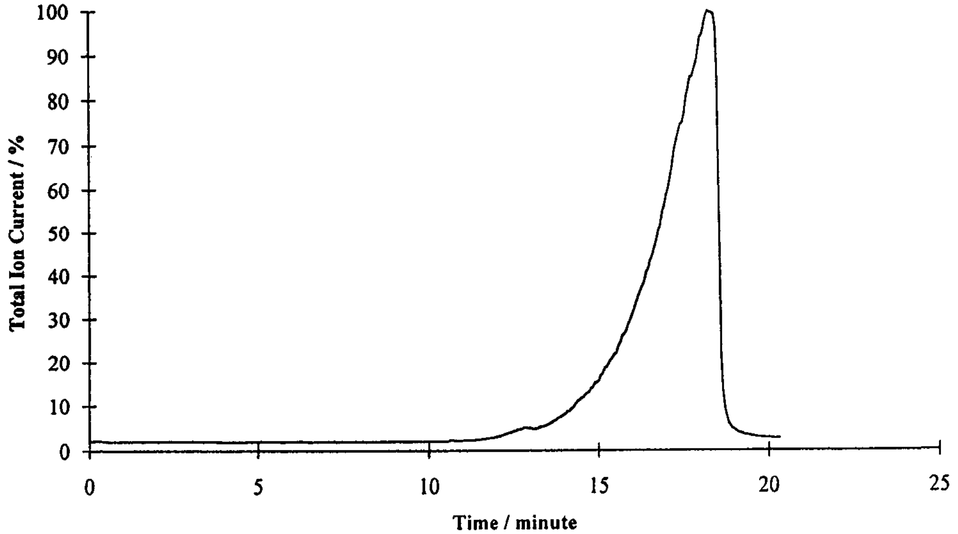

Fig. 10(i) TIC curve produced by TP-SIP-MS analysis of Irganox MD 1024

It is clear that TP-SIP-MS and SEM X-ray microanalysis are complementary techniques, each being applicable to different types of sample. SEM X-ray microanalysis gives an elemental composition for elements with relative atomic mass >16, it is ideal for materials which are involatile, even at 1000°C, and is suitable for microscopic particles. TP-SIP-MS is appropriate to the analysis of

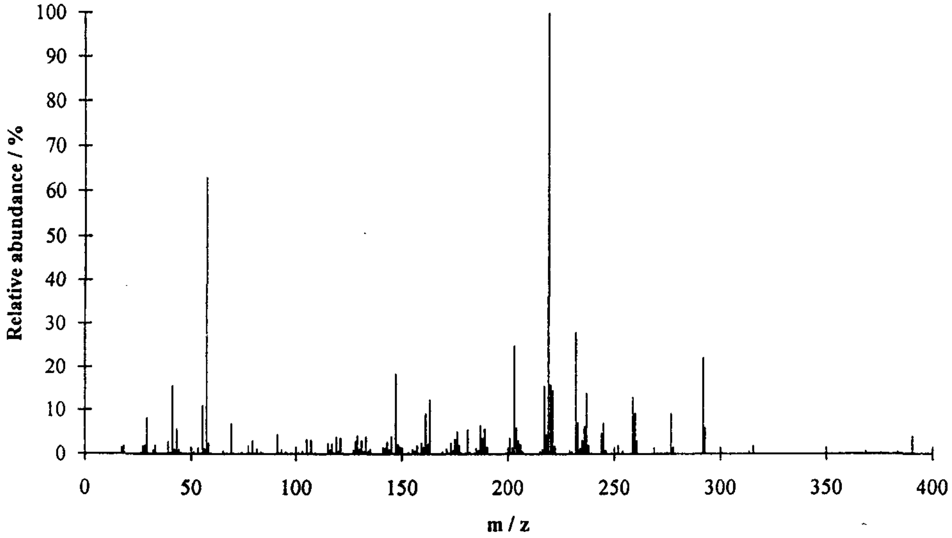

Fig. 10(ii) Mass spectrum produced by TP-SIP-MS analysis of Irganox MD 1024

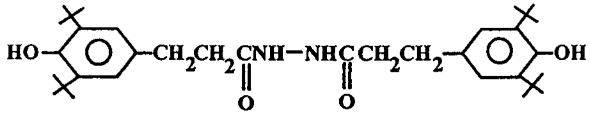

Fig. 11 The chemical structure of Irganox MD 1024

small solid particles which are volatile, or produce volatile decomposition products. It provides information on the molecular composition of the material and is suitable for the analysis of compounds containing all elements.

The identification of the foreign particle enabled the source of the product failure to be traced to one of its constituents, i.e. Irganox. In the light of this, the company was able to take the necessary steps to prevent recurrence of the problem.

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Zusammenfassung — Die Analyse von sehr kleinen Partikeln kann zum Problem werden. Vorliegend wird die Anwendung von TP-SIP-MS, von Scanning-Elektronenmikroskopie und SEM Röntgenmikroanalyse zur Identifizierung von Fremdstoffpartikeln in Industrieprodukten beschrieben. Dabei werden die relativen Vorteile und Grenzen der Technik beschrieben. Es wird gezeigt, daß TP-SIP-MS ein gut geeignetes Instrument für eine derartige Aufgabe ist und die Anwendung herkömmlicher mikroanalytischer Methoden gut ergänzt.