Identification and analysis of polymer additives using packed-column supercritical fluid chromatography with APCI mass spectrometric detection

The Analyst

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Packed-column supercritical fluid chromatography (pSFC) with detection using atmospheric pressure chemical ionisation (APCI) mass spectrometry (MS) provides a versatile method for the detection and quantification of 20 polymer additives, including common antioxidants, light stabilisers and slip agents. Using MS with APCI in both positive and negative ion modes both molecular mass data and informative fragmentation patterns were obtained. The pSFC-MS technique was shown to be linear over a wide concentration range (0.05–25 μg ml^{-1}) and picogram limits of detection with positive ion APCI (single ion monitoring) were determined for Tinuvin 327 (68 pg) and Irganox 1010 (390 pg). The corresponding figures for negative ion APCI were 150 and 470 pg, respectively. Standard mixtures of additives could be separated in less than 15 min with a high degree of resolution. Experiments on additives extracted from polyethylene confirmed these observations, and it was possible not only to identify a number of the additives, but also, in the case of the antioxidant Irgafos 168, an oxidation product.

Introduction

An additive is a compound which is physically dispersed in the matrix without significantly affecting the molecular structure of the polymer.[1] Such additives fulfil several functions, both in processing the material and improving the properties of the product, and can act, for example, as antioxidants, light stabilisers, slip additives, antistatic agents, flame retardants or plasticisers.[2]

There are a number of reasons why the analysis of polymer additives is important. First, health and environmental considerations arise from the use of plastics for an application such as food packaging.[3] Possible leaching of the additives into the food requires the determination of the levels of additives in the plastic and the environment.[4] Recent discoveries that some additives appear to have oestrogenic properties, which have been linked to a drop in the male sperm count,[5] have highlighted the environmental risks from these compounds. As polymer additives are used in processing and to improve the properties of the finished product, any failure of the polymer to meet the desired specification may be due to either insufficient levels of the additive in the product or decomposition of the additives. Therefore, the identification and quantification of additives present, and their possible breakdown products, are invaluable for product quality control.

Direct analysis of additives in the polymer matrix is difficult owing to the small amounts present (often in the ppm range), and chromatographic analysis of polymer extracts is therefore commonly employed. As additives generally have high molecular masses, HPLC has been the most widely used method for analysis of the additives. However, there remains a need for a sensitive universal detector capable of giving molecular identification and structural information; this problem has been overcome to some extent by using MS with a moving belt interface,[6] but this causes problems with thermally labile samples. A recent paper has reported the use of solvent-elimination Fourier-transform infrared (FTIR) spectroscopic detection of polymer additives following separation using HPLC.[7] This technique, however, uses time-consuming off-line detection, and has detection limits in the low- to mid-nanogram range.

Supercritical fluid chromatography (SFC) has been applied to high molecular mass, moderately polar and thermally unstable compounds. In addition, high-resolution separations are possible and a wide variety of gas chromatographic (GC) and LC detectors may be employed.[8] Therefore, SFC offers a suitable alternative to traditional techniques for the separation, identification and quantification of polymer additives. Capillary SFC (cSFC) has been demonstrated to provide high-resolution separation of 21 polymer additives[9] and combination with FTIR spectroscopy permitted identification of the compounds. cSFC has also been coupled with MS using a standard electron impact/chemical ionisation (EI/CI) source for the analysis of standard compounds[10] and additives in real products such as microwave packaging[4] and polyurethanes.[11]

The separation step has been coupled with supercritical fluid extraction (SFE) to provide on-line extraction and analysis of additives in polyethylene[12] and polypropylene.[13] SFE has been linked to cSFC-FTIR to analyse antioxidants in polyethylene.[14] In addition, on-line SFE-cSFC-MS studies on polymer additives have been reported.[15,16] All of these applications have used capillary columns, which are capable of providing high resolution, with analysis times between 40 and 60 min. However, most polymers contain relatively few additives, and therefore the high resolving power of capillary columns is not required, and separations have been achieved in less than 10 min using pSFC.[17] This work employed a single-wavelength ultraviolet (UV) detector, however, which gave no structural information, and was not adequate to characterise unknown additives in real analytical problems. However, on-line SFE-pSFC-FTIR has been used to characterise additives and oligomers in nylon and polystyrene, where specific identification of analytes was achieved.[18]

The use of packed-column SFC coupled with atmospheric pressure chemical ionisation (APCI) MS for the rapid separation and identification of complex and thermally sensitive analytes has been reported.[19,20] A similar study on cannabinoids has also recently been reported.[21] Here we report the use of

pSFC-MS (with APCI) for the identification and analysis of a range of typical polymer additives. The characterisation of single standard samples is described, together with the separation and identification of mixtures of additives. Limits of detection were determined for positive and negative ionisation modes of the mass spectrometer. Finally, the application of the technique to a mixture of additives extracted by SFE from a polythene sample is also demonstrated. The techniques described enable rapid separation and identification of polymer additives to be achieved. The range of fragmentation patterns found using MS with APCI gives a great deal of structural information in a short analysis time.

Experimental

All SFC analyses were performed using a Gilson packed column SFC system (Anachem, Luton, UK) coupled to the APCI source of a Trio 2000 quadrupole mass spectrometer (VG Biotech, Altrincham, UK). The SFC mobile phase was delivered using two Gilson piston pumps. A microprocessor-controlled Gilson Model 308 pump, fitted with a chiller unit (Anachem) to cool the pump head to −10 °C, was used to deliver SFC-grade CO_2 (99.99%, BOC, London, UK). A Gilson Model 306 pump was used for the programmed addition of methanol modifier to the mobile phase. The pumps were connected to a Gilson Model 311C dynamic mixer to ensure homogeneity of the mobile phase.

Separations of the polymer additive standards and extracts were achieved using a 25 cm × 4.6 mm id column with a C_{18} stationary phase. Samples were introduced using a 10 μl injection loop and eluted using a CO_2 mobile phase with a methanol modifier gradient. The modifier programme started at 2% methanol for 1 min followed by a linear gradient to 10% after 10 min and held for 5 min at the final value. A flow rate of 2 ml min^{-1} produced a pressure of 200 bar at the column inlet.

The packed-column SFC system was interfaced to APCI-MS using a tapered 75 μm id restrictor, with a heated tip, inserted into the APCI probe. The position of the restrictor and probe, the gas flow rates and probe temperature were all separately optimised.[22,23] Comparison with UV chromatograms showed that the interface had no deleterious effect on the chromatographic resolution. Thus there is no evidence for mass-transfer problems leading to a two-phase system and impaired resolution.[24] The mass spectrometer was operated in both positive and negative ion modes. Full scan spectra were recorded for identification of the additives and single ion monitoring was used for determining limits of detection and linearity of the detector response.

In order to carry out the analysis in the negative ion mode, the bath gas, sheath gas and source temperature were optimised using replicate injections of the additive Tinuvin 327, 0.05 mg ml^{-1} in methanol. Compressed air was used for the sheath and bath gas, as oxygen was required to initiate the ionisation process for negative ion APCI. Ions were extracted and focused into the mass spectrometer using a −30 to −100 V accelerating voltage applied to the sampling cone.

Chemicals

A range of 25 polymer additives (Fig. 1), including antioxidants, light stabilisers, antistatic agents and slip additives, were supplied by British Petroleum (Sunbury, UK). A polyethylene sample was obtained from the same source to test the system in a real situation.

Extraction

The polyethylene sample was extracted using SFE (the extraction apparatus has been described previously in detail[25]). Briefly, about 2.0 g of ground polyethylene were loaded into an 8 ml extraction vessel, placed in the oven at 80 °C and allowed to equilibrate for 30 min prior to extraction. The sample was extracted in the dynamic mode with pure CO_2 at 350 bar (flow rate 4 ml min^{-1}) and a temperature of 80 °C for 1 h. Extracted material was collected in a vial containing a small amount of methanol after depressurisation at a Jasco (Tokyo, Japan) (Model 880-81) back-pressure regulator. The extract was diluted to 10 ml in a calibrated flask and analysed by pSFC-APCI-MS.

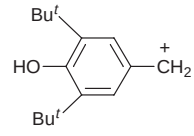
Results and discussion

Standard compounds

The additives shown in Fig. 1 were all studied individually to establish their suitability for SFC-APCI-MS analysis. Injections of individual additives, 0.05 mg ml^{-1} in methanol (HPLC grade), were made to determine the retention times and obtain reference spectra. These solutions correspond to 500 ng of each sample being injected on to the column.

Using the mass spectrometer in the positive ion mode, most of the additives were eluted in less than 15 min under the conditions used; the retention times and mass spectral data are summarised in Table 1. Five additives were not eluted: Chimassorb 944, Tinuvin 770, Irganox 1425, Tinuvin 622 and Synprolam; further increases in the pressure to 300 bar and in the modifier concentration to 20% still failed to elute these compounds. Chimassorb 944 and Tinuvin 622 are high molecular mass polymeric additives, which are more suited to HPLC.[26] Tinuvin 770 is a secondary amine, and the use of a basic additive such as isopropylamine in the modifier[27] may be required to elute this basic compound. Irganox 1425 is an ionic compound and can only be eluted by the addition of a polar additive such as trifluoroacetic acid to the modifier to suppress ionisation of the solute.[28] Most of the additives eluted have good peak shapes, although UV531, Topanol CA and 2-hydroxy-4-methoxybenzophenone gave broad and tailing peaks owing to interactions with active sites on the column.

All of the eluted additives gave a response in the positive ion mode; however, in a number of cases the intensity of the protonated molecule ion was low or zero, notably for the Irganox based antioxidants, which often produced spectra with extensive fragmentation and no protonated molecule ion. The spectra for Irganox 1330, Irganox 3114 and Irganox 1010 are all highly fragmented and exhibit a characteristic ion at *m/z* 219,[11] due to $C_{15}H_{23}O^+$, which has the following structure:



Irganox 1330 has a low intensity molecule ion at *m/z* 774 and a mass peak at *m/z* 569 which corresponds to the loss of one of the hindered phenol groups. Irganox 245 and Irganox 1076 were also found to give weak protonated molecule ions in addition to numerous fragments, and the relative intensities of ions in the spectra at 30 V are summarised in Table 1. In addition to the base peak at *m/z* 219, the spectrum for Irganox 1010 contains a number of higher mass peaks which are separated by 56 mass units, due to the consecutive loss of *tert*-butyl groups from the fragment ions. The base peak in the spectrum for Irganox 1035

occurs at *m/z* 249 and two other fragments are present at *m/z* 193 and 309.

Even at very low cone voltages, extensive fragmentation occurred. For initial identification, and for quantification, it would be very much better to be able to obtain the molecule ion. As all of the Irganox series contain hydroxyl groups, negative ion APCI (to produce deprotonated molecule ions) would be a more suitable technique for these compounds.

The negative ion mass spectra of the antioxidant additives, obtained with an accelerating voltage of −30 V, show less fragmentation than the corresponding positive ion spectra and generally provide molecular mass information. Butylated hydroxytoluene (BHT) exhibits a single mass peak at *m/z* 219 due to the $[M - H]^-$ ion. The mass spectra for Irganox 1035, Irganox 1330, Irganox 1076 and Irganox 245 contain peaks due to M^- and $[M - H]^-$ ions. In addition, owing to the large carbon skeleton of these compounds, which may contain between 38 and 73 carbon atoms, there is a significant contribution from ^{13}C observed in the spectra of the Irganox species mentioned which results in additional mass peaks at 1 mass unit above the expected values. The mass peaks due to M^- and $[M - H]^-$ appear to indicate that ionisation is occurring *via* both charge exchange and proton abstraction. Other Irganox based antioxidants, such as Irganox 1010 and Topanol CA, produced good CI spectra in the negative ion mode without extensive fragmentation. The only exceptions to this were Irganox 3114 and Irgafos 168, which did not exhibit molecule ions and had base peaks in the spectra at *m/z* 346 and 473, respectively. The ions present in the spectra and their relative intensities in the negative ion mode with a cone voltage of −30 V are summarised in Table 1.

In addition to the antioxidants, several other additives were found to be suitable for analysis by negative ion APCI, particularly those with a phenolic hydroxyl group. Thus, the light stabilisers Tinuvin 327, Tinuvin 440 and Tinuvin 328 gave typical negative ion APCI spectra with $[M - H]^-$ ions at *m/z* 356 for Tinuvin 327, *m/z* 434 for Tinuvin 440 and *m/z* 446 for Tinuvin 328.

As in the positive ion mode, structural information can be obtained for the additives in the negative ion mode by increasing the accelerating voltage applied to the sampling cone. In some cases, where fragmentation could be observed in

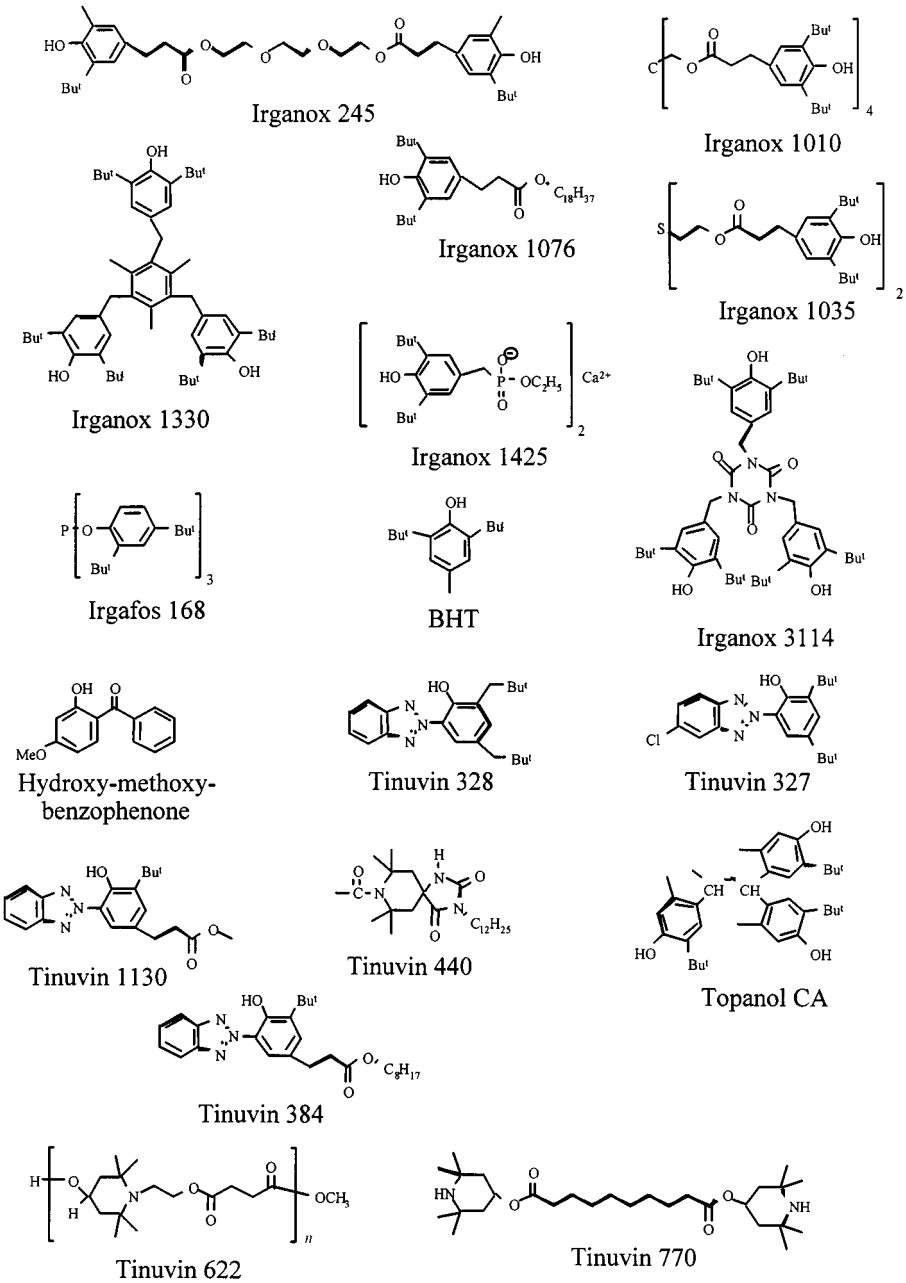


Fig. 1 Structures of polymer additives.

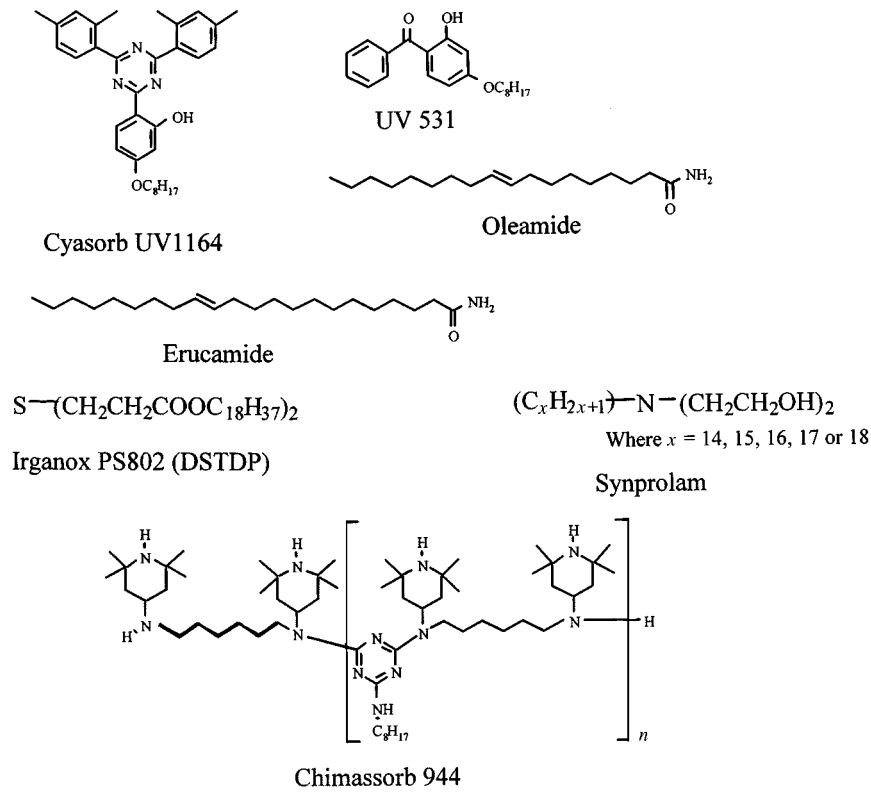


Fig. 1 *Continued*.

both positive and negative ion modes, there were significant differences in the two cases. For example, Fig. 2 shows the positive ion mass spectra for Tinuvin 327 at 30 and 80 V and the negative ion mass spectra at −30 and −100 V. In the positive ion mode the fragment ions arise from loss of the *tert*-butyl groups, but this mechanism was not observed when using negative ion APCI, where the initial breakdown appears to occur by loss of oxygen and chlorine atoms.

The range of structural information obtained by a combination of positive and negative ion mass spectra and several different cone voltages show that pSFC-APCI-MS is a very powerful method for the identification of polymer additives. If a user has also built up a library of mass spectra of polymer additives using the pSFC-APCI-MS technique, then this technique will be very valuable in the structural elucidation of 'unknown'additives.

Table 1 Summary of APCI-MS data for the analysis of polymer additives

Compound	M_r	Retention time/min	Positive ion mode (% rel. int.)[a]	Negative ion mode (% rel int.)[a]
Tinuvin 327	357	4.4	360 (34), 358 (100)	358 (23), 356 (100)
Tinuvin 328	447	7.0	449 (24), 448 (100)	447 (35), 446 (100)
Tinuvin 440	435	4.9	437 (17), 436 (100), 394 (16)	435 (10), 434 (100)
Tinuvin 384	451	5.3	453 (32), 452 (100)	451 (78), 450 (100)
Hydroxy-methoxy benzophenone	228	2.5	230 (10), 229 (100)	228 (15), 227 (100)
UV531	326	4.00	328 (21), 327 (100)	326 (50), 325 (100)
Erucamide	337	7.11	329 (21), 338 (100)	No response
Oleamide	281	4.38	283 (15), 282 (100)	No response
Irgafos 168	646	5.6	648 (21), 647 (100)	474 (89), 473 (100), 205 (36)
Butylated hydroxytoluene (BHT)	220	1.8	221 (50), 220 (100)	220 (12), 219 (100)
Tinuvin 1130	353	4.03	355 (27), 354 (100)	Not run in negative ion mode
Cyasorb UV1164	509	12.1	51(31), 510 (100)	No response
DSTDP (Irganox PS802)	682	9.35	684 (62), 683 (100)	Not run in negative ion mode
Irganox 1330	774	9.2	774 (10), 570 (19), 569 (22), 220 (10), 219 (100)	775 (55), 774 (100), 773 (78)
Irganox 3114	747	5.8	220 (12), 219 (100)	565 (8), 347 (61), 346 (100), 233 (14), 128 (76)
Irganox 1035	642	4.1	309 (27), 250 (14), 249 (100), 193 (12)	643 (42), 642 (100), 641 (80)
Topanol CA	544	5.4	191 (100)	545 (28), 544 (100), 543 (65)
Irganox 1010	1176	10.7	953 (18), 897 (17), 841 (32), 785 (32), 731 (90), 675 (57), 619 (55), 563 (96), 291 (23), 235 (50), 219 (100)	1175 (100), 291 (25), 233 (40)
Irganox 1076	530	4.9	531 (16), 530 (38), 475 (26), 419 (54), 291 (30), 259 (29), 235 (65), 219 (30), 167 (100)	531 (35), 530 (35), 529 (100)
Irganox 245	586	4.0	587 (19), 531 (37), 475 (47), 263 (100), 207 (77)	587 (20), 586 (42), 585 (100)

[a] Ion intensities for the most significant peaks in the mass spectra obtained using cone voltages of +30 and −30 V for positive and negative ionisation modes respectively. Numbers in parentheses are the relative peak intensities.

Linearity of response and limits of detection

For quantification purposes, the detector should give a linear response over the required concentration range and provide low limits of detection. The linearity of the detector response and the limits of detection were determined for an antioxidant and a light stabiliser, Irganox 1010 and Tinuvin 327, respectively. A series of standard solutions was prepared for each additive in the concentration range 25–0.05 μg ml^{-1} in methanol. The mass spectrometer was operated at a cone voltage of +30 V in the single ion monitoring mode with a dwell time of 0.5 s and a span of 0.4 u for each ion monitored. In positive ion mode, the protonated molecule ion at *m/z* 358 was monitored for Tinuvin 327 and the most intense fragment ion at *m/z* 219 was recorded for Irganox 1010. Calibration graphs for the amount injected *versus* the peak area gave a straight line plot with correlation coefficients of 0.998 and 0.997 for Tinuvin 327 and Irganox 1010, respectively, indicating good linearity for the detector response over the concentration range of the standard solutions.

The limits of detection were estimated (for a signal-to-noise ratio of 3 : 1) to be 68 pg for Tinuvin 327 and 390 pg for Irganox 1010.

Similar experiments were carried out in the negative ion mode with a cone voltage of −30 V, showing that the detector response remained linear, with detection limits of 150 pg for Tinuvin 327 and 470 pg for Irganox 1010 (using $[M - H]^-$ ions at *m/z* 356, 1175, respectively). The higher detection limits in the negative ion mode are due to the existence of more than one ionisation mechanism, giving a larger number of peaks in the mass spectrum and reducing the intensities of the base peaks.[22]

In both the positive and negative ion modes, however, the linearities of response and the limits of detection show that the pSFC-APCI-MS method can be used for the analysis of a wide range of polymer additives.

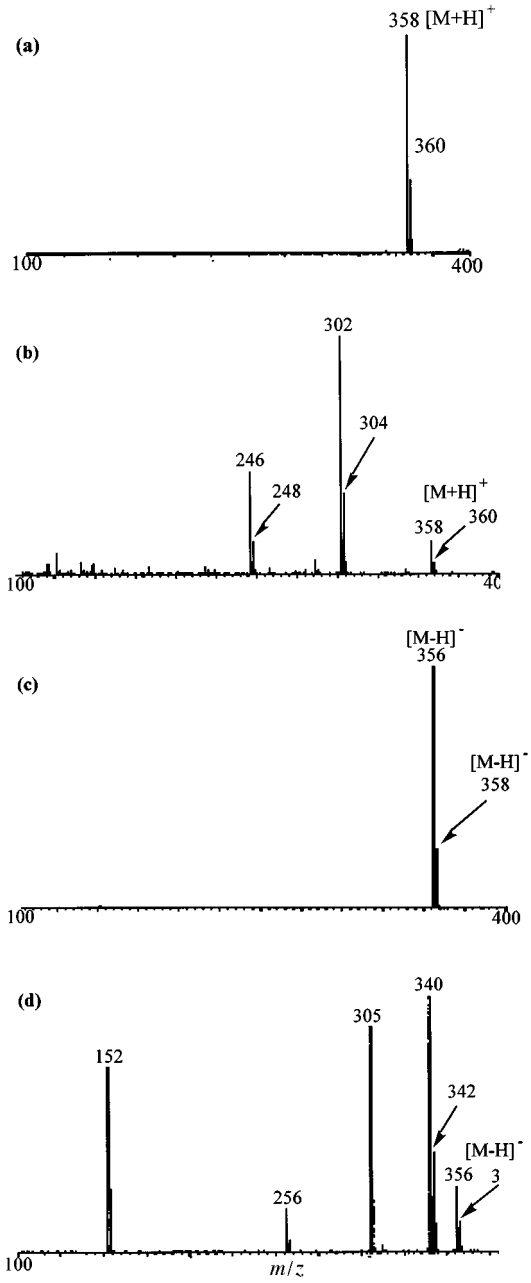


Fig. 2 APCI mass spectra of Tinuvin 327: (a) positive ion mode, accelerating voltage +30 V; (b) positive ion mode, accelerating voltage +80 V; (c) negative ion mode, accelerating voltage −30 V; (d) negative ion mode, accelerating voltage −100 V.

Additive mixtures

Fig. 3 shows the TIC (positive ion mode) chromatogram for the separation of a synthetic mixture of additives consisting of the light stabilisers Tinuvin 327, Tinuvin 328 and Cyasorb UV1164, the antioxidants Irganox 1010 and Irgafos 168 and the slip agent erucamide. The peak shapes are good, and the separation was complete in less than 15 min. The mass spectra obtained with an accelerating voltage of 30 V exhibit protonated molecule ions for all of the additives and very little fragmentation, except for Irganox 1010. Characteristic fragment ions for structure elucidation and identification can be obtained by increasing the accelerating voltage applied to the sampling cone, and polymer additive spectra were generated using cone voltages between 60 and 100 V.

The TIC chromatogram for the same mixture under negative ion conditions (Fig. 4) shows only four peaks. Erucamide and Cyasorb 1164, as expected from the standard samples, gave no response, but all of the remaining additives, including Irganox

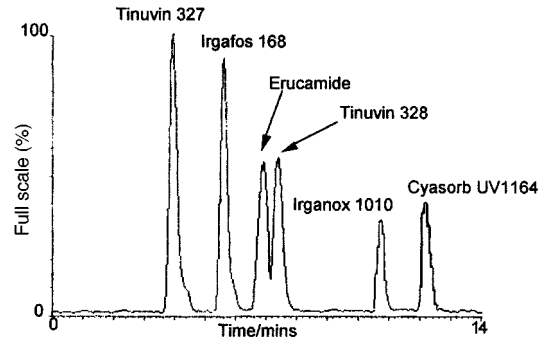


Fig. 3 TIC (positive ion mode) for the separation of six polymer additives.

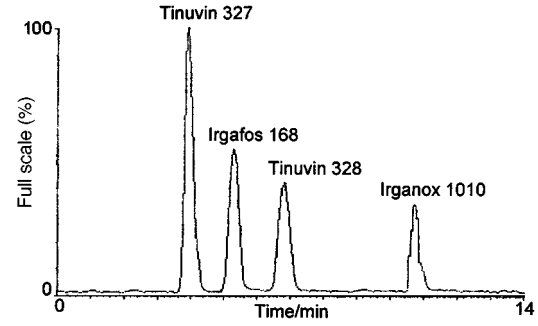


Fig. 4 TIC (negative ion mode) for the separation of four polymer additives.

1010, showed deprotonated molecule ions at low cone voltage.

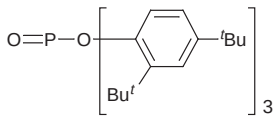
These results, with 500 ng samples injected on-column, show that the separation of polymer additives can be carried out with high sensitivity, and much more rapidly than with capillary SFC.

An additive sample extracted from polyethylene

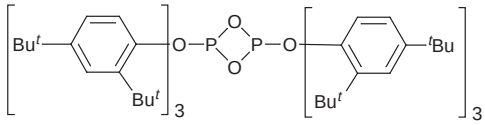
A polyethylene sample was extracted according to the procedure described in the Experimental section. The polymer extract was subsequently analysed by SFC-APCI-MS, using positive and negative ionisation. The positive ion chromatogram, obtained at an accelerating voltage of 30 V, is shown in Fig. 5.

The major component in the extract is the peak at 4.7 min, labelled A. This can be tentatively identified from the corresponding mass spectrum as the peak at *m/z* 647 corresponds to the $[M + H]^+$ ion of Irgafos 168. For positive identification of the additive, the analysis was repeated using a cone voltage of 100 V to produce a spectrum with structurally informative fragments. Comparison of the spectrum with the standard spectrum obtained previously confirmed the identity of the additive as that of Irgafos 168.

The spectrum of peak B at a cone voltage of 30 V has a high-mass peak at *m/z* 1325, which is greater than the mass of any of the standard additives we have analysed to date; in addition there is an ion at *m/z* 663. Increasing the cone voltage to 100 V produces a spectrum with a series of ions separated by 56 mass units corresponding to consecutive losses of *tert*-butyl groups. The feature at *m/z* 663, *i.e.*, 16 mass units higher than for Irgafos 168, corresponds to the protonated molecule ion of the oxidised form of that additive, *i.e.*, Irgafos 168 phosphate (relative molecular mass = 662):



The peak at *m/z* 1325 corresponds to the protonated molecule ion of the dimer of this species, which has a relative molecular mass of 1324:



The fragment species observed at higher cone voltage are consistent with these assignments.

The mass spectrum corresponding to peak C is consistent with that of Irganox 1010, showing extensive fragmentation, by comparison with standard spectra.

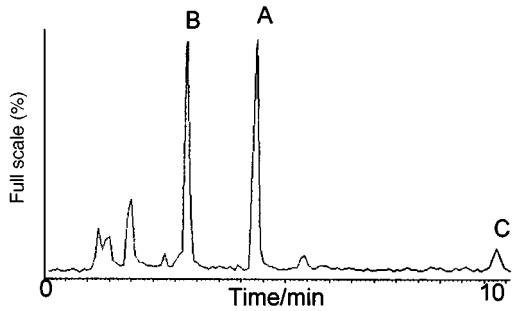


Fig. 5 TIC (positive ion mode) for a supercritical extract of a polyethylene sample.

A negative ion chromatogram of the same extract was therefore obtained, and this showed only peaks A and C. The mass spectrum for the former confirmed the assignment of this to Irgafos 168, and the latter showed a very clear peak at *m/z* 1175, due to the deprotonated molecule ion of Irganox 1010, providing conclusive proof for that assignment.

Several smaller peaks were seen in the positive ion chromatogram, for which mass spectra were obtained. These did not correspond to any of the known additives, and at present these have not been identified.

Conclusions

Packed-column SFC in combination with APCI-MS has been applied to a wide range of polymer additives using both positive and negative ionisation. Except for the hindered phenol type antioxidants, typically the Irganox-based additives (which showed extensive fragmentation), the additives generated good spectra in the positive ion mode. Negative ionisation was found to be ideal for the Irganox species, as these compounds now provided intense molecular ion peaks and informative fragmentation. Some compounds, such as Tinuvin 327, produced good spectra under both ionisation modes, with different fragment ions in the two cases. Both ionisation modes can therefore be used to produce complementary information for identification of the additives.

Low limits of detection (mid- to low-picogram range) in both ionisation modes were obtained for a typical light stabiliser and an antioxidant. The detector response was also shown to be linear over a wide concentration range.

Data from the standard compounds were then employed to identify positively the additives in an extract of a real polyethylene sample.

Thus we have shown that packed-column SFC with APCI-MS detection is an extremely sensitive and versatile method for the detection and identification of a large number of different types of common polymer additives. By comparison with GC, a much wider mass range is accessible, without any need for derivatisation. In addition, our system gives analyses in a much shorter time than can be achieved using capillary SFC.

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