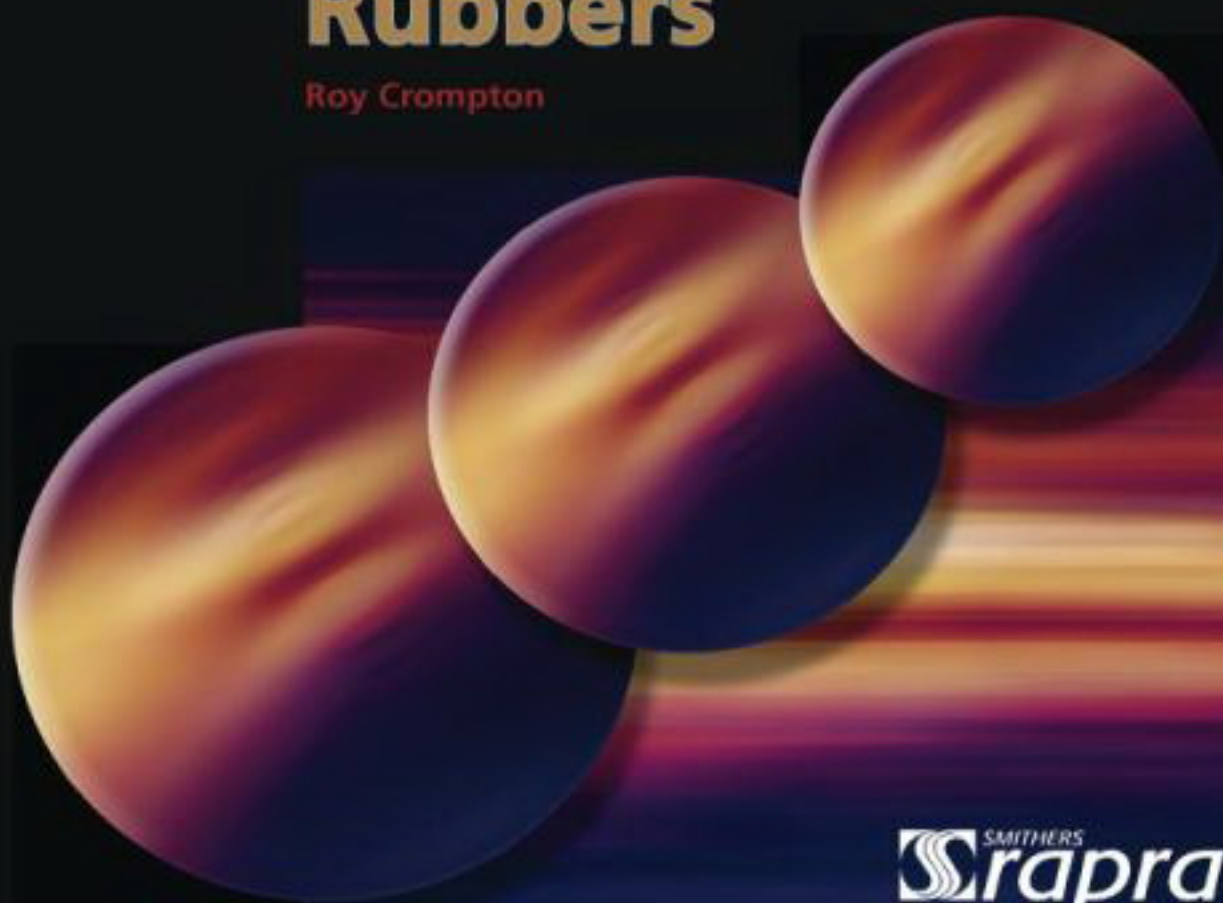# Determination of Additives in Polymers and Rubbers

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SMITHERS rapra

Determination of Additives in Polymers and Rubbers

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A Smithers Group Company

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Determination of Additives in Polymers and Rubbers

Preface

This book is designed as a practical text for use in the laboratories of the plastic producer and user industries and by others such as universities and other institutions who are concerned with problems associated with additives and adventitious impurities in polymers, their breakdown mechanisms and their analysis.

It is now about 30 years since the author wrote his first book on this subject and much has happened in the field since then.

For example powerful new analytical tools have been made available to the chemist by a combination of various chromatographic techniques with methods of identifying separated additives and their degradation products by techniques based on infrared and mass spectrometry. In particular supercritical fluid chromatography combined with mass spectrometry has come to the fore. Combinations of polymer pyrolysis with gas chromatography with mass spectrometric identification of the pyrolysis products is throwing new light on what happens to antioxidants and other polymer additives during polymer processing and products life. Similarly evolved gas analysis and thermogravimetry and dynamic scanning calorimetry are proving very useful in studies of antioxidant loss during polymer processing and service life.

The book is an up-to-date coverage of the present state of knowledge on the subject of polymer additive systems and as such should be extremely useful to workers in the field.

T Roy Crompton
March 2007

Determination of Additives in Polymers and Rubbers

1 Direct Determination of Additives in Polymers and Rubbers

In general, the direct determination of additives in plastics, as opposed to carrying out a preliminary extraction technique, such as is discussed in Chapter 2, is less time consuming and more reproducible. The direct determination of all the additives in such extracts is not always possible because of spectral interferences from other additives, low relative molecular weight (MW), mass matrix oligomers and the extracting solvent. Infrared (IR), and ultraviolet (UV) spectrometric techniques have been used successfully in some cases; in others where the extract is a complex mixture, prior chromatographic separation of the additives is necessary. Methods based on a preliminary extraction of additives from the polymer, then chromatographic separation before the analytical finish are obviously much more time consuming than methods based on direct analysis of the polymer.

Much recent work on the development of direct methods has been carried out and is discussed next.

Chemometrics is the art of extracting chemically relevant information out of data produced in chemical experiments with the use of mathematical and statistical methods [2]. The main issue is to structure the chemical problem in a form that can be expressed as a mathematical problem. Chemometrics have become an integral part of spectroscopy and other areas of chemistry.

Calibration methods seek to express the dependent variable as a linear function of the independent variables. *Linearisation* of variables before calibration will make the calibration model less complicated. According to Beer's law, the concentration and the film thickness are proportional to the absorbance. A transformation from transmittance to absorbance is therefore recommended. Varying film thicknesses might give a multiplicative effect to the absorption spectra. The effect of different thicknesses can be reduced either by scaling the data before calibration or by including the film thickness in the calibration as an extra variable. The unscrambler function multiplicative signal correction (MSC) is a normalisation function which calculates a multiplicative (*B*) and/or additive (*A*) factor for each sample to compensate for differences between the samples [1]:

$$\mathrm{M}_{\mathrm{after}\,(i,\,j)} = \{\mathrm{M}_{\mathrm{before}\,(i,j)} - A_{(i)}\}/B_{(i)} \tag{1.1}$$

where $M_{(i,j)}$ is the absorbance for sample i at wavenumber j before and after scaling. The scaling factors for each sample are calculated from the spectra in regions where spectra based on different concentrations of additives are believed to be approximately equal.

Principal component analysis (PCA) is a statistical technique which, over the last decade, has become a regular tool for analysing chemical data [3-6]. If there is a relationship among any samples in a data set, the PCA will separate the samples into groups.

Partial least squares (PLS) regression is often used for multivariate calibration [7-9]. PLS differs from other regression methods by using the dependent variable (concentrations) actively during the decomposition of the spectra. By balancing the information in the spectra and the related concentrations, the method reduces the impact of large, but irrelevant, variations in the spectra. For each variable, the calibration gives a linear regression equation of the form:

$$[\text{concs}] = B_0 + B_1 A(\lambda_1) + B_2 A(\lambda_2)$$
$$+ \dots + B_n A(\lambda_n) \tag{1.2}$$

where $A(\lambda_n)$ is the absorbance at wavenumber n, where n may represent a single wavenumber or an average.

To discuss the prediction error, one must validate the calibration model [2]. There are two sorts of validation. One method is based on a new set of objects (external prediction). It requires a large and representative set of objects which have to be kept apart from the calibration for testing purposes only. The other validation method is based on the calibration data themselves (internal validation). In most cases, internal validation methods such as cross-validation and leverage correction [2] give sensible results with valuable information about the prediction ability. Cross-validation seeks to validate the calibration model with independent test data, but contrary to external validation it does not use data for testing only. The cross-validation is performed a number of times, each time with the use of only a few calibration samples as a test set. From the validation set it is possible to compare the prediction ability for the models, expressed by the estimated prediction mean square error.

1.1 Infrared Spectroscopic Methods

Vigerust and co-workers [1] used multivariate calibration methods to establish a new method for measurement of three additives in low-density polyethylene (LDPE). The determination of the concentrations of silica, erucamide and butylated hydroxyl toluene (BHT) is based on infrared spectroscopy and a calibration model compared to traditional methods - this method is both time- and cost-effective and is more precise.

A Perkin Elmer FTIR model 1710 was used to record spectra in the region 4000-400 cm^{-1}. As shown in **Figures 1.1-1.3**, silica has intense broad bands in the region 650 to 450 and 1500 to 750 cm^{-1} with little interference or overlap from the polymer itself. BHT, which
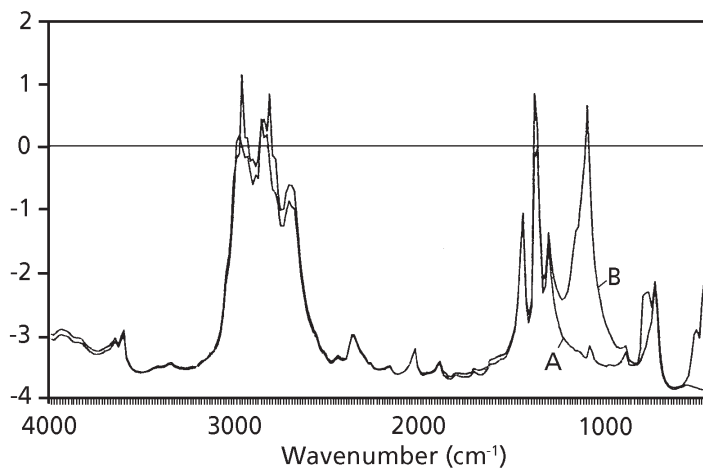
Figure 1.1 Absorbance infrared spectra of pure polymer (A) and polymer 10,000 wt/ppm silica content (B)
Reproduced with permission from B. Vigerust, K. Kolset, S. Nordenson, A. Henricsen and K. Kleveland, Applied Spectroscopy, 45, 173. ©1991, Society for Applied Spectroscopy, MD, USA [1],
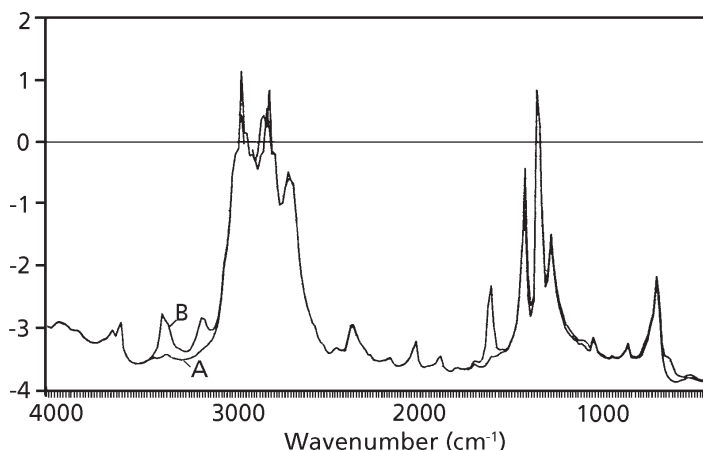
Figure 1.2 Absorbance infrared spectra of pure polymer (A) and polymer with 9300 wt/ppm erucamide content (B)
Reproduced with permission from B. Vigerust, K. Kolset, S. Nordenson, A. Henricsen and K. Kleveland, Applied Spectroscopy, 45, 173. ©1991, Society for Applied Spectroscopy, MD, USA [1],
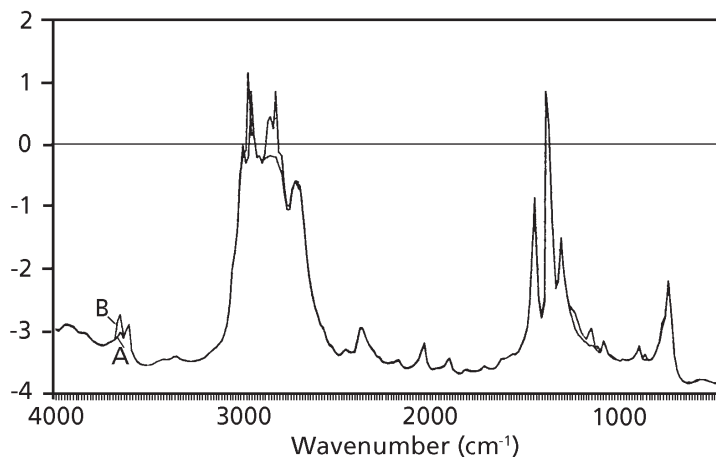
Figure 1.3 Absorbance infrared spectra of pure polymer (A) and polymer with 3400 wt/ppm
BHT content (B)
*Reproduced with permission from B. Vigerust, K. Kolset, S. Nordenson, A. Henricsen and K.
Kleveland, Applied Spectroscopy, **45**, 173. ©1991, Society for Applied Spectroscopy, MD, USA [1]*

is a steric hindered phenol, has sharp bands around 3650 cm^{-1} and some small sharp
bands in areas dominated by silica. Erucamide has broad bands in the region 1700 to
1600 and 3500 to 3100 cm^{-1}. The infrared signals from BHT and erucamide are weaker,
and both have overlapping regions with the polymer. The selective weighting functions
used for the additives in the regression models were especially necessary in order to obtain
good enough prediction results for BHT. But introduction of these functions will make
the models more sensitive to noise when the important infrared signals are small. Thus,
noise from the spectrophotometer in important infrared response areas would also be
weighted and could disturb the prediction ability of the regression models. In contrast
to silica, BHT and erucamide are reactive and can be partly consumed during extrusion
and sample preparation.

The results from the regression analysis are shown in **Table 1.1**. Best results were obtained
for silica with a correlation coefficient (R^2) of 0.99. For BHT the correlation coefficient
was 0.84 and for erucamide 0.91.

Polyethylene glycols (PEG) are used as antistatic agents in polyethylene (PE) resins. PEG is
a difficult additive to analyse. It cannot be extracted either quantitatively or reproducibly.
A simple, rapid and reliable method is required for PEG in PE. Kumar [10] has described
a direct Fourier transform infrared (FTIR) spectrometric approach for successfully
determining low concentrations (<0.05% m/m) of Carbowax (PEG 400) in high-density
polyethylene (HDPE).

Table 1.1 Regression output			
Additive	BHT	Erucamide	Silica
Standard error of estimate (wt/ppm)	69	72	30
Correlation coefficient (squared)	0.84	0.91	0.99
Number of observations	19	19	19
Degrees of freedom	18	18	18
Regression coefficient	1.01	0.96	1.00
Standard error of coefficient	0.03	0.03	0.01
Reproduced with permission from B. Vigerust, K. Kolset, S. Nordenson, A. Henricksen and K. Klevelond, Applied Spectroscopy, 45, 173. ©1991, Society for Applied Spectroscopy, MD, USA [1]			

The PEG analytical band at 1110 cm^{-1}, due to the C-O-C linkage, is first isolated from the overlapping PE bands by spectral subtraction - the integrated absorbance (1000-1170 cm^{-1}) per unit thickness then gives a measure of the PEG concentration in the resin. The detection limit is about 0.02% *m/m*, and the analysis time is 10 minutes excluding sample preparation which involves melt-pressing the sample into 0.25-0.38 mm plaques. The speed and simplicity of the analysis make the method suitable for use in quality control laboratories.

Infrared spectra were collected using a Nicolet 7199 FTIR spectrometer, equipped with a Model 1280 data acquisition system, a liquid nitrogen cooled narrow-band mercury – cadmium – telluride detector with a potassium bromide window, a water-cooled globar (silicon carbide) source and a Ge/KBr beam splitter. The interferograms were obtained with a four wavenumber resolution (number of data points = 4096) and a medium interscan correlation. A Happ-Genzel apodisation was used to transform the interferometric data into a single-beam spectrum over the spectrometer range (4000-600 cm^{-1}). The corresponding single-beam spectra were ratioed against the single-beam instrumental background recorded without the sample in the IR beam path. Sixty-four co-added scans yielded an adequate signal-to-noise ratio in the spectra.

Figure 1.4 shows the IR spectrum of Carbowax PEG 400 indicating the prominent bands due to the C-O-C ether linkage (1110 cm^{-1}) and the broad hydroxyl band (3380 cm^{-1}). The broad, intense band at 1110 cm^{-1} was chosen for determining the PEG concentration. **Figure 1.5(a)** shows the scale-expanded (1240-1000 cm^{-1}) spectra of HDPE resins containing 0, 0.04, 0.08, 0.12, 0.16 and 0.20% *m/m* Carbowax PEG 400. The PE bands in this region are sharp, but the PE background absorption severely overlaps the PEG
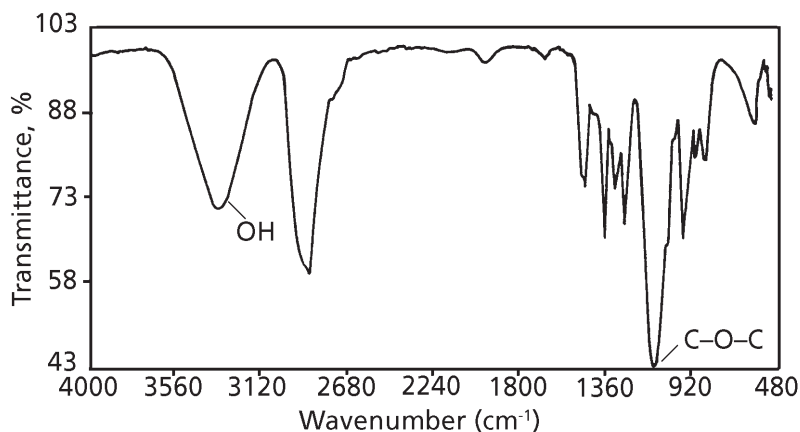
Figure 1.4 IR spectrum of Carbowax PEG 400 showing characteristic absorptions due to the OH and C-O-C structures
Reproduced from Kumar, RSC [10]

analytical band. However, it can also be seen that the PEG band intensity marginally increases with increasing PEG concentration in the resin. Owing to spectral overlap and slight increases in PEG absorbance, the measurement of absorbance at the peak maximum or integrated absorbance in these overlapping spectra will be inaccurate and imprecise.

In order to measure the PEG band intensity or area correctly, the spectral subtraction approach was used to isolate the PEG band. First, the spectrum of PEG-free HDPE was obtained and then the HDPE background absorption from each of the standards was subtracted. **Figure 1.5(b)** shows the corresponding difference spectra of the four standards by adjusting the scaling factor until the PE reference band at 2019 cm^{-1} is cancelled out. It can be seen that the PEG band is clearly isolated in each spectrum, allowing the PEG concentration to be measured precisely and determined reliably. The band area (1170-1000 cm^{-1}) and peak maximum per mm were measured for each difference spectrum of the standards. The linear calibration graphs showing area and peak height per mm *versus* PEG concentration in HDPE are shown in **Figure 1.6**.

Using this method PEG 400 concentrations of 0.195% *w/w* were found for a polymer known to contain 0.18-0.2% PEG 400.

For resins with completely unknown compositions, this method is not applicable because the analyst cannot determine the possible interferences. For instance, the Si-O band in silica and silicates, often used as antiblock agents, overlaps the C-O-C band in PEG. As the crystallinity in HDPE can also vary, spectral subtraction could cause some uncertainty from incomplete removal of the PE crystallinity band absorption at 1075 cm^{-1}.
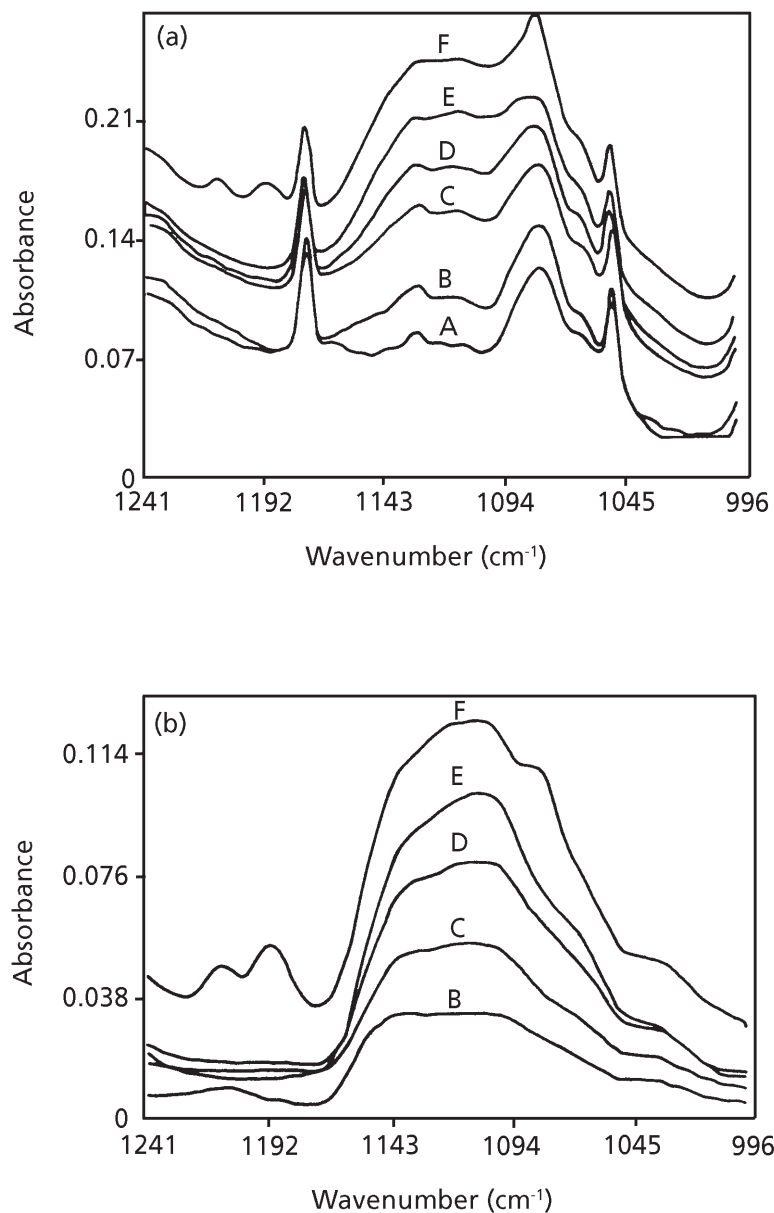
Figure 1.5 Scale-expanded spectra (1240-1000 cm^{-1}) of HDPE containing A, 0; B, 0.04; C, 0.08; D, 0.12; E, 0.16; and F, 0.20% *m/m* PEG 400. (a) Original spectra and (b) difference spectra showing the PEG analytical band.
Reproduced from Kumar, RSC [10]
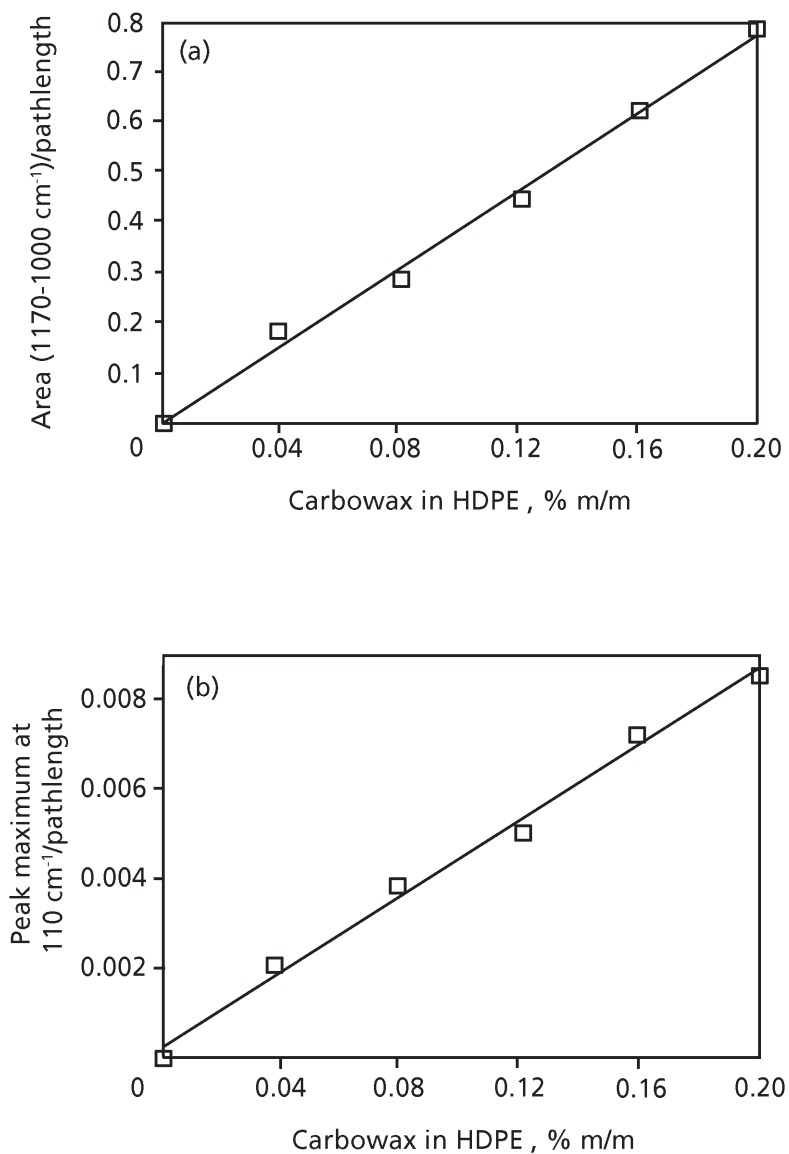
Figure 1.6 Linear calibration graphs for PEG 400 in HDPE. (a) Area: slope = 3.7857; intercept = 8.1 x 10^{-3}; r^2 = 0.996. (b) Peak maximum: slope = 4.27 10^{-2}; intercept = 1.6 x 10^{-4}; r^2 = 0.998
Reproduced from Kumar, RSC [10]

Crecely and Day [11] prepared thin films of thermoplastic polymers for IR spectroscopy by hot pressing at an appropriate temperature and thickness. Their IR spectra display peaks are unique to certain additives. Quantitative data can be obtained from measured absorbance, measured film thickness and the absorptivity given in **Table 1.2**. This assumes that the polymer is the solvent. Polyolefins lend themselves best to this technique, because their IR spectra have few interfering bands. Usually the quantitative measure of organic additives can be expected to be at least ±10% relative standard deviation, except in the case of inorganics where the result is only a reasonable estimate of concentration.

Direct measurement of concentration can also be used for some UV absorbing additives by using thin films and a UV spectrophotometer.

Karlsson [12] in his review article on recycled polyolefins discusses the characterisation of recycled polymers in terms of polymer degradation, polymer composition and the presence of low MW compounds (degradation products of matrix and additives, initiator or catalyst residues, solvents and so on) using spectroscopic (UV, IR, nuclear magnetic

Table 1.2 Direct IR measurements				
Polymer	Press temperature (°C)	Additive	Peak (µm)[a]	Absorptivity (A/mil/100%)[b]
Polyethylene	140	Talc	9.85	10
Polyethylene	140	Kaolin clay	9.95	8.5
Polyethylene	140	Zinc stearate	6.47	3.4
Polyethylene	140	Stearic acid	5.85	5.3
Acrylonitrile-butadiene-styrene	150	Ethylene distearamide	3.03	4.0
Acetal	200	Nylon	6.08	8.5
Polypropylene	160	Antimony oxide	26	2.1

$$\frac{Measured\ absorbance \times 100}{Absorptivity \times sample\ thickness\ (mil)} = wt\%$$

[a]*A given wavelength, x (µm) and wave number, y (cm⁻³) can be interconverted by the formula xy = 10,000*

[b]*1 mil = 0.001*

1 inch = 0.0254 mm

Reproduced with permission from R.W. Crecely and C.E. Day in Plastics Additives: An A-Z Reference, *Ed., G. Pritchard, Chapman and Hall, London, UK, p.26-31. ©1998, Chapman and Hall [11]*

resonance (NMR)), chromatographic (high performance liquid chromatography, gas chromatography (GC), gel permeation chromatography (GPC)) and thermal dynamic scanning calorimetry (DSC) analytical techniques and examples of their applications are described.

Near IR spectroscopy of PE powder was carried out before compounding with Irganox 1010 and Irgafos 168. It was observed that the identification and selection of specific bands or unique spectral features in the spectra is difficult. The variation in baselines is due to differences in scattering properties of the analytes. Multiplicative scattering correction or derivation can eliminate these variations [13, 14].

A certain relationship between the samples that contain antioxidants exists, since they are gathered in two clusters, whereas the non-stabilised sample differs from the rest. By PCA the cluster on the left side is built by samples that contain a total amount of antioxidants lower or equal to 2,200 ppm and the cluster on the right side is made up of samples having total antioxidant concentrations above 2,500 ppm. The difference between virgin HDPE and stabilised samples may also be explained by the degradation of the virgin sample during extrusion, which has been confirmed by the presence of carbonyl groups and changes in crystallinity as measured by FTIR and DSC, respectively. The virgin sample showed a carbonyl index (CI) equal to 0.29 whereas the samples containing Irgafos 168 above 300 ppm did not show carbonyl groups at all. Samples with concentrations of Irgafos 168 below 300 ppm were slightly degraded, the CI was in the range 0-0.09. Small differences in the DSC crystallinity were observed among the stabilised samples, their values were in the 62-65% interval. However, a lower crystallinity value, 57% was obtained for the virgin specimen. The root mean square errors of prediction for Irganox 1010 and Irgafos 168 were 45 and 95 ppm, respectively. The models were obtained using a PLS regression with four factors over the 5000-9000 cm^{-1} spectral segment.

Nishikawa and co-workers [15] developed dynamic compression modulation attenuated total reflection - Fourier transform infrared (ATR-FTIR) spectroscopic methods for characterising polymer films. To obtain dynamic compression polarised ATR spectra, internal reflection element (IRE) secure assemblies made of tungsten carbide with very high hardness (Knoop hardness of >1000 kgf/mm^2) were designed. These assemblies are mounted on the Harrick Seagull ATR attachment and measured by step-scan FTIR spectroscopy. The effect of static compression, air gaps, and refractive index changes were examined. Experimental and simulated results showed that the effect of air gaps between the sample and IRE and refractive index changes of the sample and IRE are negligible at values larger than a static torque of 40 cN-m and good signal-to-noise ratios and reproducible data can be obtained. Uniaxially and biaxially drawn polyethylene terephthalate (PET) films were measured by this method. Both bipolar and unipolar bands were observed in the dynamic in-phase ATR spectra, which can be associated with their micro-structural environmental changes. This technique shows promise in evaluating

various polymer film materials, including biaxially oriented films, multilayer coated film surfaces, and molecular interactions between polymer-polymer and polymer-additives at the film surface.

Various workers have reviewed the application of IR spectroscopy to the determination of additives [16, 17, 18]. Other recent applications of IR spectroscopy include the determination of slip agents in PE [19], ethyl acetate and ethanol in HDPE [20], stearic acid in polystyrene (PS) [21], talc, antimony trioxide and decabromophenylether flame retardants in polyvinyl chloride (PVC) [22-24], mould release agents [25] and binders in aged paint film [26].

1.2 Ultraviolet Spectroscopy

This technique has found very limited applications in the direct analysis of additives in polymers.

Soucek and Jelinkova [27] have also used this differential principle to determine in polypropylene (PP) two antioxidants (2,6-di-*tert*-butyl 4 methylphenol and 4-substituted 2,6-xylenol) which have virtually identical UV absorption spectra in the absence of alkali. The antioxidants can be distinguished in alkaline medium, where 4-substituted 2,6-xylenol forms phosphonate readily, thus allowing the utilisation of the bathochromic shift for its determination. The use of derivative spectroscopy reduces light scattering and matrix interferences when extracts from PP samples are measured.

Lutzen and co-workers [28] describe an in-line monitoring, UV method for the determination of polymer additives such as thermal and UV stabilisers and antioxidants in polymers.

Thermal UV spectroscopy has been used to identify and determine organic and inorganic pigments in polymers.

Organic and inorganic pigments are used for coloration of polymers, polymer films and polymer coatings on metal containers. Vapour phase UV absorption spectrometry at 200 nm has been used to identify such pigments [29]. In this method powdered samples are directly vapourised in the heated graphite atomiser. Thermal UV profiles of organic pigments show absorption bands between 300 and 900 °C, while profiles of inorganic pigments are characterised by absorption bands at temperatures above 900 °C. Temperature, relative intensity, and width of the bands allow the identification of the pigments. The technique shows fast acquisition of thermal UV profiles (2-3 minutes for each run), good repeatability and wide thermal range (from 150 to 2300 °C). The method has been applied to a variety of polymers.

A practical example of the identification of pigments is given in **Figure 1.7**. A 1:1 mixture of organic pigment yellow (2-nitro-*p*-toluidine coupled with acetoacetanilide) and inorganic PY 34 (lead chromate) was vapourised using the conditions quoted in **Figure 1.1(a)**. The thermal UV profile clearly shows two absorption bands at about 500 °C and 1250 °C. The first band is attributable to the vapours which originate from the decomposition and pyrolysis of the organic pigment, the second band corresponds to the decomposition and vapourisation of lead chromate at high temperature (mp = 844 °C). It is possible therefore to determine by a rapid run whether the pigment is a mixture or belongs to the organic or inorganic group.

Blue and green organic pigments are commonly derivatives of copper phthalocyanine, which is characterised by remarkable resistance to thermal treatments. In fact these pigments show UV absorption at temperatures higher (about 800-900 °C) than those observed for yellow and red pigments **Figure 1.7(b)**.

Albarino [30] has stated that analysis of PE additives by means of UV spectroscopy is limited by excessive beam dispersion due to light scattering from the polymer crystalline regions. Additives at low concentrations (0.1%) require sample thicknesses which mean that analysis must be performed in the presence of a high level of scattering which may change unpredictably with wavelength. At lower levels of concentration and correspondingly greater sample thicknesses, unacceptable signal-to-noise ratios exist. Nevertheless, UV spectroscopy remains an attractive method for analysis of many additives. Principal advantages over IR analysis include greater sensitivity arising from higher extinction coefficients and a lack of interfering absorptions from the PE matrix. These advantages can be realised, however, only if background scattering from the polymer can be reduced.

Albarino [30] demonstrated the feasibility of quantitative UV analysis of additives in PE at temperatures above the polymer melting point where the crystallites, which account for much of the scattering, are eliminated. Greater sample thickness and analytical sensitivity are possible compared to analysis of solid samples at room temperature. In this work, sample thickness was controlled by brass shims held between Suprasil grade silica windows (Heraeus Amersil, Inc.) by a faceplate bolted to the cell body.

PE samples were prepared for analysis by calculating the weight required to fill the shim opening in the melt. Samples were inserted into the shim opening as pressed films cut to size; several layers were required for greater thicknesses. After gently tightening the faceplate, the cell was rapidly heated to 120 to 125 °C by supplying about 65 W to the heater. By proper tightening of the faceplate, the shim space was uniformly filled with PE, after which the cell was transferred to the sample compartment of a spectrometer. Upon warmup to the melt, an input power of 29 W maintained cell temperature within the limits given in **Table 1.3** during scanning. Cell temperature was regulated only to the extent of maintaining the melt between 121 to 135 °C. A small temperature increase, given
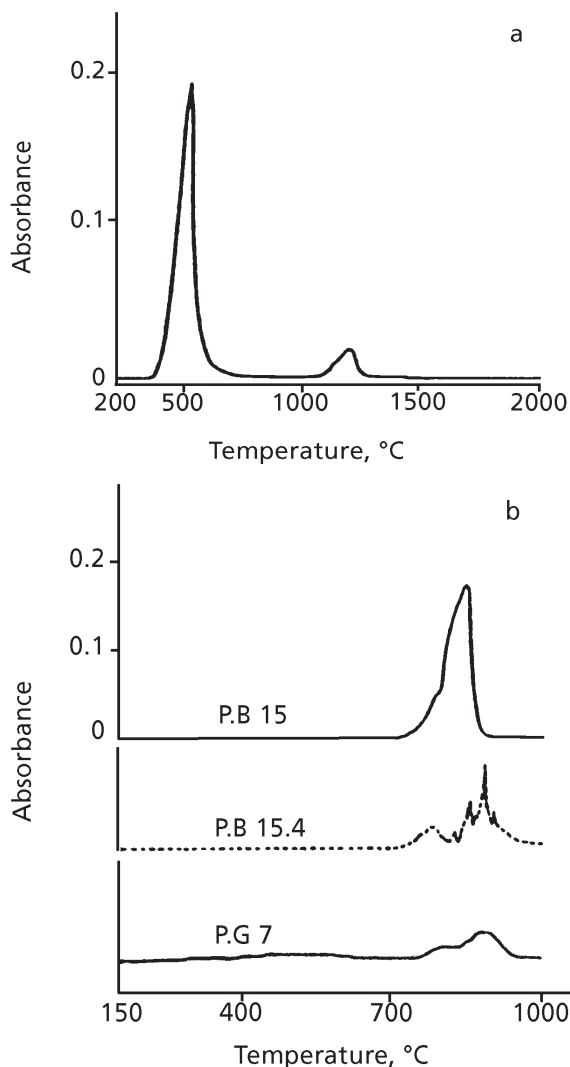
Figure 1.7 Thermal UV profile of (a) 1:1 mixture of organic pigment yellow (2-nitro-*p*-toluidine coupled with acetoacetanilide and inorganic pigment PY 34 (lead chromate). (b) PB 15.4 copper phthalocyanine (beta form); PG 7 polychlorinated copper phthalocyanine (14-16 chlorine atoms)

Thermal cycle	1	2	3
Temperature, °C	200	2000	2650
Ramp times, s	10	8	2
Hold temperature, °C	25	10	5
Time constant		0.5	

Source: Author's own files

	Composition Irganox 1010 in PE (%)	Thickness (cm)	Temperature (°C)	Sample absorbance at 2800 Å	Baseline absorbance at 2800 Å	Antioxidant absorbance at 2800 Å
Table 1.3 Analysis of Irganox 1010 antioxidant in molten polyethylene						
1	0.101	0.030	121-129	0.212	0.032	0.180
2	0.101	0.058	122-126	0.347	0.044	0.303
3	0.101	0.081	122-125	0.511	0.053	0.458
4	0.101	0.112	123	0.678	0.065	0.613
5	0.051	0.218	124-125	0.692	0.107	0.585
6	0.051	0.056	122-127	0.217	0.043	0.174
7	0.051	0.109	124-127	0.378	0.06	0.314
8	0.051	0.165	124	0.548	0.086	0.462
9	0.010	0.274	123-128	0.278	0.129	0.149
10	0.010	0.508	122-124	0.486	0.222	0.264
11	0.010	0.612	125-128	0.585	0.264	0.321
12	0.010	0.780	127-135	0.753	0.330	0.423
13	0	0.058	123-124	0.278	0.058	
14	0	0.266	126-129	0.486	0.130	
15	0	0.508	124-132	0.585	0.218	
16	0	0.780	123-131	0.753	0.333	
Reproduced with permission from R.V. Albarino, Applied Spectroscopy, *27, 1, 47. ©1973, Society for Applied Spectroscopy, MD, USA [30]*						

by the intervals of **Table 1.3** was generally allowed. Spectra were found to be insensitive to temperature in the intervals 128 ± 4 °C to 145 ± 4 °C; a thermometer in contact with 'woods metal' (low melting point alloy) was used to indicate initial cell temperature and temperature upon completion of spectra. Possible temperature gradients across the PE melt were considered unimportant in view of the insensitivity of spectra to melt temperature.

Micrometer measurements of thickness were made on the solidified PE samples. Errors due to polymer contraction on solidification were small, as the process of solidification generally results in a net volume change of the solid in the absence of constraints. As the polymer samples were not constrained in any dimension, contraction occurred along the length and width of the specimen as well as the thickness. That portion of the contraction resulting in a decrease in sample thickness was observed to be non-uniform across the face of the sample; micrometer measurements on this face were taken as true melt thickness.

Shims designed to allow an outflow of excess molten polyethylene would facilitate thickness measurements as melt thickness would correspond to shim thickness.

Albarino [30] used standards consisting of PE and Irganox 1010. These were made by milling at temperatures of about 127 °C. Samples containing 0.051 and 0.010% Irganox 1010 were made from a masterbatch containing 0.101% Irganox 1010. These standards and an unstabilised control were moulded into sheets 0.064 to 0.076 cm thick for use in the analysis.

The effect of sample melting on scattering is illustrated in **Figure 1.8**. **Figure 1.9** is the spectrum of a 0.045 cm PE specimen containing 0.101% Irganox 1010 at room
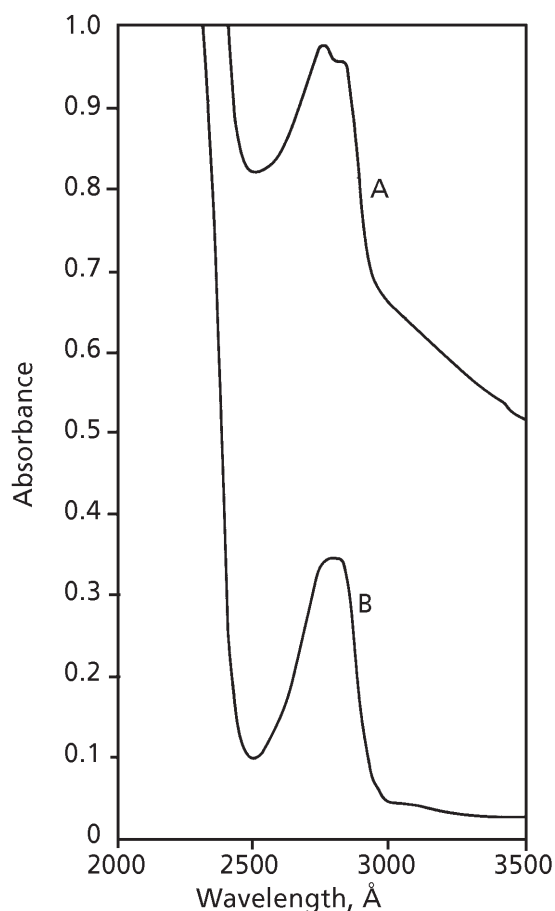
Figure 1.8 Direct UV spectra of 0.101% Irganox 1010 in polyethylene, A: 0.0045 cm, B: 0.058 cm, 122-126 ºC
Reproduced from R.V. Albarino, Applied Spectroscopy [30]
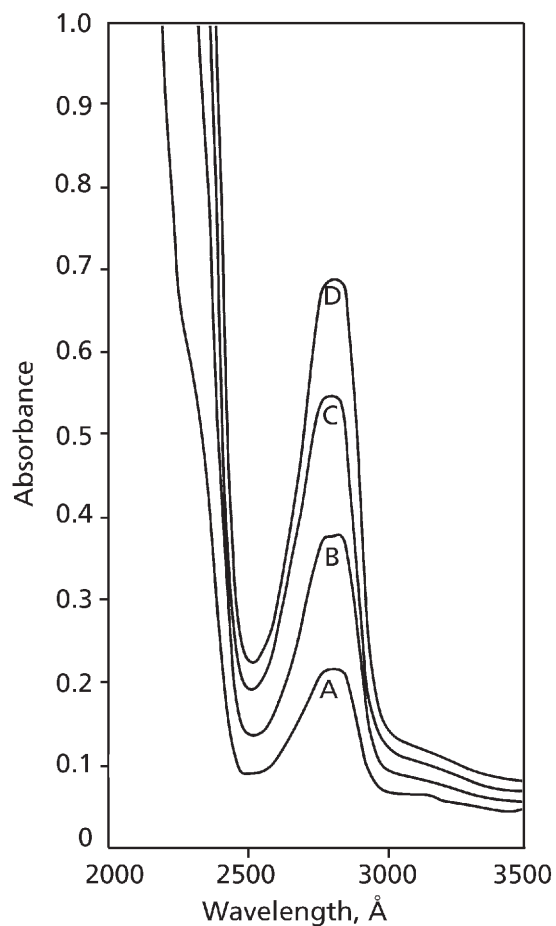
Figure 1.9 Direct UV spectra of 0.051% Irganox 1010 in polyethylene. A: 0.056 cm, 122-127 ºC, B: 0.109 cm, 124-127 ºC, C: 0.165, 124 ° C, D: 0.218 cm, 124-125 ºC
Reproduced with permission from Albarino, Applied Spectroscopy [30]

temperature. **Figure 1.9** was recorded at 122 to 126 °C with a 0.058 cm specimen. A very substantial decrease in scattering has resulted with little change in the antioxidant absorption at 2800 Å.

1.3 Raman Spectroscopy

Fourier transfer near infrared Raman spectroscopy (400-10,000 cm⁻¹) is useful for the examination of additives in polymer extracts [31].

An example of the application of Raman spectroscopy is the identification of additives in fire retardant PP. When a sample of PP was examined by IR spectroscopy the strongest bands (9.8 and 14.9 μm) were due to a talc-type material and bands of medium intensity were assigned to PP and possibly antimony trioxide (13.4 μm). Additional weak bands in the 7.3-7.7 μm region were possibly due to decabromodiphenyl ether. In the Raman spectrum, however, the strongest bands (250 and 185 cm^{-1} shift) confirmed the presence of antimony trioxide and some bands of medium intensity confirmed the presence of decabromodiphenyl ether (doublet at 140, triplet at 220 cm^{-1} shift) and PP (800, 835, 1150, 1325, 1450 and 2900 cm^{-1} shift). The silicate bands that obscured the regions of the IR spectrum were not observed in the Raman spectrum.

Although both of these spectroscopic methods have a wide use in their own right, this example demonstrates well the complementary value of the two methods, taking advantage of the fact that elements of high atomic number, e.g., antimony and bromine, have relatively more intense Raman spectra but the lighter elements show up clearly in the IR spectra.

Other applications of Raman spectroscopy include monomers in polymethylmethacrylate [32] and additives in PVC [33].

1.4 Mass Spectrometry

Mass spectrometry (MS) involves the study of ions in the vapour phase. This analytical method has a number of features and advantages that make it an extremely valuable tool for the identification and structural elucidation of organic molecules - including synthetic polymers: (a) the amount of sample needed is small (microgram level or less); (b) the molar mass of the material can be obtained directly by measuring the mass of the molecular (or quasimolecular) ion; (c) molecular structures can be elucidated by examining molar masses, ion fragmentation patterns, and atomic compositions determined by mass spectrometry; and (d) mixtures can be analysed by using 'soft' ionisation methods and hyphenated techniques (such as GC-MS, liquid chromatography-mass spectrometry (LC-MS), and MS/MS).

Mass spectrometric methods are routinely used to characterise a wide variety of biopolymers, such as proteins, polysaccharides, and nucleic acids. Nevertheless, despite its advantages, MS has been under utilised in the past for studying synthetic polymer systems. It is fair to say that, until recently, polymer scientists have been rather unfamiliar with the advances made in the field of MS.

However, MS in recent years has rapidly become an indispensable tool in polymer analysis, and modern MS today complements in many ways the structural data provided by NMR and IR methods. Contemporary MS of polymers is capable of changing the

protocols which have been established for years, for the molecular and structural analysis of macromolecules.

Some of the most significant applications of modern MS to synthetic polymers are (a) chemical structure and end-group analysis, (b) direct measurement of molar mass and molar mass distribution, (c) copolymer composition and sequence distribution, and (d) detection and identification of impurities and additives in polymeric materials.

In order to analyse any material by MS, the sample must first be vapourised (or desorbed) and ionised into the instrument's vacuum system. Since polymers are generally nonvolatile, many mass spectral methods have involved *degradation* of the polymeric material before analysis of the more volatile fragments.

Two traditional methods to examine polymers have been flash-pyrolysis GC-MS and direct pyrolysis in the ion source of the instrument.

In recent years, however, there has been a marked tendency toward the use of *direct* MS techniques. While a continued effort to introduce MS as a major technique for the structural analysis of polymers has been made over the past three decades, MS analysts did not have a great impact upon the polymer community until the past five years or so. During this period outstanding progress has been made in the application of MS to some crucial problems involving the characterisation of synthetic polymers.

Developments in two general areas have spurred this progress. Sector and quadrupole mass *analysers,* the traditional methods of separation of ions in MS, have recently been complemented by the development of powerful Fourier transform (FT-MS) and time-of-flight (TOF-MS) instruments. The TOF analysers are particularly well-suited for detecting higher molar-mass species present in polymers.

Parallel to this, new *ionisation methods* have been developed that are based on the direct desorption of ions from polymer surfaces. With the introduction of 'desorption/ionisation' techniques, it has become possible to eject large molecules into the gas phase directly from the sample surface, and thereby mass spectra of intact polymer molecules have been produced. The term 'desorption/ionisation' refers to a method in which the desorption/vapourisation and ionisation steps essentially occur simultaneously.

Fortunately, the use of MS for polymer analysis took on a new dimension at the turn of the century. Up until the mid-1990s there was a steady - but not dramatic - increase in the number of journal publications on polymer mass spectrometry. Starting in 1995, however, there has been a marked increase in the number of polymer mass spectrometry reports in the literature. Also the number of symposia and conferences devoted to the subject has grown considerably in the last few years.

The major reason for this increase has been the use of matrix-assisted laser desorption/ionisation-MS (MALDI-MS) for numerous polymer applications. MALDI is by no means the only mass spectral method that is useful for polymer analysis, but it has provided the impetus to get polymer people interested in what mass spectrometry can do.

Hayes and Altenau [34] were the first to report the use of MS to directly characterise antioxidants and processing oil additives in synthetic rubbers. Since then, various MS techniques have been applied to the analysis of rubber and polymer additives either as extracts or on the sample surface by laser techniques as reviewed by Lattimer and Harris [35]. Lattimer reviewed the present situation regarding MS in polymer analysis [36]. Analysis of polymer extracts by MS has proved challenging. Electron impact mass spectra (EI-MS) are often difficult to interpret due to the high concentration of processing oils and the additives in the extract, and excessive fragmentation of the molecular ions. Desorption/ionisation techniques such as field desorption (FD) and fast atom bombardment (FAB) have been found to be the most effective means for analysing polymer and rubber extracts [37, 38].

FD-MS has proved to be a particularly useful technique, since molecular ion abundances are high with respect to fragmented ions [39]. Electrospray ionisation MS (ESI-MS and ESI-MS-MS) has also been used for the analysis of polymer additive mixtures [40].

Extraction and separation procedures are time consuming, rendering additive characterisation a slow and laborious process, there is the possibility that the extraction process may compromise the integrity of the additive mixture, leading to an inaccurate picture of polymer composition.

Attempts at direct MS characterisation of additives in bulk polymer samples have centred on direct thermal adsorption of additives for the bulk polymer, followed by EI-MS, chemical ionisation (CI-MS) or field ionisation (FI-MS). However, this approach is linked to polymer additives that are stable or can provide meaningful fragment ions at elevated temperatures. Desorption/ionisation methods such as fast ion bombardment (FAB) [41], laser desorption [42, 43] and secondary ion MS (SIMS) have also been applied to the analysis of additives in bulk polymer samples. However, these single step techniques suffer to varying degrees from matrix interferences in the resulting mass spectra.

Laser desorption/laser photoionisation time-of-flight MS (LPToFMS) is a technique that has great potential for the direct analysis of molecular species from complex host matrices. This two-step approach circumvents many of the problems, discussed previously, that have been encountered with other techniques.

These various experimental techniques are discussed further next.

Earlier Experimental Techniques

In 1986, Peltonen [44] applied MS to the identification of volatile breakdown products of heated PS. The early work includes that of Rudewicz and Munson [45] who vaporised Ionox 330 and Irganox 168 and UV 531 additives from PP in a heatable glass probe under chemical ionisation conditions using 1.4% ammonia in methane reagent gas. The dominant species in this mixture, NH_4^+, is a low energy reagent ion that reacts with the additives to give very simple spectra of $(M + H)^+$ or $(M + NH_4)^+$ ions with little fragmentation.

Lattimer and co-workers [46] have applied MS to the determination of organic additives (antioxidants and antiozonants) in rubber vulcanisates. Direct thermal desorption was used with three different ionisation methods (EI, CI, FI). The vulcanisates were also examined by direct FAB-MS as a means for surface desorption/ionisation.

Rubber extracts were examined directly by the four ionisation methods. Of the vaporisation/ionisation methods, it appears that field ionisation is the most efficient for identifying typical organic additives in rubber vulcanisates.

Other earlier applications include those of Bletsos and co-workers [47] who produced time-of-flight ion MS of additives in polydimethylsiloxane and polytetrafluoroethylene, MS of organic additives in carbon black filled styrene-butadiene rubber [48] and oxidative ageing of antioxidants present on polymer surfaces [49, 36].

In principle, the most straightforward way to identify organic additives in a compounded polymer is to heat the material to thermally desorb the volatile components. The evolved chemicals may then be directed into a MS ion source for analysis. EI is the traditional method of ionisation in MS, and in the early years of MS, it was the only method that was readily available. Several studies from the 1970s and the early 1980s describe heating rubber compounds (or their extracts) *in vacuo* to vapourise the components into an EI ion source [34, 50-52]. These studies were in general hampered by (a) extensive EI fragmentation and (b) intense signals from the processing oil that is contained in most rubber recipes.

Later systemic studies by Lattimer described the use of 'soft' ionisation methods (CI and FI) in the direct analysis of model vulcanisates [46] as well as uncured compounds [48]. The resulting 'survey' spectra were much simpler in nature – and thus easier to interpret – than those obtained via EI-MS. All of these studies, which used single-stage MS methods, describe the identification of various organic ingredients in the elastomers [50-53]. In later work, tandem mass spectrometry (MS-MS) was shown to be effective for increasing the specificity and sensitivity of detection and identification of additives in direct rubber compound [54, 55]. Pyrolysis field ionisation (Py-FI-MS) was shown to be a good technique for analysis of both organic additives and rubber components in the

same experiment [56]. Results of literature reports through 1989 were summarised in a review article on rubber-compound analysis [57].

Relatively few descriptions of direct mass spectral analysis of plastics compounds have appeared in the literature. In a rather early report, additives in PP compounds were thermally desorbed into a heated reservoir inlet for mass spectral analysis [58]. It was found that numerous stabilisers could be identified via 80 eV EI-MS. Thermal, desorption of additives via direct probe introduction of PP compounds was described in a later report [59]. A more recent paper considered the mass spectral analysis of both rubber and plastic compounds. This report was an overview, without much detail. Analysis of additives in PP compounds via direct thermal desorption CI-MS has also been described [45].

Ammonia as a reagent gas was found to yield very simple CI mass spectra. Finally, a recent report analysed a number of additives (antioxidants and light stabilisers) in PP compounds. Three ionisation methods (El, CI, FI) were used, and supplemental MS-MS and atomic composition (AC-MS) results were used for chemical structure elucidation/confirmation of various ingredients.

Soft Ionisation, Tandem (MS-MS) and High Resolution (Atomic Composition-MS) Mass Spectrometry

Lattimer [60] has recently reported a method of the mass spectral identification of components (particularly residual volatile chemicals, organic additives, and degradation products) in a number of commercial elastomer compounds of unknown composition. Programmed direct probe heating of the compounded elastomer was used with three different methods of ionisation: 70 eV EI-MS, isobutane CI-MS, and FI-MS. It should be understood that both thermal desorption and pyrolysis are taking place. That is, residual volatile chemicals and most organic additives are thermally desorbed at lower temperatures (less than ~250 °C), while polymeric components are thermally decomposed (pyrolysed) at higher temperatures (greater than ~250 °C). In some cases, tandem mass spectrometry (MS-MS) and or high resolution mass analysis (for atomic compositions, AC-MS) was carried out to improve the specificity of the analysis. Lattimer gives examples to illustrate the various modern MS approaches that may be used in practical problem-solving applications.

The first step in the analysis of an unknown elastomer compound is to obtain and examine low-resolution 'survey' MS from the material. These spectra cover a wide mass range (typically ~ 50-1000 Da) and give an 'overview' of the sample composition. The most useful ionisation method for this is generally field ionisation, since the simplest possible spectrum is obtained. In the FI spectrum molecular ions are dominant, which facilitates the characterisation of the complex organic additive mixtures that are present in typical elastomer compounds.

The first example is a competitive elastomeric (ethylene-propylene-diene terpolymer; EPDM) bearing used in an aerospace application. The rubber was examined by heating in the direct probe over the range 20-400 °C. **Figure 1.10** is a composite FI-MS survey scan covering the sample heating range ~70-230 °C; the probe heating rate was 18 °C/min. For comparison, a composite 70 eV EI-MS covering the same heating range is shown in **Figure 1.11**. The EI spectrum is considerably more complex due to the large number of fragment ions from processing oil and other ingredients.

After survey scans are acquired, the next step was to identify the molecular ions. In some cases the identities may be obvious from the molecular weights alone. In most cases involving unknowns, however, the supplemental techniques of MS-MS and/or AC-MS are used. The basic concept of MS-MS is to put two mass analysers (MS-1 and MS-2) in tandem. After passing through MS-1, the ions traverse a collision chamber, where a low-pressure gas induces decomposition (fragmentation). In the Finnigan MAT 95Q, MS-1 is a double-focussing (BE) mass analyser, and the collision chamber is contained in an octapole field to enhance transmission. The secondary fragment (or product) ions are then mass-separated in MS-2 and subsequently detected. In the Finnigan MAT 95Q, MS-2 is a quadrupole mass filter. The most common MS-MS experiment is the *product ion scan*. In this a precursor (or parent) ion of interest is selected (focussed) in MS-1 and decomposed in the collision cell; the resulting product (or fragment) ions are then mass-separated in MS-2 and detected.

Figure 1.12 is a typical product ion scan (EI-MS-MS) for a volatile component from the rubber bearing. The precursor ion is M^+ 136, obtained by El ionisation. (Either El or CI is normally used for MS-MS experiments, since the ion current is more stable and intense compared to that obtained by FI-MS). The spectrum in **Figure 1.12** closely resembles that of cumyl alcohol as found in libraries of standard El spectra. The principal product ions are m/z 121 $(M - CH_3)^+$ and m/z 43 $(C_2H_3O^+)$.

To determine unambiguously the molecular formula (or atomic composition) of an ion of interest, the supplemental technique of 'high resolution' MS (AC-MS) was used. In this, masses of ions were measured accurately to three or four decimal places with increased resolution of the instrument. This is accomplished by 'matching' known reference peaks (usually $C_xF_y^+$ ions from perfluorokerosene) with the unknown peaks in the sample. In the Finnigan MAT 95Q, this operation is facilitated with computerised peak matching algorithms.

Masses measured with a few parts per million (ppm) accuracy can provide an unequivocal identification of the atomic composition. This is due to the fact that the atomic weights of the nuclides are not exact whole numbers on the ^{12}C mass scale (e.g., $^{1}H = 1.007825$, $^{16}O = 15.99491$, $^{14}N = 14.00307$, $^{32}S = 31.97207$). Accurate mass measurements are most often carried out with El or CI ionisation, since the signal-to-noise ratio, stabilities of ions, and availability of reference peaks are better in these modes (as compared to FI).
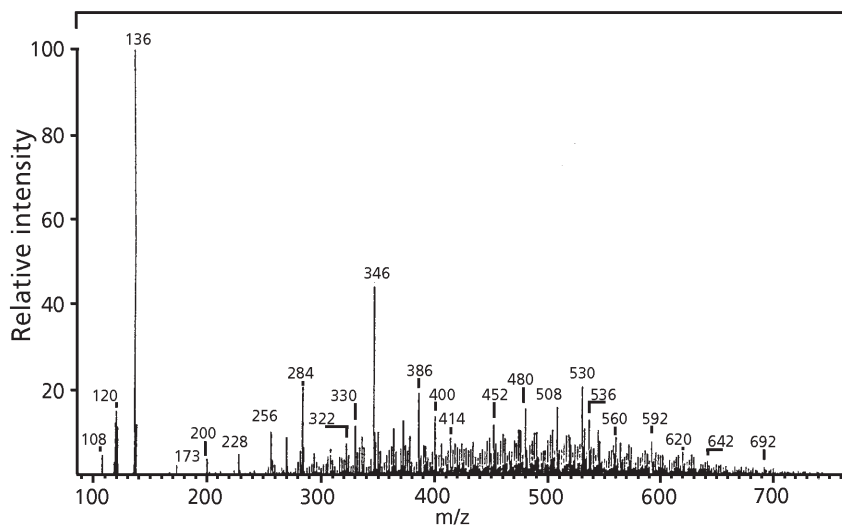
Figure 1.10 FI-MS survey scan of EPDM bearing (70-230 °C)
Reproduced with permission from Lattimer and co-workers, Rubber Chemistry and Technology
[60]
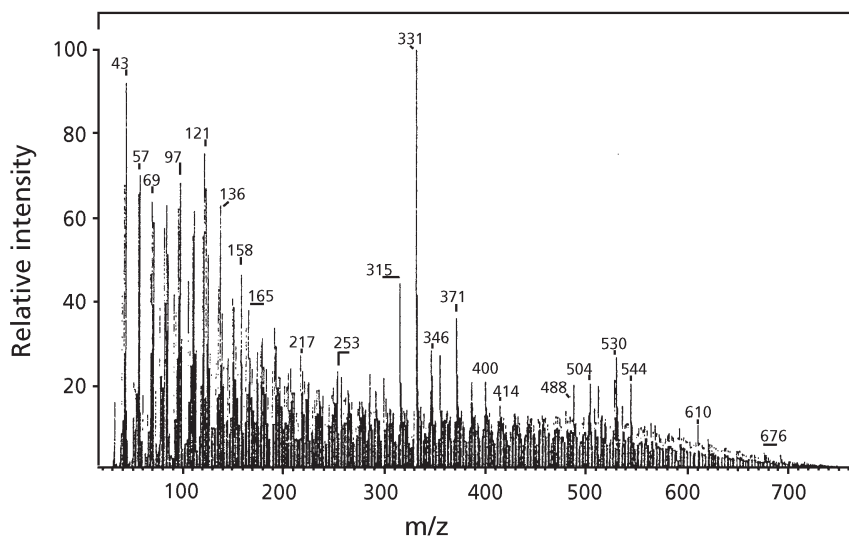
Figure 1.11 EI-MS survey scan of EPDM bearing (70-230 °C)
Reproduced with permission from Lattimer and co-workers, Rubber Chemistry and Technology
[60]

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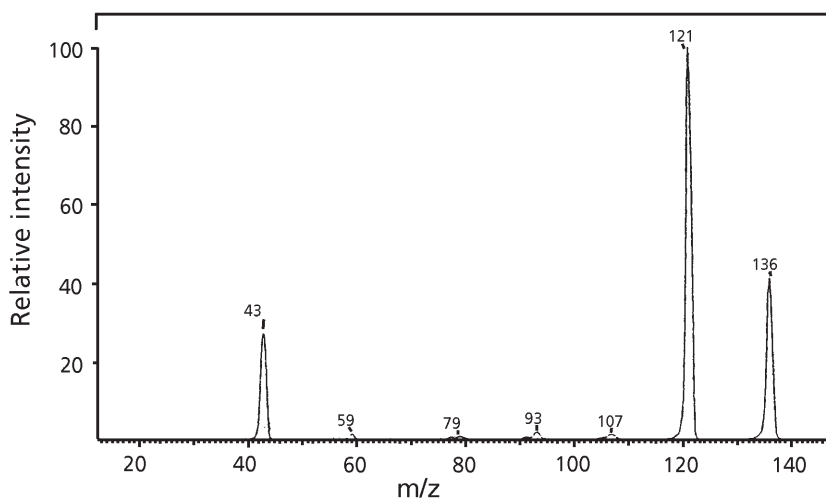
Figure 1.12 Product ion scan (El-MS/MS) of M+ 136 from EPDM bearing
Reproduced with permission from Lattimer and co-workers, Rubber Chemistry and Technology
[60]

In the case of the M+ 136 ion from the rubber bearing, an El accurate mass measurement gave the value of *m/z* as 136.0892. Computer calculations showed that the best atomic composition match for this mass is $C_9H_{12}O$, which has a calculated *m/z* of 136.0888. The observed value differs from the calculated number by 3 ppm, which is an acceptable match. With the combination of the product ion scan (fragmentation pattern) obtained by MS-MS and the formula obtained by accurate mass measurement, the MW 136 component can confidently be assigned to the cumyl alcohol molecule.

In summary, the organic additives in this competitive EPDM bearing were found to be a light aliphatic processing oil, polytrimethyldihydroquinoline and Irganox 1076 antioxidants, and fatty acids/esters. The curing agent was cumyl peroxide. One additional peak of interest in the FI MS is *m/z* 108, which was found by EI-MS-MS to be residual methylnorbornene from the EPDM polymer.

Similarly application of this methodology to a rubber V-shaped belt showed it contained paraffin wax, a light unsaturated oil (wax, antiozonant, disphenylamine/acetone resin antioxidant, fatty acids, rosin acids and *N-t*-butyl 2-benzothiazole (sulfenamide accelerator).

Sulfenamide Accelerators

Other applications of the tandem MS-MS technique include, determination in rubbers of general additives [55, 60] and the determination in polymers of antioxidants [61] and acrylate, methylmethacrylate and butyl acrylate monomers in acrylic thermoplastics [62].

Laser Mass Desorption/Electron Ionisation MS

Johlman and co-workers [63] compared laser desorption/ionisation FT-MS (LD-FT-MS) with FAB spectra of the same materials in the analysis of non volatile polymer additives.

Both a pulsed carbon dioxide laser and a neodymium-YAG laser with outputs of 10.6 and 1.064 µm, respectively, were used to obtain LD-FT-MS spectra of all samples. Three sterically hindered phenols and other additives containing a variety of functionalities including thioester, phosphite, phosphonite, and hindered amine groups were examined. In general, FAB spectra show undesirably large amounts of fragmentation, while molecular ion species dominate LD-FT-MS spectra. It is concluded that LD-FT-MS spectra are superior to FAB spectra for analysis of these common polymer additives. This is illustrated in **Figure 1.13**. In the FAB spectrum of dilaurylthiopropionate in **Figure 1.13** only a small peak resulting from the potassium attached molecular species appears. Fragmentation is substantial and corresponds to cleavage of the ester links with an *m/z* of 329, which further fragments to yield prominent ions with *m/z* of 133, 144 and 161. Laser desorption spectra acquired by carbon dioxide (**Figure 1.13b**) and Nd:YAG (**Figure 1.13c**) laser absorption, contrast substantially with the FAB spectra. Abundant molecular ion species are observed in the laser absorption spectra.

These ions are a combination of (M + H)[+], (M + Na)[+], and (M + K)[+], depending upon the relative abundance of alkali metal salts present in the sample. Present in the CO_2 spectra of both dilaurylthiodipropionate (DLTDP) in **Figure 1.13b** are fragment ions with *m/z* 329 and *m/z* 413 that correspond to ester cleavages, as observed in the FAB spectra. In contrast, Nd:YAG spectra of DLTDP in **Figure 1.13c** each primarily contain a strong ion signal corresponding to cation attachment to the intact molecules.

In addition to dialkylthiopropionate secondary antioxidants a similar situation was shown to apply in the case of higher MW compounds with thioester functionalities, e.g., Seenox 4125 with a MW of 1156, also hindered phenols, alkyl phosphites are polyhindered amines and Irganox 1050.

Waddell and co-workers [64] applied this technique to Neoprene rubber compound surfaces. The LD-MS of the sulfur-vulcanised natural rubber (NR) Compounds #1 and
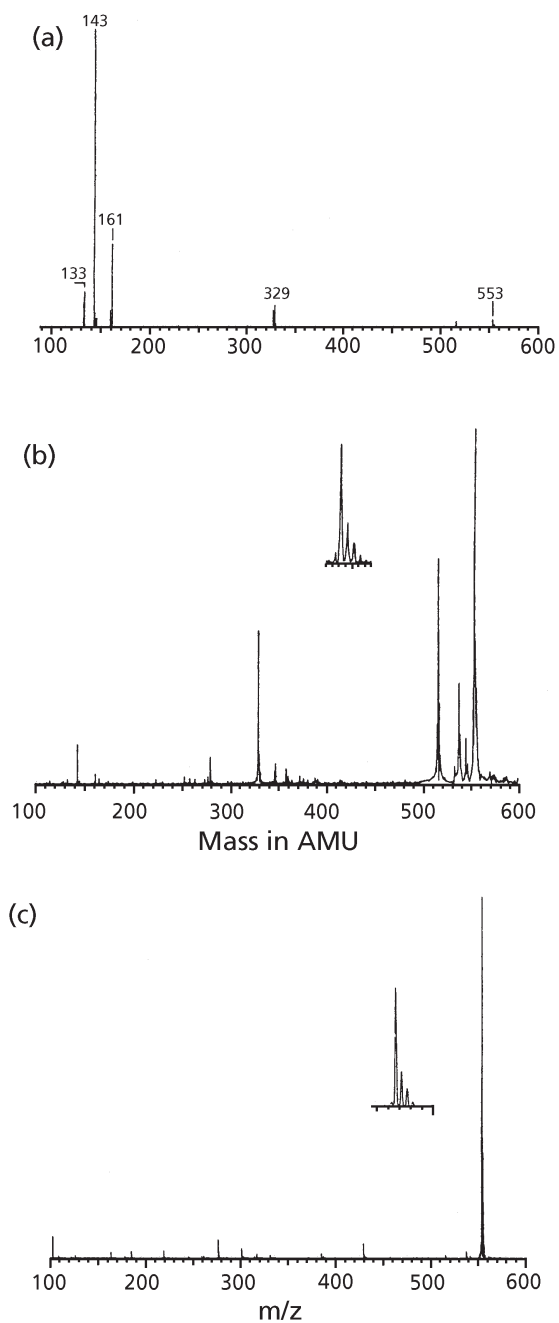
Figure 1.13 Comparison of positive ion spectra of DLTDP acquired by (a) FAB, (b) CO$_2$ LD-FTMS and (c) Nd:YAG LD-FTMS
Reproduced from Johlman and co-workers, American Chemical Society [63]

#2 obtained using the LAMMA 1000 at high laser power, essentially show a continuous series of peaks up to approximately a mass-to-charge ratio *(m/z)* of 250, and were relatively uninformative. Using reduced laser power and focusing on a fresh surface area, the spectrum shown in **Figure 1.14** was obtained for Compound #2. Similar mass spectra were also recorded for the unfilled Compound #1 and the silica-filled Compound #3. Thus the peaks observed in **Figure 1.14** are thought to result from extensive fragmentation of the NR backbone since the *m/z* 68 peak thought indicative of the isopropenyl ion $(C_6H_8^+)$ is present, but no peaks greater than approximately *m/z* 200 are present. The laser mass spectrum differs from that obtained using pyrolysis methods which show isoprene oligomers up to *m/z* 900.

The following compounds were identified in a range of Neoprene samples (**Table 1.4**), NSA carbon black filler, Sundex 8125 processing oils, Wingstay 300 antiozonant, Wingstay 100 antioxidant and sulfur curing agent.
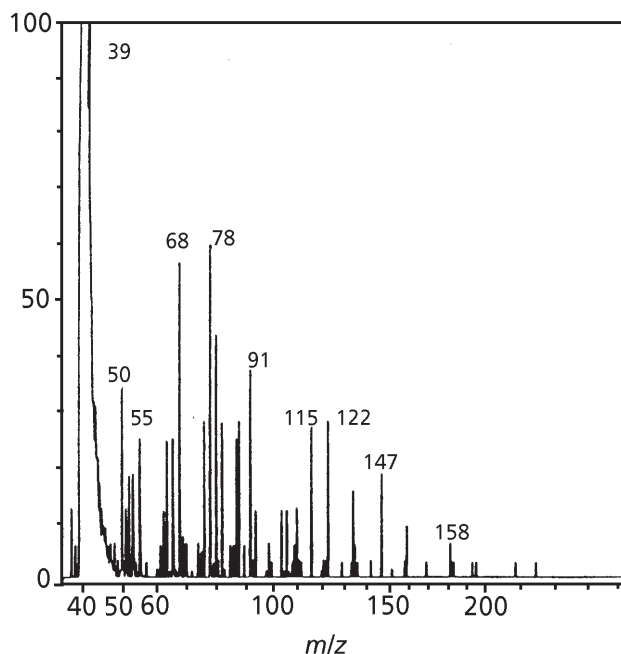
Figure 1.14 Laser desorption mass spectrum of Compound #2, the carbon-black filled vulcanised rubber compound, obtained using the LAMMA 1000 spectrometer
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]

Table 1.4 Rubber compound formulas (parts per hundred rubber, phr)								
Compound	1	2	3	4	5	6	7	8
Natural rubber	100	100	100	100	100	100	100	100
ISAF carbon black	0	50	0	50			0	50
HI-SUL 233 silica	0	0	50	0	0	0	50	0
Sulfur	2	2	2	2	2	2	2	2
Zinc oxide	3	3	3	3	3	3	3	3
Mercaptobenzothiazole	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Sundex 8125 processing oil	0	0	0	4	0	0	0	0
Wingstay 300 antiozonant	0	0	0	0	4	4	4	2
Wingstay 100 antioxidant	0	0	0	0	0	0	0	2
ISAF								
Reprinted with permission from W. Waddell, K. Benzing, L. Evans, S. Mowdood, D. Weil, J. McMahon, R. Cody, Jr., and J. Kinsinger, Rubber Chemistry and Technology, 64, 4, 622. ©1991, Rubber Division, ACS [64]								

Regarding the processing oil, GPC of an authentic sample of Sundex 8125 aromatic processing oil and of an extract of cured Neoprene rubber containing this oil (**Figure 1.15**) shows that the processing oil is a mixture having components with a broad distribution of MW. Using a hydrocarbon as the GPC standard, the average MW of the processing oil is assigned a value of 200, however, using PS as a standard, affords a MW of 340. The MW reported by the manufacturer is 395. The direct surface analysis of Compound #4 by LD-MS (**Figure 1.16**) gives a spectrum having a series of mass peaks with values ranging from *m/z* of about 200 to 360, centred around an *m/z* value of approximately 260. These peaks are thought to be due to the molecular ions (M^+) of the various components comprising the aromatic processing oil created by loss of an electron from the aromatic ring.

The discrepancy in MW distribution of the oil from that reported might be due to the relative diffusion characteristics of the lower MW and more volatile components in the oil which can be expected to result in their higher rubber surface concentrations as determined by direct analysis of the compound by LD-MS.

The ATR-IR spectrum of rubber Compound #6 that contains the antiozonant has one clearly visible additional peak at 1470 cm^{-1}, **Figure 1.17** (arrow). The IR difference spectrum (Compound #6 - Compound #2), in **Figure 1.18** reveals approximately six peaks (checkmarks) thought to be characteristic of the added antiozonant that might be used for its identification in a cured rubber compound since these peaks are present in the IR of the antiozonant, **Figure 1.18b** (checkmarks).
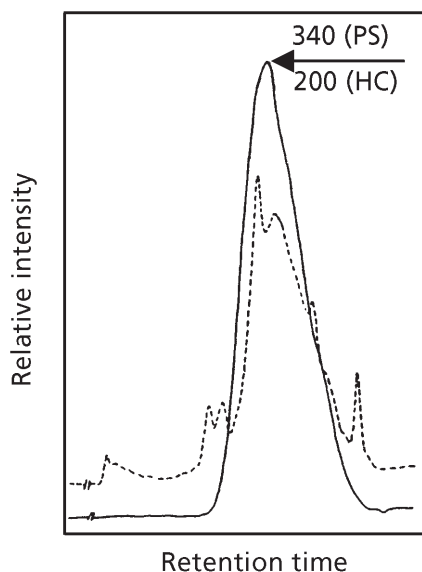
Figure 1.15 Gel permeation chromatographs of the aromatic processing oil (solid line) and the rubber extract (dotted line)
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]
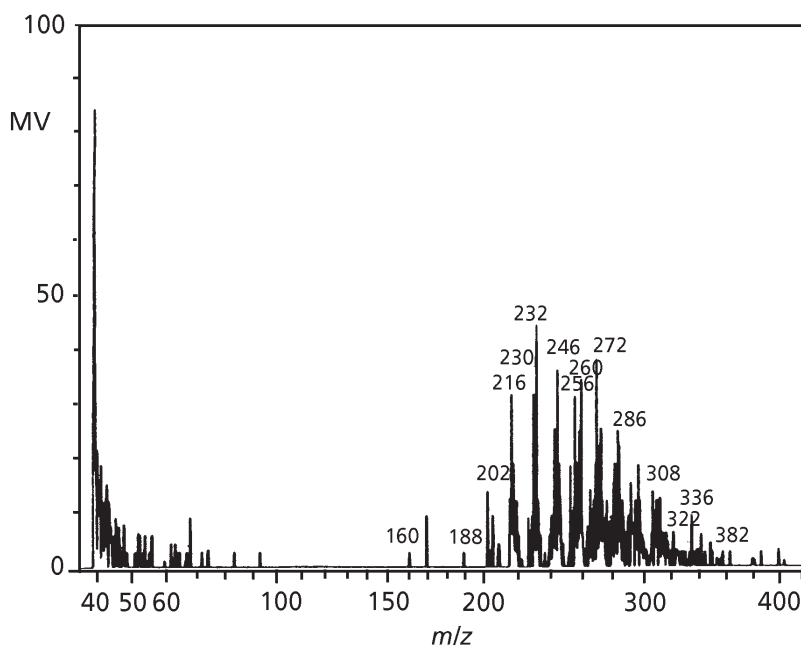
Figure 1.16 LAMMA 1000 spectrum of Compound #4, the carbon-black filled, vulcanised rubber compound containing the aromatic processing oil, Sundex 8125
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]

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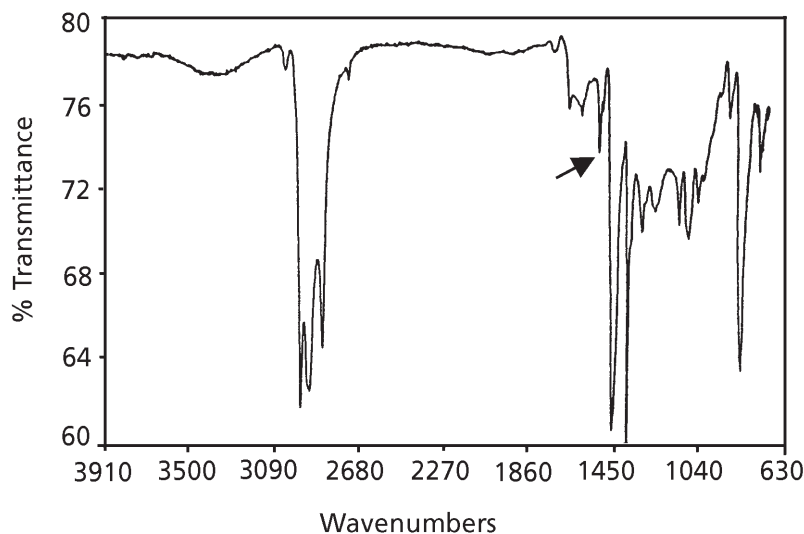
Figure 1.17 Attenuated total reflectance Fourier transform infrared spectrum of Compound #6, the carbon-black filled, vulcanised rubber compound containing the antiozonant. The arrow highlights the only peak visibly different from the ATR-IR spectrum of Compound #2, which does not contain the antiozonant
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]

The LAMMA 1000 LD-MS of Compound #6 has five new peaks present at *m/z* values of 268, 253, 211, 183, and 168, **Figure 1.19** (checkmarks). Peaks thought to be representative of polymer backbone fragmentation are present at *m/z* values less than about *m/z* 120, including the *m/z* 68 peak, thought to be due to the isopropenyl ion. These new peaks are thought to result specifically from laser desorption and ionisation of the aromatic antiozonant present on the rubber surface.

The LD-MS of Compound #8, which contains the Wingstay 300 antiozonant and an aromatic antioxidant, has characteristic peaks at *m/z* 268, 211, and 183 representative of the antiozonant and new peaks present at *m/z* 352, 288, 274, and 260. These latter three peaks are thought to represent the three molecular ions of the components of the antioxidant mixture in Goodyear's Wingstay 100, an aromatic amine antioxidant.

LD-MS has proven a uniquely useful technique for the direct characterisation of rubber-compound surface species. Mass spectra were obtained for intact molecular ions (M$^+$) of organic chemical rubber additives such as the aromatic processing oil, and the aromatic antiozonant and antioxidants incorporated to protect the rubber. MW information from
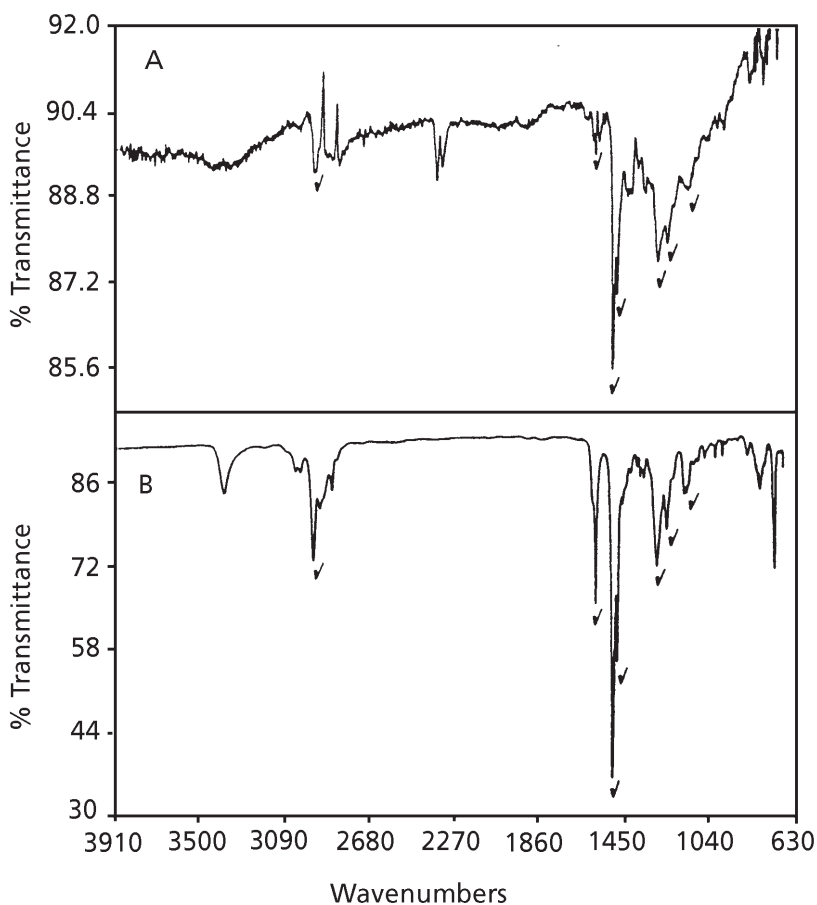
Figure 1.18 A: Infrared difference spectrum obtained by computer subtraction of the ATR-IR spectra of Compound #2 from Compound #6, B: Infrared transmission spectrum of a thin film of the antiozonant on a NaCl plate. Checkmarks highlight those peaks characteristic of the *para*-phenylenediamine antiozonant
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]

the molecular ions and structural information from the fragmentation ions could be obtained without interference from the fragmentation peaks of the rubber backbone.

Laser and thermal desorption mass spectral techniques provided complementary structural information, and when coupled with current analytical methods to characterise rubber compounds, can provide the necessary information to positively identify various organic species present on the surfaces of vulcanised rubber.
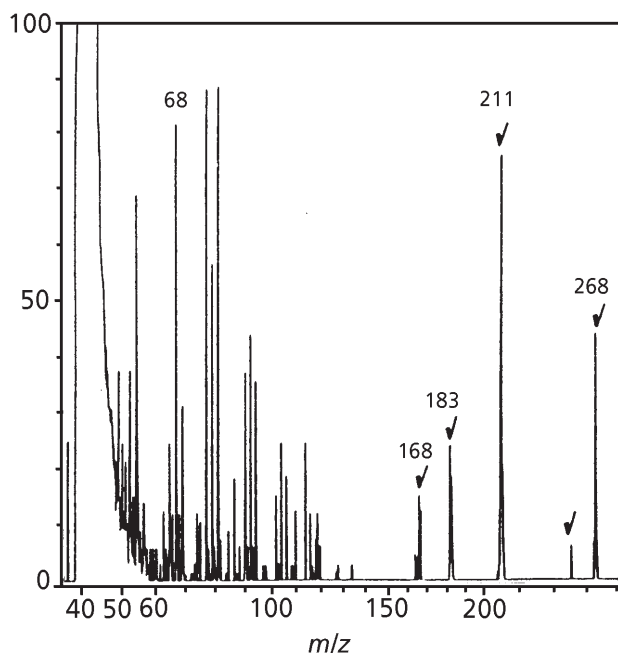
Figure 1.19 LAMMA 1000 spectrum of Compound #6, the carbon-black filled, vulcanised rubber compound containing the antiozonant. Checkmarks highlight those peaks characteristic of the *para*-phenylenediamine antiozonant
Reproduced with permission from Waddell and co-workers, Rubber Chemistry and Technology [64]

Wright and co-workers [61] have used a two-step laser desorption/laser photoionisation time-of-flight MS (L2MS) for selective *in situ* detection of polymer additives in PP and polyoxymethylene.

A pulsed CO_2 laser was used to desorb the additives as neutral species into the gas phase, where they were post-ionised using a second UV laser operating at either 266 or 193 nm.

For all the antioxidants studied, the 266 nm photoionisation mass spectra are dominated by the molecular ion peak; very little fragmentation is observed. In contrast, at 193 nm, the molecular ion peak is usually absent from the photoionisation mass spectra. Similar behaviour is exhibited by the UV stabilisers (Tinuvin) in their photoionisation mass spectra. This wavelength-dependent fragmentation can be exploited for unambiguous identification of many polymer additives. For example, it is shown that the isomeric UV stabilisers Tinuvin 320, Tinuvin 343, and Tinuvin 329 can be differentiated on the basis of

the extent or nature of the observed fragmentation in their photoionisation mass spectra. Several commercial polymer formulations containing these types of additives have also been analysed using this experimental approach: the samples were interrogated directly without any pretreatment or extraction. It is shown that UV laser post-ionisation enables selective detection of the additives in preference to the polymer, providing unambiguous *in situ* identification. The potential of this technique for surface analysis and depth profiling is also discussed.

There are many advantages to be gained in being able to chemically speciate additives *directly* from the polymer matrix as opposed to methods involving a preliminary solvent extraction of the additives from the polymer prior to MS (see Chapter 3) [43, 61, 65-73].

Laser desorption/laser photoionisation time-of-flight mass spectrometry is a technique that has great potential for the direct analysis of molecular species from complex host matrices. This two-step approach circumvents many of the problems that have been encountered with other techniques. In this method, a pulsed CO_2 laser is used to desorb the analyte into the gas phase as a neutral species, *directly* from the sample of interest. A second pulse from a UV laser is then used to post-ionise these gas phase neutral species, generally using a resonance-enhanced multiphoton ionisation (REMPI) scheme. The benefits of this two-step approach lie in the spatial and temporal separation of the desorption and ionisation events, thereby enabling the independent optimisation of each process. This provides a number of advantages for the *in situ* analysis of bulk polymer samples: (i) desorption of neutral target molecules from the host polymer matrix with minimal decomposition, (ii) soft ionisation of the desorbed neutral species, resulting in readily interpretable mass spectra, (iii) selective ionisation of polymer additives which have a significant one-photon absorption cross section at the chosen ionisation wavelength, and (iv) highly sensitive detection of many polymer additive species.

The two different ionisation laser wavelengths result in markedly different mass spectra. These mass spectral differences are a valuable aid in the unambiguous identification of the additives. Wright and co-workers [61] also reported that the spectra obtained show not only that it is possible to directly detect these additives in the polymer formulations, but also that chemical changes undergone by antioxidants, due to either processing or ageing, can also be observed.

The additives included in this study are shown in **Table 1.5**.

Antioxidants. The mass spectra obtained for Irganox 1330, Irgafos 168, and Santowhite using 266 and 193 nm photoionisation are shown in **Figure 1.20**. In the case of Irganox 1330, the spectra at both these wavelengths are dominated by the molecular ion peak at *m/z* = 774. However, it is evident that 266 nm photoionisation results in the production of fragment ions different than those observed at 193 nm. At 266 nm, a fragment is observed

Table 1.5 Nomenclature and structure of polymer additives			
Trivial name	**Chemical name**	**Structure**	**Molecular weight**
Irganox 1330	1 ,3,5,-tris(3,5-di-*tert*-4-butyl-4-hydroxybenzyl)-2,4,6,trimethylbenzene		774
Irganox 1076	Octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl) propionate		530
Irgafos 168	Tris(2,4-di-*tert*-butylphenyl) phosphite		646
Santowhite	4,4′-Butylidene bis-6-(4-methyl-2-*tert*-butylphenol)		382
Tinuvin P	2-(2′-Hydroxy-5′-methylphenyl)-2H-benzotriazole		225
Tinuvin 326	2-(2′-Hydroxy-3′-methyl-5′-*tert*-butylphenyl)-2H-5-chlorobenzotriazole		315
Tinuvin 327	2-(2′-Hydroxy-3′,5′-di-*tert*-butylphenyl)-2H-5-chlorobenzotriazole		357
Tinuvin 320	2-(2′-Hydroxy-3′,5′-di-*tert*-butylphenyl)-2H-benzotriazole		323

Table 1.5 Cont'd…			
Trivial name	Chemical name	Structure	Molecular weight
Tinuvin 343	2-(2′-Hydroxy-3′-*tert*-butyl-5′-(1-methyl)-propylphenyl)-2H-benzotriazole		323
Tinuvin 329	2-(2′-Hydroxy-5′-(1,1,3,3-di-methyl)-butylphenyl)-2H-benzotriazole		323
Reproduced with permission from S.J. Wright, M.J. Dale, P.R.R. Langridge-Smith, Q. Zhan and R. Zenobi, Analytical Chemistry, *68, 20, 3585. ©1996, ACS [61]*			
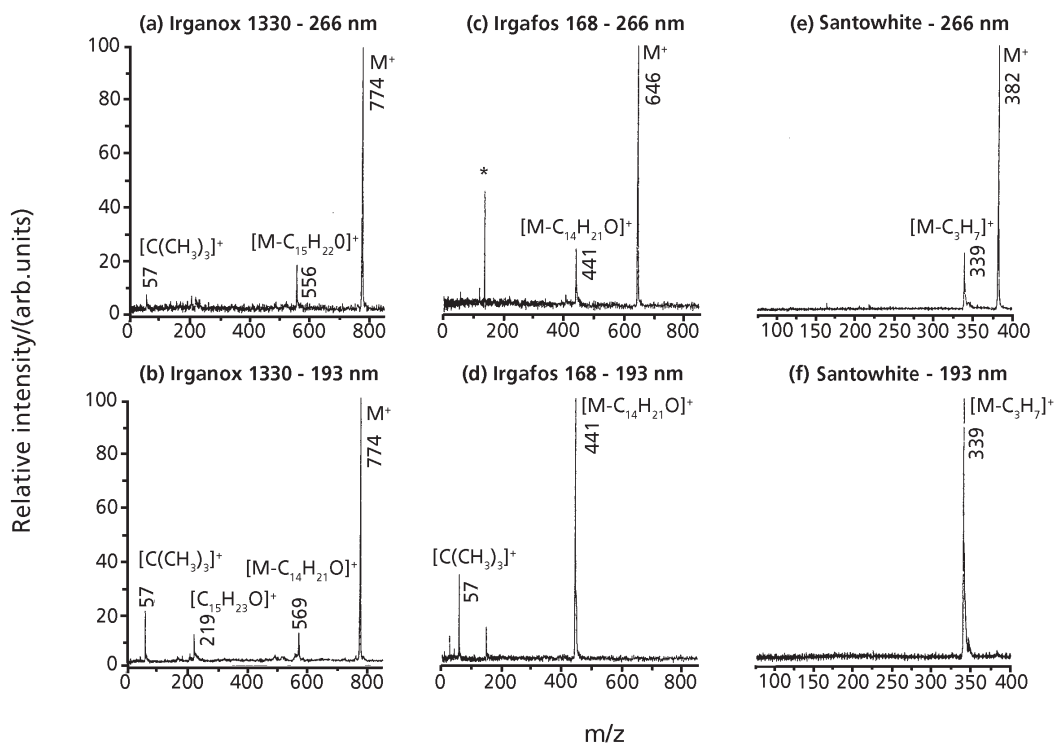
Figure 1.20 Photoionisation mass spectra for Irganox 1330 at (a) 266 and (b) 193 nm; Irgafos 168 at (c) 266 and (d) 193 nm; and Santowhite powder at (e) 266 and (f) 193 nm. The peak marked with an asterisk in spectrum (c) is due to an internal mass standard, 4-aminobenzoic acid (m/z = 137)
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at *m/z* = 556. This is thought to result from loss of a 3,5-di-*tert*-butyl-4-hydroxybenzyl side group, with a concomitant hydrogen rearrangement. A weaker fragment peak at *m/z* = 57, due to the *tert*-butyl ion, can also be seen.

Photoionisation of Irganox 1330 at 193 nm produces fragments at *m/z* = 57, 219, and 569. The fragment at *m/z* = 569 corresponds to the loss of a 3,5-di-*tert*-butyl-4-phenol side group via direct cleavage rather than rearrangement. The peak at *m/z* = 219 is characteristic of positive ion mass spectra of dibutyl phenols and corresponds to the 3,5-di-*tert*-butyl-4-hydroxybenzyl ion. The peak at *m/z* = 57 corresponds to the *tert*-butyl ion.

Similar characteristics were observed in the mass spectra for Irganox 1076 (not shown). When 266 nm radiation is used, the molecular ion can be clearly identified at *m/z* = 530. At 193 nm, no molecular ion peak is seen. Instead, the base peak of the mass spectrum is at *m/z* = 515, corresponding to the loss of a methyl radical from the molecular ion.

In summary, for all the antioxidants studied, the mass spectra obtained using photoionisation at 266 nm are dominated by molecular ion signals, with very little fragmentation. With the exception of Irganox 1330, photoionisation using 193 nm radiation generated little or no molecular ion signal. There are two possible explanations for this apparent wavelength dependence. Most organic molecules have ionisation potentials (IP) in the range 7-10 eV. The energy of 266 nm photons is ~4.66 eV, whereas a 193 nm photon has an associated energy of 6.42 eV. In both cases, therefore, absorption of two photons is required in order to achieve ionisation. However, absorption of the first 193 nm photon can result in different intermediate electronic states being accessed compared to excitation at 266 nm, such as Rydberg states. It is possible that this may lead to different ionisation pathways being promoted, resulting in differing mass spectra at 193 *versus* 266 nm. Alternatively, the difference may simply be due to the difference in excess energy deposited initially in the molecular ion. Assuming an ionisation potential of 8 eV, photoionisation at 266 nm will produce a molecular ion with up to 1.32 eV of excess energy. This is small compared to the excess energy of up to 4.84 eV possible following photoionisation at 193 nm. This larger excess energy may be sufficient to exceed the appearance potential for the production of the most facile fragment ions. Therefore, at 193 nm, ionisation would be accompanied by facile fragmentation. The data available do not permit identification of which of these two mechanisms may be responsible for the different fragmentation patterns observed.

UV Stabilisers

Similarly 266 and 193 nm photoionisation mass spectral data showed that in general the photoionisation mass spectra of the Tinuvin UV stabilisers examined differ markedly at 266 and 193 nm. At 266 nm, the mass spectra are dominated by molecular ion signals,

with very little associated fragmentation. This nicely illustrates the advantage of L2MS as a soft ionisation technique, enabling readily interpretable mass spectra to be generated. Photoionisation at 193 nm, however, results in mass spectra in which the base peaks are fragment ions. This difference in behaviour may be due either to the difference in excess energy deposited in the molecular ion or to excitation via different intermediate states, as discussed earlier.

Clearly, any technique that can provide chemical analysis of target analytes at trace levels directly from their host matrix represents an attractive and rapid methodology. The feature of the technique that allows this to be achieved is the selectivity provided by the photoionisation process. Most organic molecules have ionisation potentials between 7 and 10 eV. To achieve ionisation, absorption of two or more UV photons is required. For efficient photoionisation, a molecule must have a significant absorption cross section at the wavelength of the ionising radiation used. Molecules that do not possess a suitable chromophore will not be efficiently ionised. Therefore, by careful choice of the ionisation laser wavelength, the target analyte of interest may be selectively detected in preference to other components present in the mixture, including the host matrix. Wright and co-workers [61] showed that polymer additives with an appreciable absorption in the UV region of the spectrum can be selectively ionised in preference to the non-UV-absorbing host polymer.

They examined a sample of PP containing 0.15 wt% of Irganox 1330 and 0.05 wt% of Irgafos 168. The mass spectra obtained using 266 and 193 nm photoionisation following direct desorption from the PP matrix are shown in **Figure 1.21**. To obtain an appreciable signal from this sample, it was necessary to increase the desorption laser power density 4-fold, to ~38 MW/cm^2, compared to the value used to desorb the pure polymer additives. The need for increased laser desorption power densities is due to the PP matrix having a very low absorbance at the desorption laser wavelength of 10.6 nm. In the spectrum obtained at 266 nm, the molecular ions for both Irganox 1330 (m/z = 774) and Irgafos 168 (m/z = 646) are present. For ionisation at 193 nm, the molecular ion signals are very much weaker. However, a strong characteristic fragment signal at m/z = 441, anticipated from the 193 nm photoionisation mass spectrum of pure Irgafos 168 (see **Figure 1.20d**), can be seen. This peak is due to the loss of a 2,4-di-*tert*-butylphenyl—O group from the molecular ion, as is seen in the corresponding spectrum for the pure compound. These spectra demonstrate that, by use of two readily available ionisation wavelengths, and with reference to the corresponding spectra for the pure additives, it is possible to unambiguously determine the presence of Irganox 1330 and Irgafos 168 directly from the host PP matrix.

An apparently anomalous peak at m/z = 662 is observed in the 266 nm photoionisation MS (see **Figure 1.21a**) which is due to a phosphate antioxidant which is generally due to an oxidation product of the Irgaflox 168 phosphite secondary antioxidant, i.e., it is possible to determine not only the active phosphate level in the polymer but also the
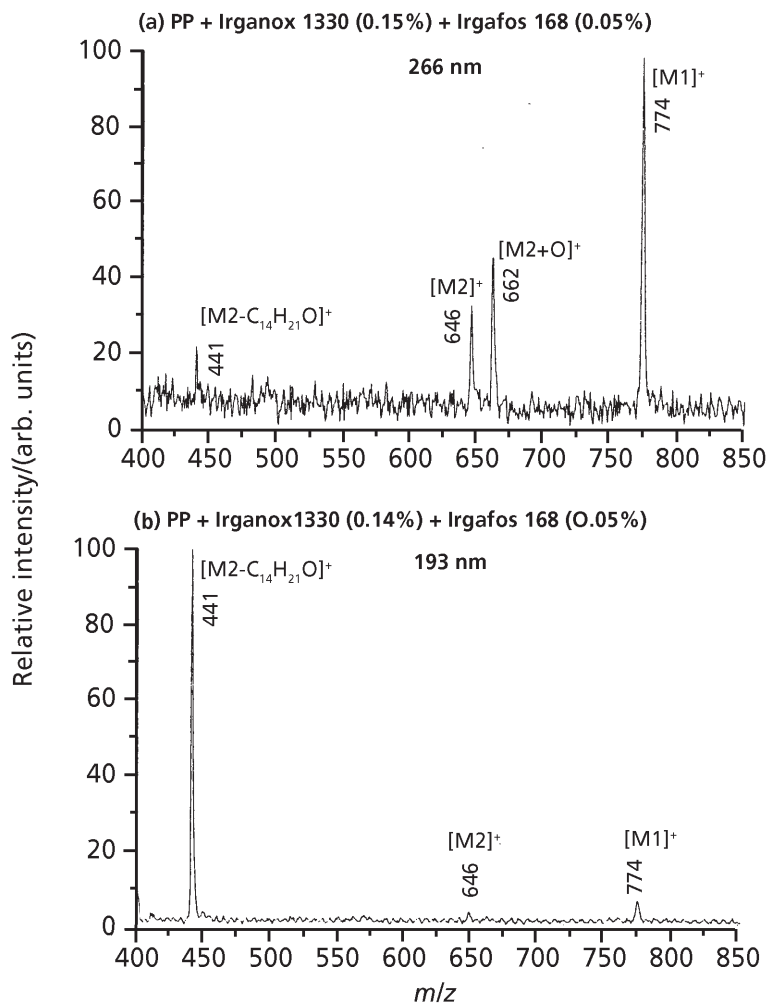
Figure 1.21 *In situ* mass spectra of polypropylene (PP) sample containing Irganox 1330 (0.15 wt%) and Irgafos 168 (0.05 wt%). Photoionisation at (a) 266 and (b) 193 nm. [M1]⁺ and [M2]⁺ denote the molecular ions of Irganox 1330 and Irgafos 168, respectively
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inactive degraded phosphate level, i.e., it is possible not only to determine the presence of additive species directly from the polymer but also to monitor chemical changes caused by the polymerisation process or subsequent exposure to heat, light, and other conditions which initiate polymer degradation.

In conclusion, Wright and co-workers [61] have shown that marked differences in the photofragmentation behaviour at 266 and 193 nm, allow unambiguous identification of these additives, even including differentiation between isomeric species. It has also proved possible to detect antioxidants and UV stabilisers in PP and polyoxymethylene polymers at concentrations consistent with commercial polymer formulations. In the case of the PP polymer formulation, it has been possible to detect an oxidation product of the antioxidant Irgafos 168 formed during either processing or natural ageing of the polymer. Such measurements could be extended to allow monitoring of additive degradation levels in aged polymer samples.

This study has also demonstrated the potential of L2MS as a surface analytical technique. It has been shown that it is possible to detect species on the surfaces of polymers which are not present in the bulk of the sample. It should prove possible to extend this work using spatially resolved desorption to probe for additive migration and aggregation.

Zhan and co-workers [65] have also reported on the application of two-step laser MS to the determination of surface antioxidants and the UV stablisers on PE and PET. They showed that laser melting-depth profiling could be achieved in polyoxymethylene, which enabled the determination of the special distribution of an antioxidant in an injection moulded test bar.

Laser Desorption EI-FT Ion Cyclotron MS (LD-EI-FT-ICR-MS)

As industrial thermoplastics are melt processed, they undergo oxidation reactions leading to changes in molecular weight and colour. Phosphite antioxidants [66-69] are generally considered to be secondary antioxidants, and their function is to control polymer molecular weight and colour. Phosphite stabilisers are used in most common thermoplastics at levels from 250 ppm to 2%. Typical phosphite loadings are often less than 1000 ppm. Phosphite stabilisers react with hydroperoxides, peroxy radicals, alkoxy radicals, and olefinic and carbonyl moieties; in addition, phosphites form co-ordination complexes with metals, changing their potential activity [70, 71].

Since the additive level in the polymer affects its stability, the analysis of polymer additives immediately poses two basic analytical questions: first, how much of the additive gets into the polymer during compounding, and second, how much of the additive that was added remains as the original phosphite form? Conventional methods for isolation and detection of phosphite additives are generally unsatisfactory.

Phosphite antioxidant tends to fragment extensively in mass spectrometric analysis. Xiang and co-workers [72] analysed Ultranox 626 diphosphite [bis(2,4-di-*tert*-butylphenyl) pentaerythritol diphosphite] and its corresponding diphosphate oxidation product, XR-2502, as well as the phosphate additive, WESTON 618 diphosphite (distearyl pentaerythritol diphosphate) by Nd:YAG laser desorption 1.064 nm) electron ionisation Fourier transform

ion cyclotron resonance mass spectrometry (LD/EI/FT/ICR/MS). For each of the isolated additives, the molecular ion (M$^+$) was observed as the predominant species with virtually no fragmentation. Moreover, abundant molecular ions were detected for Ultranox 626 diphosphite in a mixed polymer of polyethylene terephthalate, PP, and acrylonitrile-butadiene-styrene (ABS) at additive concentrations as low as 0.1% by direct analysis of the polymer film when the probe was heated to about 200 °C prior to laser desorption. The elevated sample temperature appears to increase the free volume of the polymer, in turn facilitating release of laser desorbed/ionised additives. LD/EI/FT/ICR/MS thus offers a sensitive and accurate means for detecting nonvolatile phosphite additives at typical concentrations in solid polymers, without the need for any chemical pretreatment.

Mass Spectra of Pure Additives

The LD/EI/FT/ICR mass spectrum of the Ultranox 626 disphosphate additive is shown in **Figure 1.22a**. The molecular ion (M$^+$) at mass-to-charge *m/z* 604 is the principal ionic species, in contrast to the pseudomolecular (M$^+$ K$^+$) ion observed in highest abundance for other kinds of additives [43, 73] by LD/FT/ICR/MS (i.e., no electron ionisation following laser desorption). By optimising the laser power (to ~50 mJ in ~10 ns in this case), it is possible to generate abundant molecular ions with virtually no fragmentation - higher laser power induces significant fragmentation.

Scheme 1.1 shows the two-stage oxidation of Ultranox 626 diphosphite to form the diphosphate compound, XR 2502. The LD/EI/FT/ICR mass spectrum in **Figure 1.22b** shows the predominant molecular ion signal *(m/z* 636) for the diphosphate, XR 2502, along with residual signals from incompletely oxidised phosphite precursor at *m/z* 620 (half-oxidised monophosphate) and *m/z* 604 (unoxidised phosphite).
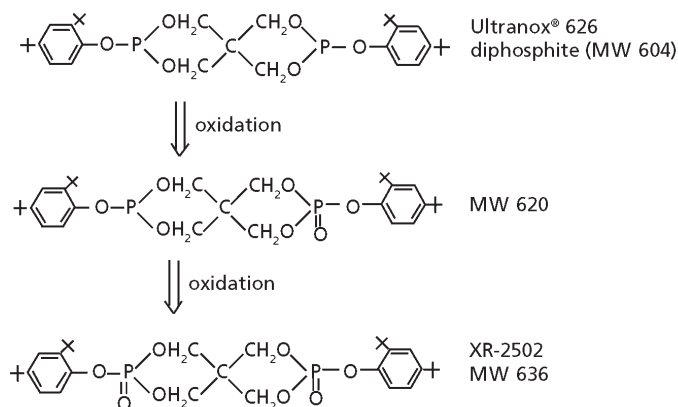
Scheme 1.1
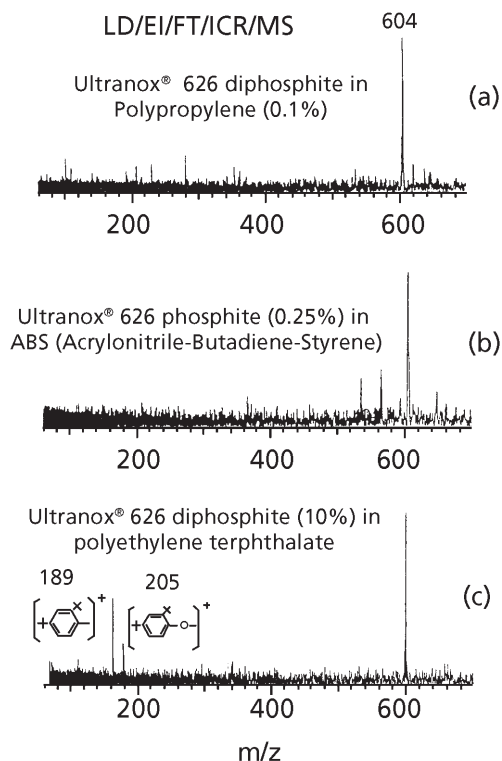
Figure 1.22 LD/EI/FT/ICR mass spectra of ULTRANOX 626 diphosphite in various solid polymers: (a) 0.1% in PP; (b) 0.25% in acrylonitrile-butadiene-styrene; (c) 10% in PET. Direct analysis of polymeric film or extraction was necessary to produce these spectra. *Reproduced from Xiang and co-workers, American Chemical Society [72]*

Figure 1.22c shows the LD/EI/FT/ICR mass spectrum of a second phosphite additive, WESTON 618 diphosphite. Although the molecular ion (*m/z* 732) is readily observed, its abundance is lower than for Ultranox 626 diphosphite or XF 2502, presumably because WESTON 618 diphosphite has saturated C_{18} hydrocarbon chains in place of aromatic rings and therefore fragments more easily. Similar behaviour has been reported for other phosphate additives [43].

Figure 1.22a shows the LD/EI/FT/ICR mass spectrum of Ultranox 626 diphosphite (~0.1% *w/w*) in PP. Although no fragment ions from the polymer itself are observed under these conditions (due to low laser power and high MW of the polymer), molecular ions from the additive in both diphosphite (*m/z* 604) and diphosphate *(m/z* 636) form are clearly detectable at ~ 0.05% each. The signal magnitude increases significantly when the probe is heated to about 200 °C prior to laser desorption. Heating evidently increases the free

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volume of the polymer to facilitate laser desorption/ionisation of the additives. Abundant ions at *m/z* 191 and 205 correspond to the following fragments:

m/z 191   and   *m/z* 205
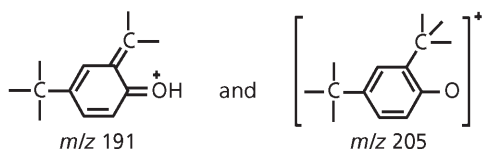
The fragment at *m/z* 205 is an obvious phosphite bond cleavage product, the other fragment was confirmed to be $C_{13}H_{19}O$ (191.143 nm) by accurate-mass measurement (191.145 nm) by internal calibration against ions of seven *m/z* ratios from perfluorotri-*n*-butylamine.

LD/EI/FT/ICR mass spectra of the same additive present at higher concentrations in PET and ABS polymers are shown in **Figure 1.22b** and **c**. This time, there does not appear to be significant oxidation of the additive, since no signals from the phosphate or diphosphate oxidation products are observed.

Laser desorption/Fourier transform ion cyclotron resonance MS has also been used to identify and determine the following types of polymer additives [74]: UV absorbents, e.g., Tinuvin [75], antioxidants, e.g., Irganox MD-1024, and amide wax antislip additives.

Potassium Ionisation of Desorbed Species (K+IDS)

Potassium ionisation of desorbed species (K+IDS) with mass spectrometric detection is an extremely useful tool for the characterisation of high performance organic coatings. K+IDS uses a commercial rapid heating probe to desorb intact molecules which are then ionised by potassium cation attachment. Based upon the molecular ions, which appear as [M]K+, coatings components can be qualitatively and quantitatively analysed. In this work K+IDS was selected as a method of soft ionisation, (i.e., producing molecular ions) because of its simplicity, wide applicability, low cost and compatibility with the quadrupole mass spectrometer. Simonsick [76] reports the application of K+IDS to polymer additives (UV stabilisers and antioxidants), catalysts (organotin), reactive diluents (vernonia oil and aliphatic epoxides) and polyurethane precursors (polyesters and isocyanates). Tikuisis and co-workers [77] also discussed this technique.

The technique is based upon rapid heating to desorb intact compounds [78]. Since ions are produced by potassium attachment and the internal energy transfer is low, primarily potassiated molecular ions with little or no fragmentation are observed [74, 79, 80]. Implementation of K+IDS required no modification of existing commercial equipment, no capital investment and is performed on quadrupole mass spectrometers [75].

This method was applied to the determination of organotin catalysts, e.g., dibutyl tin dilaurate, stablisers, e.g., Cyanox 1790, a hindered phenol antioxidant and Tinuvin 292, a hindered amine light stabiliser (HALS) and reactive diluents (such as aliphatic epoxides, epichlorohydrin, vernonial oil and so on) in acrylate resins.

Figure 1.23 shows the K+IDS MS spectrum of Cyanox 1790 antioxidant.

Figure 1.23 is the K+IDS mass spectrum of Cyanox-1790 a commercially available hindered phenolic antioxidant (American Cyanamid, Wayne, NJ). The molecular weight of this chemical is 699 Da; hence, under K+IDS conditions we would expect an ion at 738 Da, i.e., 699 + 39 (39 being the atomic weight of potassium). We see from the spectrum that this material is relatively pure.

This paper demonstrates the utility of K+IDS for the characterisation of individual coating components. Molecular weight data and complementary isotope patterns permits a rapid (10 minutes) assignment of specific structures to the materials contained in coatings.

A change in mass is usually involved in an organic reaction. The products differ from the reactants in molecular weight. Hence, K+IDS is an excellent probe for monitoring the success of derivatisation reactions and for elucidating the reactions which occur in model
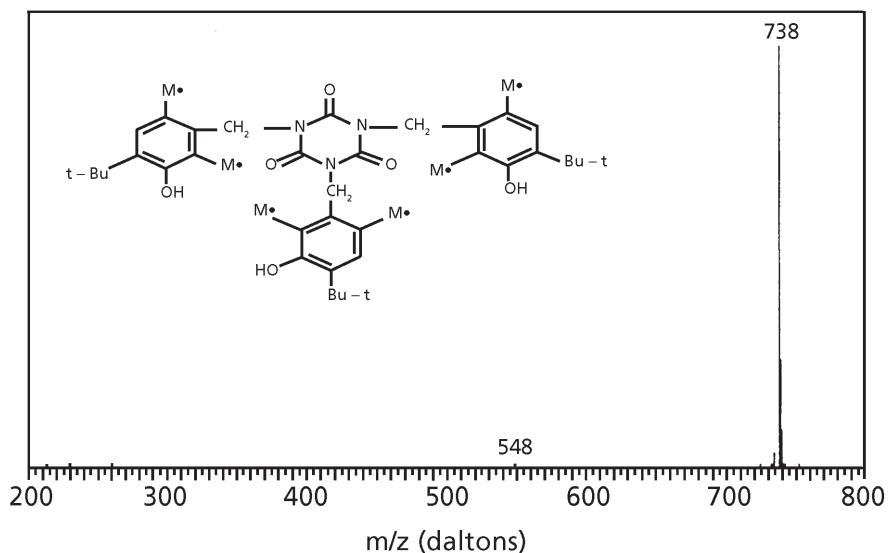
Figure 1.23 K+IDS MS of Cyanox-1790, a commercial antioxidant
*Reproduced from W.J. Simonsick Jr., Progress in Organic Coatings, 1992, **20**, 3-4, 411 [76]*

crosslinking chemistries. Finally, using selective chemical degradation coupled with K$^+$IDS analysis of the products, one is able to assemble the original network structure.

Fast Atom Bombardment (FAB)

Sterically hindered phenols and other additives containing thioesters, phosphonites and hindered amine moieties were analysed by LD-FT-MS and FAB-MS [81]. The LD technique was preferred for analysis of polymer additives because of undesirable fragmentation from FAB techniques.

Chang and co-workers applied FAB-MS to the measurement of HALS in polymers. The technique has also been applied to the measurement of oligomers up to decamer in polymers [82].

High Frequency Collision Induced Dissociation (CID)

This technique has been used to analyse the effect of internal energy deposition on the collision induced dissociation (CID) fragmentation spectra of Irganox 1076. Four different ionisation techniques were compared. The variation in the relative yields of the different fragmentation ions was attributed to differences in the amount of internal energy transferred to the precursor ions during the ionisation process. A five component mixture of antioxidants and UV stabilisers has been analysed by high energy MS and high energy CID using a four sector instrument and a time-of-flight MS [83] and by electrospray ionisation with high energy CID [84].

Secondary Ion Mass Spectrometry (SIMS)

The principles of this technique have been discussed by Shick and co-workers [85] and O'Toole and co-workers [86]. Time-of-flight SIMS with either gallium or indium primary beams has been evaluated as a method for measuring the homogeneity of distribution of a hindered amine antioxidant in low-density polyethylene. The parent ion for the oligomer at *m/z* 599 was so weak that it could not be used to map the distribution of the additive throughout its most commonly used concentration range (0.1 to 0.5% *w/w*) in polyethylene. Instead a mass fragment at *m/z* 58 was found to be sufficiently clear of interferences for use as a surrogate for the parent ion. As a result, imaging of the antioxidant distribution was possible to concentrations as low as 0.1% and a linear concentration calibration curve was obtained. The use of an indium primary beam improved the correlation of the antioxidant. Furthermore, indium reduced the contribution from the polyethylene background at *m/z* 58 in relation to the total counts acquired.

Rudewicz and Munson [45] used this technique for the direct determination of additives in PP. The technique has also been used to determine oligomers in polyacrylates, PEG, siloxanes and polycarbonates [87], polyglycols [88] and adhesion promoters, primers and additives in the surface of PET film [89], volatile antioxidants in styrene-butadiene rubbers [34, 50], mercaptobenzothiazole sulfenamide accelerator in rubber vulcanisates [90] and divinyl benzene in styrene-divinyl benzene copolymer [91].

Maldi Mass Spectrometry

Hanton [92] applied MALDI spectroscopy and electrospray ionisation MS to the characterisation of polymers used in coatings. Taguchi and co-workers [93] have developed a novel method for the direct analysis of small amounts of an oligomeric HALS occluded in PP material to study its photostabilising action on the basis of matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS) using a solid sampling technique while avoiding troublesome solvent extraction. In this sampling protocol, the powdered mixture of PP composite sample containing trace amounts of an oligomeric HALS, Adekastab LA-68LD (MW = 1900), and the matrix reagent (dithranol) was spotted on the sample plate, then ion exchanged water was deposited onto the mixture to make a suspension, and finally, the dried mixture adhered on the plate was subjected to MALDI-MS measurement. On the mass spectrum thus obtained by the solid sampling MALDI, the molecular ions of the HALS desorbed from the PP composite were clearly observed as three major series of the HALS components in the range up to about m/z 7000 with little interference by the PP substrate and the other additives. Moreover, in the MALDI-MS spectra for the UV-exposed sample, the satellite peaks around the major HALS components proved were enhanced significantly, reflecting the ability of the oxidised HALS species at the tetramethylpiperidine units to cause the photostabilising action. In addition, hydrolysed HALS species were also observed for the irradiated sample. These results suggest that not only the oxidation reaction but also the hydrolysis or decomposition of the oligomeric HALS components competitively proceeds in the PP composites during UV exposure.

Figure 1.24 shows a typical MALDI mass spectrum of intact Adekastab LA-68LD measured by the conventional dried droplet method in linear mode along with the assigned structures of the major components. **Table 1.6** summarises the calculated molar mass for the assigned structures and the observed peak top m/z values of the major components. Three series of the HALS components are mainly observed as the molecular ions (M^+) on the mass spectrum in the range up to about m/z 8000. Here, the precise m/z values of b_1 used as an internal standard for mass calibration were determined by an additional MALDI-MS measurement in reflector mode, confirming that the observed ions are mostly M^+. Among these, the constituents designated with b_n, which are the HALS molecules completely end capped with tetramethylpiperidyl groups, show the most intense peaks. In addition, the

Table 1.6 Calculated molar mass for the assigned structures and observed peak top *m/z* values of major components of HALS		
Component	Calculated molar mass[a]	Observed *m/z* value
a_0	665.9	666.3
b_0	791.1	791.5
c_0	938.2	938.6
a_1	1446.9	1447.1
b_1	1572.1	1572.1[b]
c_1	1719.2	1719.5
a_2	2227.9	2228.2
b_2	2353.1	2353.3
c_2	2500.2	2500.6
a_3	3008.9	3009.5
b_3	3134.1	2124.5
c_{13}	3281.2	3281.6
a_4	3789.9	3789.9
b_4	3915.1	3915.6
c_4	4062.2	4063.0
a_5	4570.9	4571.9
b_5	4696.1	4696.7
c_5	4843.2	4843.7
a_6	5351.9	5352.9
b_6	5477.1	5478.0
c_6	5624.2	5623.8
a_7	6132.9	6133.0
b_7	3258.1	6258.3
c_7	3405.2	6407.1
a_8	6913.9	6915.1
b_8	7039.1	7039.1[b]
c_8	7186.2	7185.3

[a]: *Isotopic abundance was taken into account*
[b]: *Used as internal standards for mass calibration: the molecular ions of b_1, m/z 1572.1 and b_8, m/z 7039.1*
Source: *Author's own files*

compounds containing a methoxy substituent (a_n) instead of a tetramethylpiperidyloxy unit of the corresponding main components (b_n) and those with a spirochain-type terminals (c_n) are also observed in fairly strong intensities. These two components are presumed to be the byproducts due to incomplete condensation or partial decomposition during synthesis of the HALS. The mass spectrum indicates that the oligomeric HALS consists
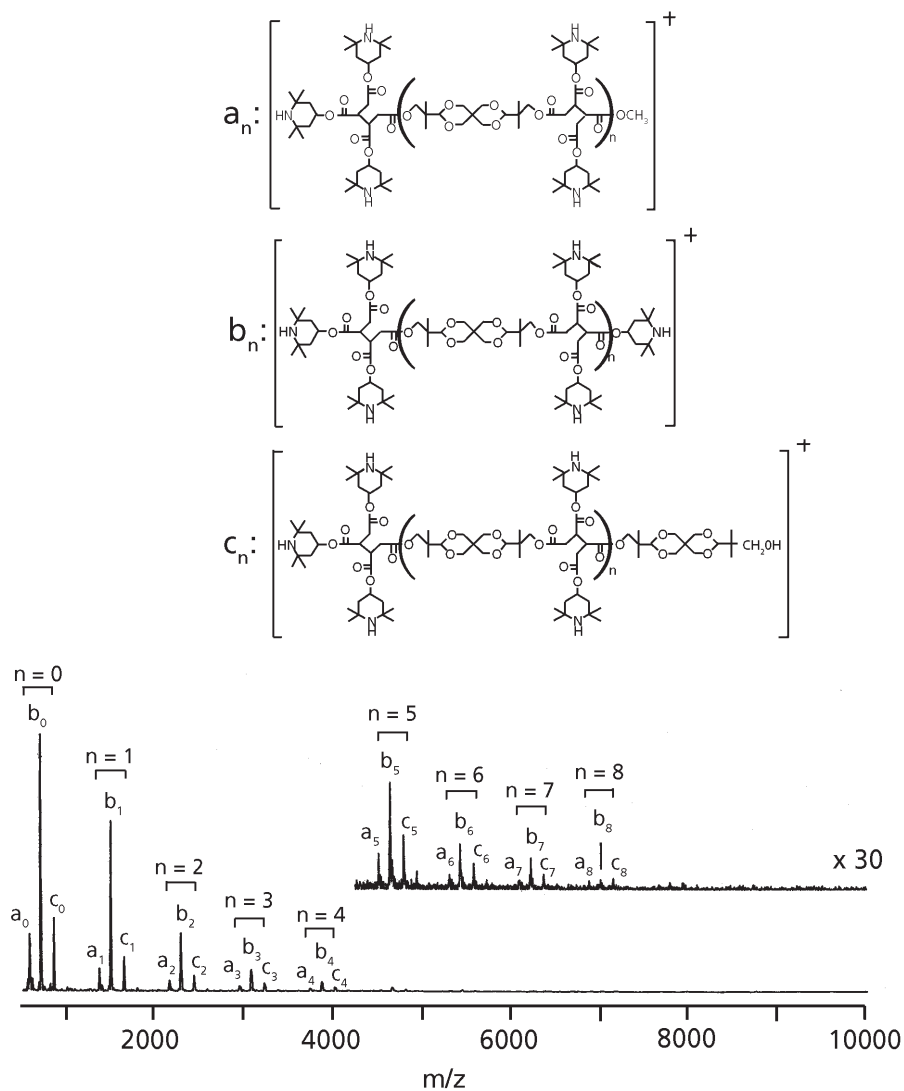
Figure 1.24 MALDI mass spectrum of Adekastab LA-68 LD obtained by conventional solution-based MALDI-MS. The weight ratio of sample/matrix was 1:10
Reproduced from Taguchi and co-workers, American Chemical Society [93]

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of a number of components with at least three kinds of different chemical structures and wide variations of molecular weights.

Figure 1.25 shows MALDI mass spectra of the HALS occluded in the PP composite (a) obtained by the dried droplet method after conventional solvent extraction from the PP
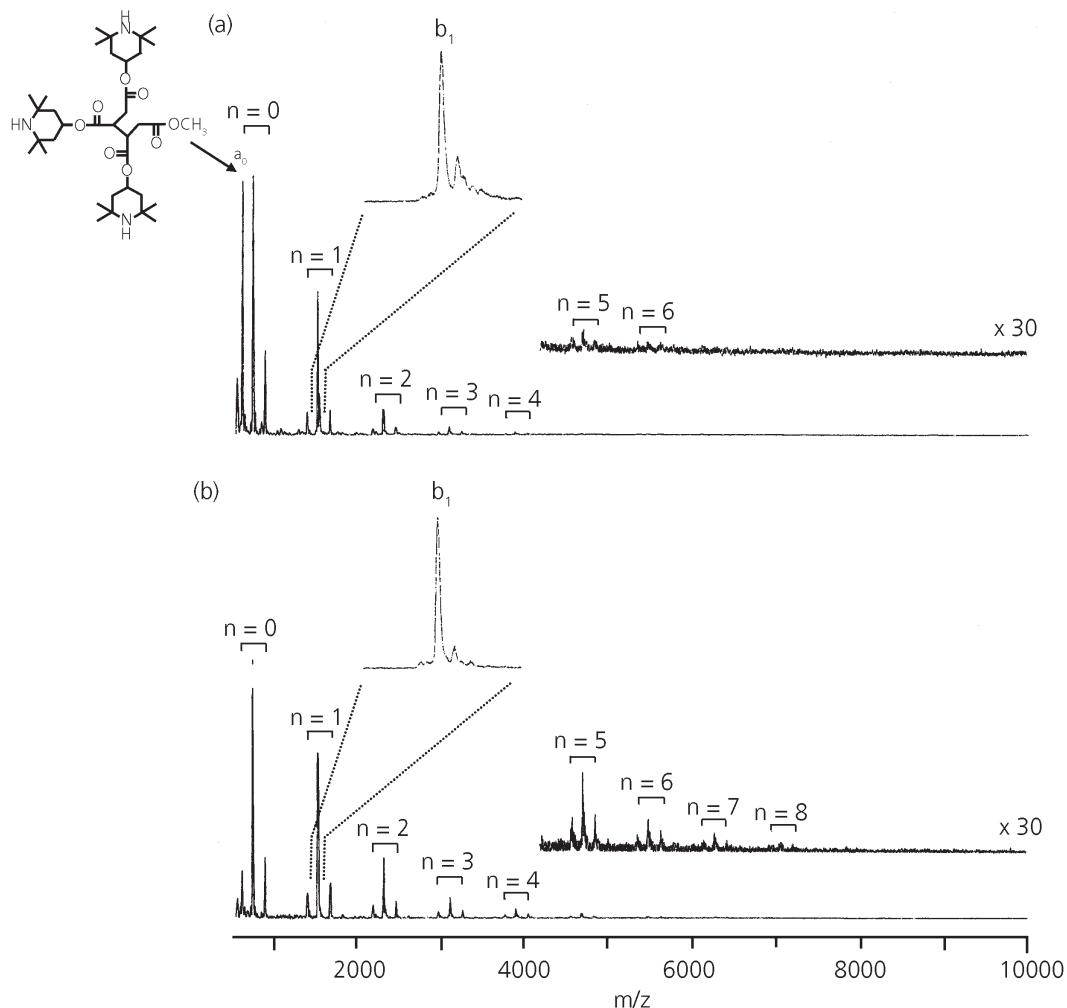
Figure 1.25 MALDI mass spectrum of HALS components in PP composite sample containing 1.0 wt% of HALS before UV irradiation: (a) solvent extracts from the sample obtained by solution-based preparation method; (b) HALS components directly desorbed from the PP composite obtained by the solid sampling technique
Reproduced from Taguchi and co-workers, American Chemical Society [93]

material and (b) directly desorbed from PP in the ionisation chamber by using the solid sampling technique. On the mass spectrum of the extracts (a), the peak of the main HALS oligomers markedly declined in comparison with those in **Figure 1.24** so that the components in $n = 6$ and higher regions were scarcely observed. Moreover, the relative peak intensity of the byproduct a_0 significantly increased and some satellite peaks around the major components such as b_1 were fairly boosted or additionally observed after the solvent extraction probably due to the decomposition of the larger components. These results suggest that not only the insufficient extraction of the higher molecular weight HALS components but also their undesirable decomposition proceeded considerably during the extraction process.

On the other hand, the mass spectrum obtained by direct MALDI-MS measurement of the PP sample (b) was almost identical to that of intact Adekastab LA-68LD shown in **Figure 1.24**. This fact suggests that the whole MW range of the HALS components was appropriately ionised during the solid sampling MALDI process through adequate contact between the matrix and the HALS molecules on the surface of the PP substrate. Here, the ions of the substrate polymer components and the antioxidants were scarcely observed on the mass spectrum under the given MALDI-MS conditions. These results demonstrate that MALDI-MS using the solid sampling method enables us to analyse the oligomeric HALS molecules occluded in the PP material directly without causing discriminative loss or decomposition of the HALS components during desorption. By using this technique, therefore, the subtle change in the molecular structure of the HALS components in PP during UV irradiation could be observed in the MALDI mass spectrum which it is possible to interpret in terms of the photostabilising action.

1.5 X-ray Photoelectron Spectroscopy (XPS)

Using x-ray photoelectron spectroscopy, Pena and co-workers [94] examined the factors affecting the adsorption of organophosphorus polymer stabilisers on to carbon black.

1.6 Thermal Methods of Analysis

1.6.1 Differential Scanning Calorimetry

Prasad and Shanker [95] used a differential scanning calorimeter (DSC) for the quantitative analysis of chemical blowing agents such as azodicarbonamide (azo) in commercial formulations. The DSC results were comparable to those obtained by the commonly used evolved gas analysis (EGA) technique. Advantages of DSC are: ease of operation,

shorter analysis time, environmental safety, and the quantitative analysis is independent of additives such as UV and antioxidant stabilisers which are normally present in carrier resins. The DSC technique is also effective in measuring azo concentrations up to 2% by weight, which is a limitation of the EGA technique. DSC can also be used to obtain the onset of the decomposition temperature and rate of decomposition of azo compounds containing Group II and Group IV metal salt activators, such as zinc oxide and zinc stearate. DSC also has the potential to detect the level of undecomposed blowing agent present in processed foam products as discussed next.

DSC measures the temperature and heat flow associated with the transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about the physical and chemical changes that involve exothermic and endothermic processes.

Figure 1.26 is a general illustration of the type of information that DSC provides in the decomposition study of a foam concentrate. The melting of a carrier resin (in this case LDPE) is an endothermic process, whereas the decomposition of the azo is exothermic.
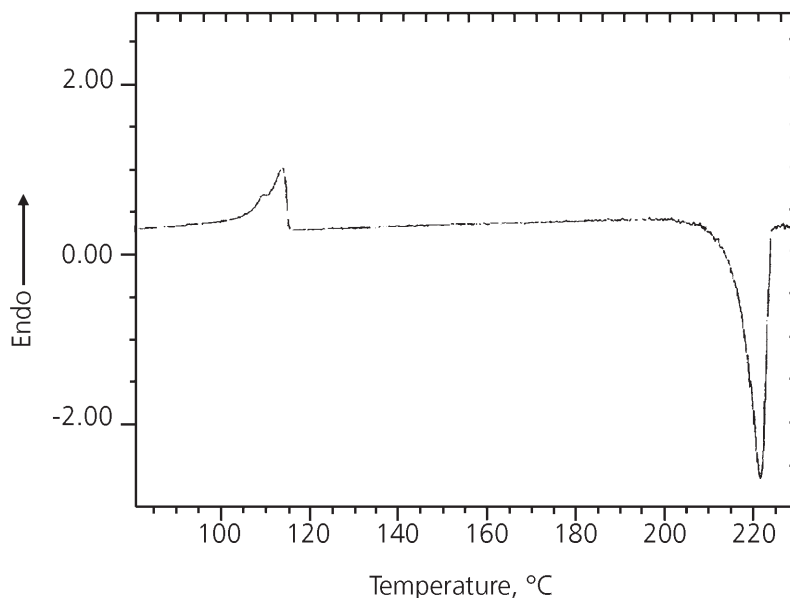
Figure 1.26 Typical DSC heating scans of azo dispersed in LDPE. The endothermic peak is due to the melting of LDPE. The exothermic peak is due to the decomposition of azo
*Reproduced with permission from A. Prasad and M. Shanker, Cellular Polymers, 1999, **18**, 1, 35. ©Rapra Technology [95]*

The breadth of the exothermic curve (195 °C to 225 °C) indicates the temperature range over which the decomposition of azo occurs. The shape of the peak indicates the uniformity of the decomposition. In addition, the size of the peak, i.e., the area under the exothermic curve, is a quantitative measure of the amount of blowing agent that has decomposed in the sample. This integrated area under the exothermic peak is referred to as heat of decomposition, AH_d.

An exothermic peak at 230 °C followed by an endothermic peak at 250 °C was observed in the DSC heating scan of pure azo (scans are not shown here). The reason for the endothermic peak in pure azo is not known. This endothermic peak at 250 °C was not observed in any of the foam concentrates. Because of the overlap of the exothermic peak with the endothermic peak, it is difficult to obtain the heat of decomposition value of the pure azo compound. However, based on the measured heat of decomposition value of samples A-F, the heat of decomposition value of pure azo was estimated to be about 1200 J/g (see **Table 1.7**).

Control samples (containing between 10% and 36% of blowing agent and between 90% and 64% of LDPE) were used to construct a calibration plot. These samples are free of any additives that would normally be present in the commercial samples. Some of the normalised DSC curves (total mass of 2.0 mg) as a function of % azo are shown in

Table 1.7 DSC results for the control foam concentrate samples					
Sample	**Exothermic peak**		**Heat of decomposition**[a]		$\Delta H_d{}^b$
	Temperature (°C)	σ	ΔH_d	σ	**(J/g of azo)**
			(J/g of sample weight)		
A	222.5	0.6	120.5	5.0	1200
B	222.5	0.9	181.0	5.0	1206
C	221.8	0.9	241.0	6.0	1205
D	222.0	0.8	301.0	5.0	1204
E	220:0	0.9	361.0	3.0	1203
F	223.0	1.0	438.0	6.0	1216
100% Azo	230.5	1.5	-	-	-
σ: *Refers to one standard deviation for n = 5 measurements* [a]: *ΔHd value obtained for the total sample weight of 2 mg, where % azo varies* [b]: *ΔHd value for 100% azo calculated from the known azo composition in samples A-F* *Reproduced with permission from A. Prasad and M. Shanker,* Cellular Polymers, *1999,* **18**, *1, 35.* ©*Rapra Technology [95]*					

Figure 1.27. This figure clearly shows that the magnitude of the exothermic curve (area of the exothermic curve) increases with the azo concentration. This figure demonstrates that the relative heat of decomposition depends strongly on the amount of azo compound present in a given sample. Therefore, in principle, the DSC data can be used to construct a calibration plot of the azo concentration against ΔH_d. Once a calibration plot has been established, routine samples run under the same conditions can simply be compared to the standard curves to measure the actual amount of azo compound present in unknown foam concentrate samples. **Figure 1.28** shows a plot of ΔH_d against percentage azo concentration for the control samples (A-F). The calibration plot of **Figure 1.28** was constructed using a total sample weight of 2 mg. In **Figure 1.28**, data points represent the average value of five runs along with the 95% confidence limit error bars ($2\sigma_{n-1}$ for $n = 5$). The data points are represented by a straight line, which, as expected, passes through the origin. The following equation was generated using a linear least square fit to the data:

$$\Delta H_d = 12.15* \% \text{ azo}$$

Thus, % azo in an unknown sample can be determined by simply dividing the ΔH_d, value by the slope of the calibration plot.
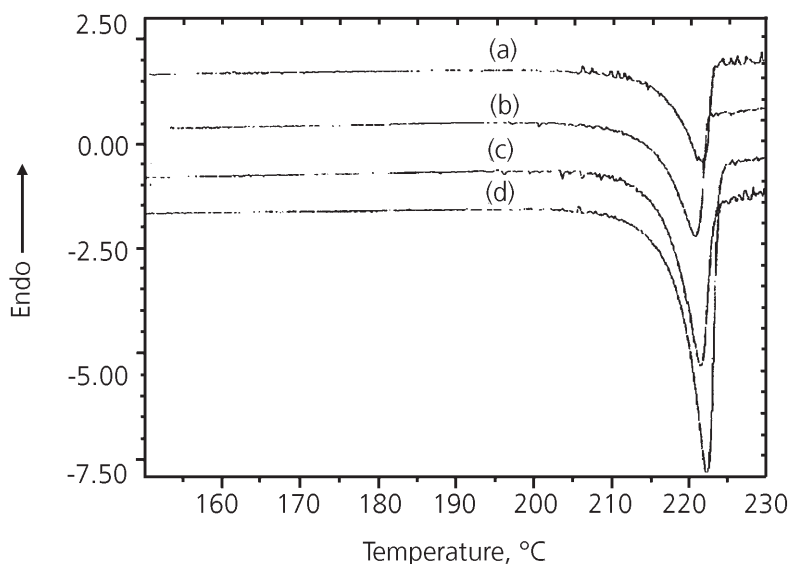
Figure 1.27 Normalised DSC scans showing the change in the exothermic peak area as a function of % azo. (a) sample B, (b) sample c, (c) sample E and (d) sample F
Reproduced with permission from A. Prasad and M. Shanker, Cellular Polymers, 1999, 18, 1, 35. ©Rapra Technology [95]From Prasad and Shankar, Cellular Polymers [95]
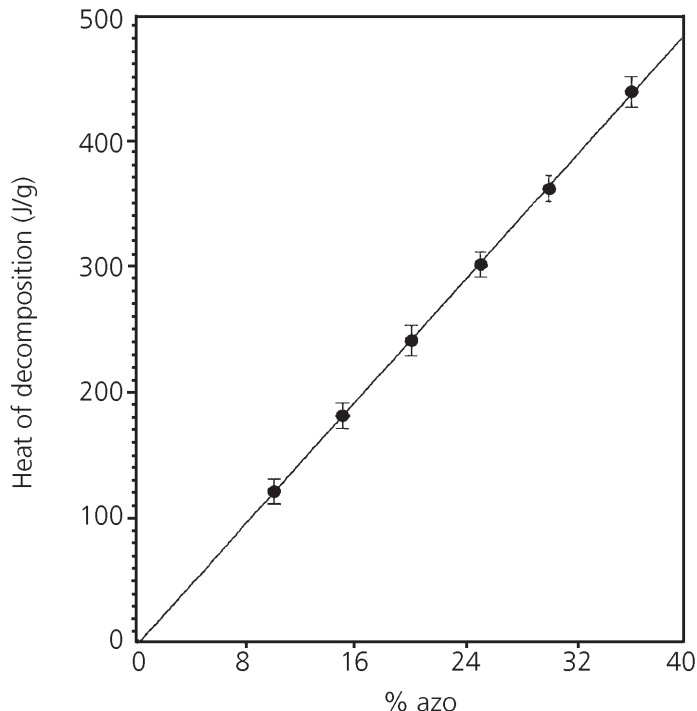
Figure 1.28 Plot of % azo against heat of decomposition by DSC of samples (A-F) for a sample mass of 2 mg. Error bars represent the 2 x σ_{n-1} limit for *n* = 5 measurements
*Reproduced with permission from A. Prasad and M. Shanker, Cellular Polymers, 1999, **18**, 1, 35. ©Rapra Technology [95]*

It has been shown that DSC is a useful, easy, fast and accurate method for the quantitative analysis of chemical blowing agents. The DSC results are comparable to the most commonly used EGA technique. It can quantitatively determine the amount of blowing agent present in both foam concentrates and finished foam sample. The most common types of additives, such as antioxidants and UV stabilisers, do not decompose in the temperature range of interest, thus making the quantitative determination of azo by DSC relatively easy. The system can be automated to reduce the operator's time. DSC can also be used to study the effects of all formulation ingredients on the decomposition of blowing agent.

Haldankar and Spencer [96] used DSC to investigate the thermal transitions occurring in polyacrylic acid and its sodium and potassium salts over a large range of water content at temperatures below the normal melting temperature of water. The bound water was identified as nonfreezing (type I), freezing with a constant melting temperature (type II), and freezing with a melting temperature dependent on the water content (type III). The

transition temperatures of the freezing states of the water were determined. Two constant melting temperatures were observed for the type II water in the sodium and potassium polyacrylates, while a single transition of this type was observed for polyacrylic acid. The sodium polyacrylate absorbed more water in the nonfreezing state than the potassium polyacrylate, and both polyelectrolytes absorbed about three times as much water in this state as the nonionic polyacrylic acid. The effects of water content on the occurrence of an exotherm at low temperature in the melting scans of the polyelectrolytes are described.

A DuPont DSC/DTA 900 thermal analyser was used with a DSC cooling attachment. The DSC was purged with nitrogen and the subambient temperature was attained with liquid nitrogen. The cell constant was determined using a sapphire disc. The temperature scale of the DSC cell was calibrated using indium (mp = 156.6 °C), water (0 °C), cyclohexane (6.5 °C), and the crystallisation temperature of cyclohexane (–87.1 °C). With careful calibration and weighing, precisions of ±2% for the enthalpy of transition and ±1 °C for the transition temperature were obtained.

1.6.2 Differential Thermal Analysis

Schwartz and co-workers [97] used isothermal differential thermal analysis to study the diffusion of Irganox 1330 (1,3,5 tris (3,5 di-*tert*-butyl-4-hydroxyl benzyl) mesitylene) in extruded sheets of isotactic polypropylene (iPP). Studies were conducted over the temperature range 80-120 °C. The measurements showed a clear relation between oxidation induction time and oxidation maximum time [both determined by isothermal dynamic thermal analysis (DTA)] and the concentration of stabiliser. It was possible to calculate the diffusion coefficients and the activation energy of diffusion of Irganox 1330 in iPP by measuring the oxidation maximum times across stacks of iPP sheets.

For quantitative determination of the concentrations of antioxidants in PP that are required for the analysis of diffusion data, an isothermal DTA technique was developed that directly uses the effect of antioxidants on the thermooxidative stability of the polymers. Especially at elevated temperatures and in the presence of oxygen, polyolefines undergo thermooxidative degradation which follows a radical mechanism [98].

The time from the start of an isothermal DTA experiment to the beginning of exothermal decomposition is the so-called oxidation induction time (OIT). After this period, which depends on the antioxidant concentration, effectiveness, and temperature used, autocatalytic oxidation produces an exothermal peak [99-102]. The time from the start of the test to the maximum of this peak is the so-called oxidation maximum time (OMT) [103], which means the complete consumption of antioxidants and the loss of thermal stability of polymer. At elevated test temperatures, corresponding to short reaction times, it was difficult, or even impossible, to determine the OIT in the usual manner. For

that reason OMT was chosen. The calibration curve, the OMT of iPP as a function of antioxidant concentration at 170 °C DTA temperature is shown in **Figure 1.29**. Each point in this figure is the average of 10 measurements carried out on iPP films with the specific antioxidant concentration. From the calibration curve it is obvious that at low levels of antioxidant concentration in the iPP film, the standard deviation is minimum. But at higher levels of antioxidant concentration, slight deviations are noted but they are within the acceptable level iPP film with 0.5% Irganox 1330, OMT = 2.50 ± 0.32 h; iPP film with 0.10% Irganox 1330, OMT = 5.77 ± 0.38 h).

Sheets of iPP with 0.03 and 0.10% antioxidant levels were chosen to determine the influence of thermooxidative degradation during storage of the materials in the circulating-air oven. The plot of reciprocal temperature of the DTA oven *versus* the OMT for the unstabilised and stabilised iPP sheets is shown in **Figure 1.30**. For an iPP sheet with 0.03% antioxidant concentration, the OMT is about 2000 h at 120 °C. So the diffusion of the antioxidant in the iPP film can be measured at 120 °C for a period of 48 h without the influence of the thermooxidative degradation and the loss of added antioxidant.

Films of iPP having the dimensions 15 mm x 15 mm x 100 µm with an antioxidant level of 0.03 or 0.10% were chosen for the diffusion measurements. Fifteen films having 0.03% antioxidant concentration were stacked and placed together and then placed over 15 films
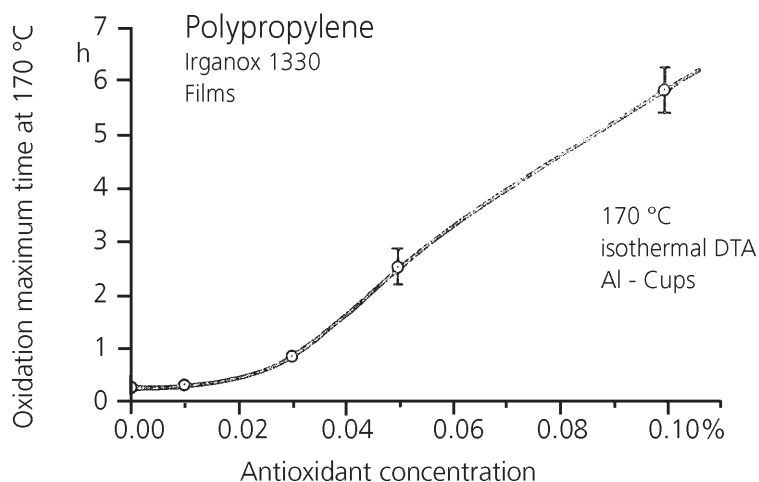
Figure 1.29 oxidation maximum times for at 170 ºC of iPP sheets as a function of antioxidant concentration (isothermal DTA)
Reproduced from Schwarz and co-workers, Journal of Applied Polymer Science [97]
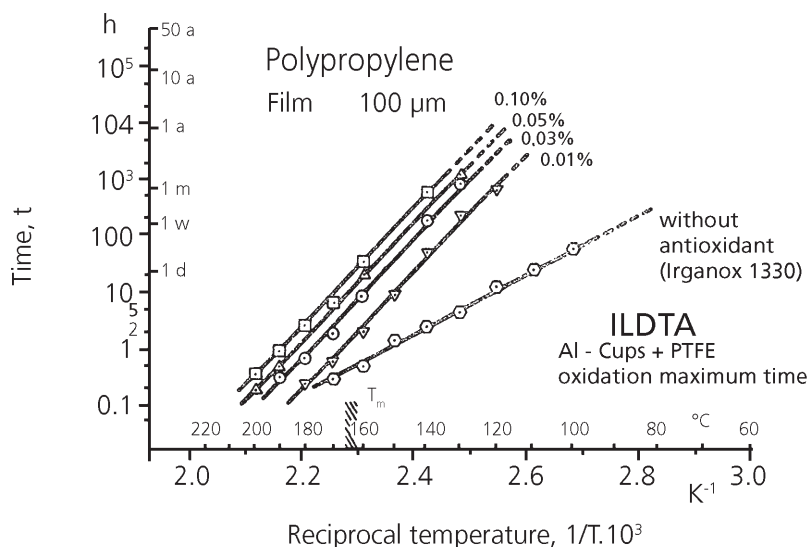
Figure 1.30 Logarithms of oxidation maximum times of isocratic PP with different antioxidant concentrations as a function of reciprocal temperature (isothermal DTA) *Reproduced from A. Prasad and M. Shanker, Cellular Polymers, 1999, **18**, 1, 35. ©Rapra Technology [95]*

with 0.10% antioxidant concentration, the whole stack of 30 sheets was kept tightly in the centre of diffusion device (two blocks of aluminium with steel bolts). This unit was placed in a circulating-air oven for several predetermined time intervals at a constant temperature. Some experiments were performed at different isothermal conditions, namely, 80, 100, 110 and 120 °C.

At the end of the run, the iPP sheets were separated and samples out of the centre of each sheet were analysed at 170 °C by isothermal DTA. This procedure is the measurement of residual stability time because the thermooxidative stability is determined after storage in the oven.

After having stored a stack of iPP sheets for 48 h at 120 °C in a circulation-air oven, the residual stability time of each sheet of this stack was determined. **Figure 1.31** shows the residual stability time at 170 °C (OIT and OMT) as a function of the thickness of the film stack. It is clear that both curves, OMT and OIT, are the same shape. Using the calibration curve shown in **Figure 1.29** the concentration profile can be determined (**Figure 1.32**).

Hatakeyama and co-workers [104] used differential thermal analysis and also DSC and TGA to determine the level of bound water in hydrophilic polymers. They were able to
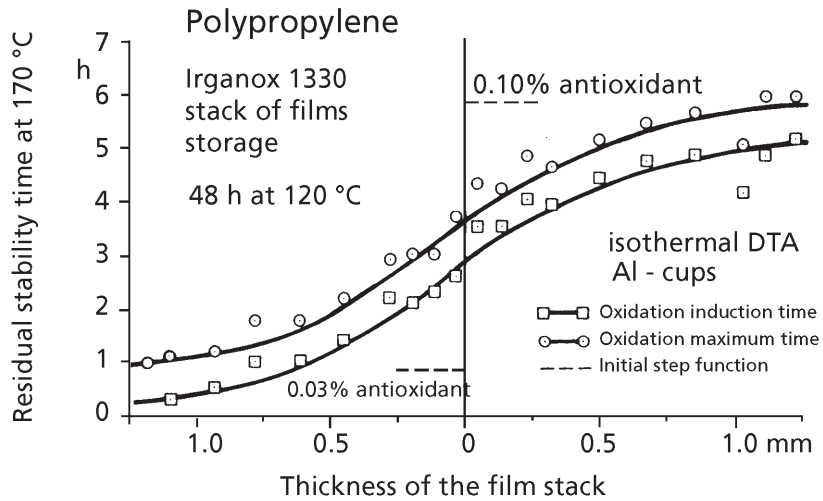
Figure 1.31 Residual stability time (OMT and OIT) at 170 °C of iPP sheets after storage of 48 h at 120 °C as a function of the thickness of the film stack (isothermal DTA)
*Reproduced from A. Prasad and M. Shanker, Cellular Polymers, 1999, **18**, 1, 35. ©Rapra Technology [95]*
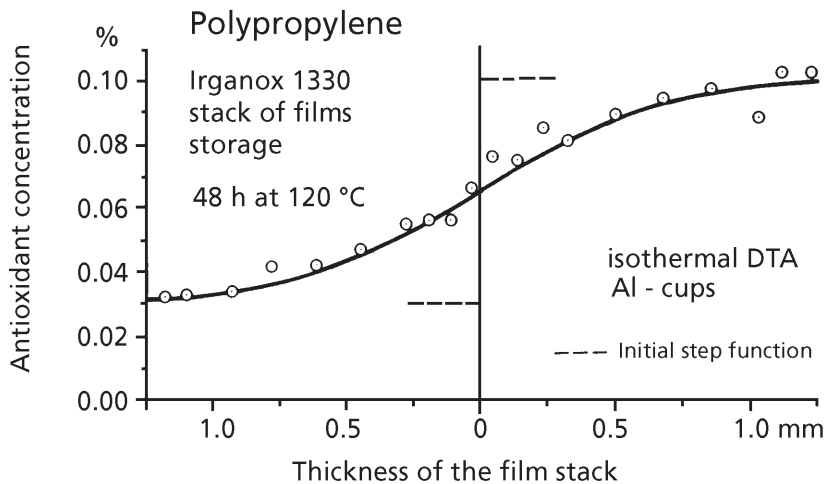
Figure 1.32 Antioxidant concentration of it iPP sheets after storage of 48 h at 120 °C as a function of the thickness of the film stack (isothermal DTA)
*Reproduced from A. Prasad and M. Shanker, Cellular Polymers, 1999, **18**, 1, 35. ©Rapra Technology [95]*

distinguish between free water in the system and water bound to the polymer. Differential thermal analysis has been used to determine blowing agents in foams [105, 106].

1.6.3 Thermogravimetric Analyses

This technique has been used to determine blowing agents in foamed plastics [105] to study liberation of stabilisers from PVC pipe at elevated temperature [107].

1.7 Vapour Phase Ultraviolet Spectroscopy

Organic and inorganic pigments are used for coloration of polymers, polymer films and polymer coatings on metal containers. Vapour/phase UV absorption spectrometry at 200 nm has been used to identify such pigments [29]. In this method powdered samples are directly vaporised in the heated graphite atomiser. Thermal UV profiles of organic pigments show absorption bands between 300 and 900 °C, while profiles of inorganic pigments are characterised by absorption bands at temperatures above 900 °C. Temperature, relative intensity, and width of the bands allow the identification of the pigments. The technique shows fast acquisition of thermal UV profiles (2-3 minutes for each run), good repeatability and wide thermal range (from 150 to 2,300 °C). A 1:1 mixture of organic pigment yellow (2-nitro-*p*-toluidine coupled with acetoacetanilide) and inorganic PY 34 (lead chromate) was vaporised. The thermal UV profile clearly shows two absorption/bands at about 500 °C and 1,250 °C. The first band is attributed to the vapours which originate from the decomposition and pyrolysis of the organic pigment, the second band corresponds to the decomposition and vaporisation of lead chromate at high temperature (mp 844 °C). It is possible therefore to determine by a rapid run whether the pigment is a mixture or belongs to the organic or inorganic group.

1.8 X-Ray Fluorescence Analysis

This technique has been applied to determining the identity of oxygen absorbers in polymers [108] also to determine traces of metals in polymers.

1.9 Nuclear Magnetic Resonance Spectroscopy

The phase partitioning of additives in styrene-butadiene polymer blends has a large impact on the performance of the blend. Since solubility characteristics and processing of the blends influences partitioning, it is necessary to be able to quantify the level of Ionol

(2,6 di-*tert*-butyl-4-methylphenol) in each phase. Smith and co-workers [109] have described an NMR method to quantify this partitioning based on the fact that the rubber phase and molecules dissolved therein, can be easily distinguished due to this phase's enhanced motional characteristics.

Table 1.8 and **Figure 1.33** give the Ionol levels in the high-impact polystyrene (HIPS) as determined by liquid chromatography (LC) and the levels found in the rubber phase by NMR. The partition coefficient is defined as the ratio of the concentration of the Ionol found in the rubber phase to that found in the rigid PS phase. The level of Ionol in the rubber phase was determined by ^{1}H NMR and the total amount in the HIPS was determined by LC.

Since the level of rubber in the HIPS (9%) was also known, the concentration of Ionol in the PS phase could be calculated by difference. The ratio of these concentrations is the partition coefficient. **Table 1.8** also lists the concentration of Ionol in the PS phase, calculated by subtracting the level in the polybutadiene from the total concentration in the HIPS, and the calculated partition coefficient for each sample. The average of these values is 2.0 and the estimated precision of these values is ±0.4. The value of 2.9 determined at low loadings of Ionol is probably due to the precision of determining Ionol by ^{1}H NMR at that low loading. The partition coefficient is fairly constant at 1.6 to 1.9 for the samples containing from 3.5 to 7.3% Ionol, indicating the rubber phase is not being saturated.

Table 1.8 Weight% Ionol and partition coefficients in HIPS standards				
Nominol weight% Ionol in the HIPS	Weight% Ionol found in the HIPS by LC	Weight% Ionol found in the rubber phase of the HIPS by NMR	Weight% Ionol in the PS phase by difference	Partition coefficient = Ionol concentration in PBD/Ionol concentration in PS
0.0	0.0	0.0	NA	NA
1.97	1.6	4.0	1.4	2.9
3.85	3.5	5.3	3.3	1.6
5.67	5.3	9.4	4.9	1.9
7.42	7.3	11.0	6.9	1.6
Reprinted with permission from P.B. Smith, W.C. Buzanowski, J.J. Gunderson, D.B. Priddy and L. Pfenninger in Proceedings of the 60th SPE Annual Technical Conference, ANTEC 2002, San Francisco, CA, USA, Paper No.421. ©2002, SPE [109]				
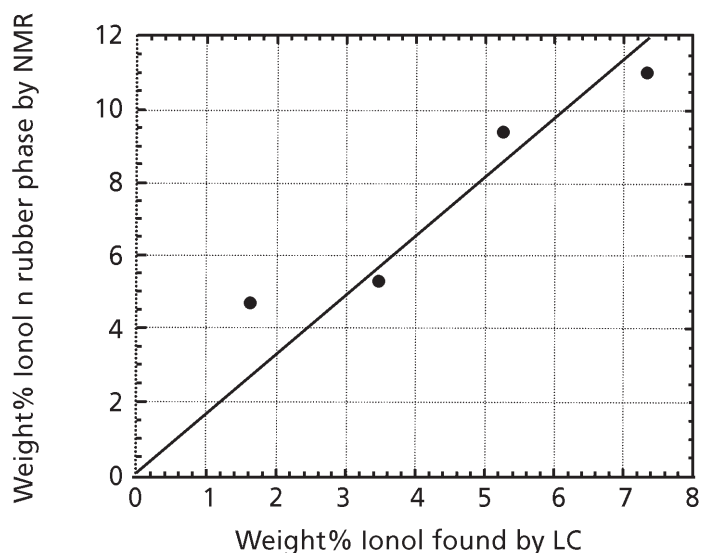
Figure 1.33 The level of Ionel determined in the rubber phase by NMR and in the HIPS by
LC, the slope giving the partition coefficient
Reproduced from Smith and co-workers, SPE [109]

NMR spectroscopy has also been used in a limited number of other applications including
the determination of stabilisers [110], water in polyols [111], starch in PE [77], degradation
products of phosphorus containing additives [112], acrylic acid in oligomers [77], and
plasticisers in PVC [112].

Wideline NMR spectroscopy has been used [113] for the determination of the plasticiser
content, (e.g., di-*iso*-octyl phthalate) of PVC. The principle of the method is that the
narrowline liquid-type NMR signal of the plasticiser is easily separated from the very broad
signal that is due to the resin - integration of the narrow-line signal permits determination
of the plasticiser. A Newport Quantity Analyser Mk I low-resolution instrument, equipped
with a 40 ml sample assembly and digital readout, has been used to determine 20 to
50% of plasticiser in PVC. The sample may be in any physical state without significantly
affecting the results, e.g., sheet samples are cut into strips 50 mm wide, which are rolled
up and placed in the sample holder. A curvilinear relationship exists between the signal
per g and the percentage by weight of the plasticiser. For highest precision, it is necessary
to know the type of plasticiser present - use of the appropriate calibration graph gives a
precision of ± 0.5%. However, one general calibration graph can be used. The precision is
then approximately ±3%. As the NMR signal is temperature dependent, the temperature
of calibration and of analysis should not differ by more than 4 °C.

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2 Extraction Techniques for Additives in Polymers

2.1 Introduction

Most polymers contain quite complex additive systems which are incorporated during manufacture to impart beneficial properties during manufacturing operations, e.g., protective antioxidants, slip agents, etc., and during end-use, e.g., antioxidants, ultraviolet (UV) stabilisers, plasticisers and antistatic agents, flame retardants, antioxidants and thermal stabilisers. The first stage in the examination of a polymer, either from the point of view of identifying the polymer or identifying and determining additives present must be to separate gross polymer from gross additives. It may then be necessary to separate the gross additive fraction into individual additives by a chromatographic procedure in order to facilitate the identification of individual additives.

Separation of gross polymer from gross additives is necessary so that examination of the polymer is not affected by interference from the additives present and also *vice versa*. Many different procedures have been studied for the removal of gross additives from the polymer and some of these are discussed next.

The main extraction procedures used are summarised in **Table 2.1** and although most of them can be carried out on material cut to a particle size of less than 2 mm diameter, it is often advantageous to produce material of a smaller size and with a larger surface area to mass ratio. This is conveniently done by grinding at the temperature of liquid nitrogen using an efficient and easily cleaned cutter mill.

The extraction of additives which are strongly adsorbed or chemisorbed onto the polymer filler matrix must be carefully watched by the analyst, as a change of the method of manufacture of, for example, the filler or in the method of compounding the plastic formulation, can also markedly alter the degree of adsorption being produced and hence invalidate an established quantitative extraction procedure. The use of 'stronger' extraction reagents can cause complications at the measurement stage and hence each system must be carefully screened and frequently checked. Polymer extraction procedures using organic solvents do not extract all types of organic additives from the polymers, also many inorganic compounds and metal inorganic compounds, e.g., calcium stearate, are

Table 2.1 Examples of extraction methods			
Extraction method	**Polymer or compound**	**Solvent**	**Additives or contamination extacted**
Single solvent (Soxhlet)	Polyvinyl chloride (PVC)	Diethyl ether	Plasticisers
Single solvent (reflux)	Polyethylene	Chloroform - 1,1,1-trichloroethane	Antioxidants
Solvent + reagent (reflux)	Polypropylene	Ethylene dichloride - trichloroacetic acid	Chemisorbed amides/amines
	Polyester	Methanol - Karl Fischer reagent	Water
Solution/precipitation	Polyolefines	Toluene - methanol, xylene - methanol	UV absorbers, antioxidants, slip agents
	Acrylics	Acetone - light petroleum	Plasticisers, lubricants
Steam/solvent distillation	Packaging films	Water - diethyl ether	Odour and taint-forming additives
Vacuum/thermal extraction	Nylon fluorocarbon polymers		Water, process fumes
Source: Author's own files			

insoluble. The presence of metals will have been indicated in the preliminary examination of the polymer. However, most types of organic polymer additives can be readily extracted from polymers with organic solvents of various types. The first stage is to solvent-extract the total additives from the polymer in high yield and with minimum contamination by low molecular polymer. Extracts should be used for analysis without delay as they may contain light or oxygen sensitive compounds. When delay is unavoidable, storage in actinic glassware under nitrogen in a refrigerator minimises the risk of decomposition.

In practice, the most commonly used procedures for the separation of gross polymer and gross additives are based on fractional precipitation and fractional extraction. In the fractional precipitation procedure a good solvent for the polymer is required, also a non-solvent for the polymer in which the additives remain soluble. Information on solvents and non-solvents for various polymers is given in **Table 2.1**. It must be realised that the solubility of a polymer depends not only on the type of polymer but also the degree of polymerisation, i.e., molecular weight and degree of branching and crosslinking and on its steric configuration. Thus a relatively low molecular weight unbranched polyethylene (PE) may have a high solubility in toluene whilst a high molecular weight highly branched

PE would have a low solubility even in hot toluene. In the case of styrene-butadiene copolymer, the uncrosslinked polymer is soluble in aromatic solvents, whilst the highly crosslinked (gel) fraction is completely insoluble and, indeed, this can be used as the basis of a method for separating gel from uncrosslinked polymer. Copolymers usually dissolve in a greater number of solvents than homopolymers. Thus, whilst PVC is only slightly soluble in acetone or methylene chloride, its copolymers with vinyl acetate or acrylates dissolve easily.

2.2 Solvent Extraction

2.2.1 Polyolefins

The scheme outlined in **Figure 2.1** has been proposed for the solvent extraction and examination of PE [1]. Some useful solvents are listed in **Table 2.2**.
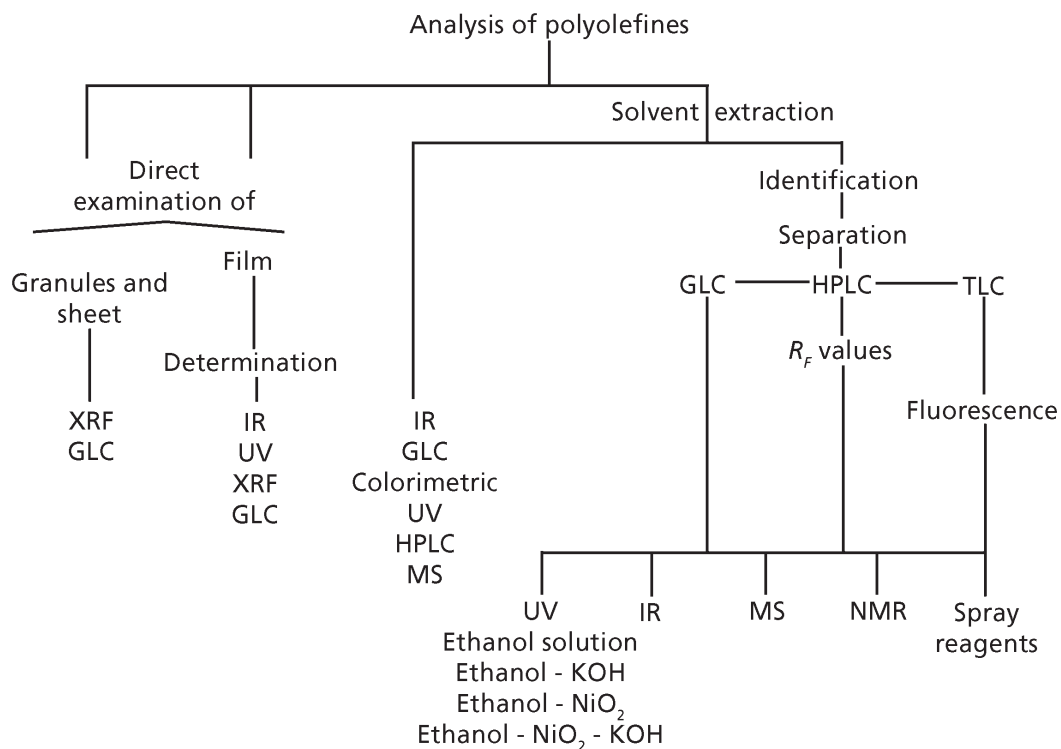
Figure 2.1 Analysis of polyolefins [1]

Table 2.2 Solvent extraction methods of additive extraction from polymers					
Polymer type	Substance extracted	Extracting solvent	Comments	Ref.	Type of extraction
PE	Cresolic and phenolic antioxidants	Chloroform	Heat at 50 °C for 3 hours in a closed container	[1]	Fractional extraction
PE	Cresolic antioxidants	Hexane	Heat at 50 °C for 24 hours	[2]	Fractional extraction
PE	Cresolic antioxidants	Ether	In the dark at 20 °C	[3]	Fractional extraction
PE	Phenolic antioxidants	Chloroform		[4]	Fractional extraction
PE	Antioxidants	Toluene	Reflux to dissolve polymer in precipitate with methanol	[5]	Fractional precipitation
PE	Antioxidants	Water	At 70 °C under nitrogen	[6]	Fractional extraction
Source: Author's own files					

Details of particular solvent extraction schemes for polyethylene are described in more detail next.

• *Toluene-Methanol Extraction System*

Total internal plus external additives can be extracted from low and high-density polyethylene (HDPE) and polystyrene (PS) by procedures involving solution or dispersion of the polymer powder or granules (3 g) in cold redistilled sulfur-free toluene (50-100 ml) followed in the case of PE, by refluxing for several hours. Rubber-modified PS does not completely dissolve in toluene if it contains gel.

• *Methylene Dichloride Extraction*

Methylene dichloride is a particularly good solvent for PP extraction because of its high volatility. In addition to additives, most solvents also extract some low molecular weight polymer with subsequent contamination of the extract. To overcome this, Slonaker and Sievers [2] have described a procedure for obtaining polymer-free additive extracts from PE based on low temperature extraction with *n*-hexane at 0 °C. This procedure is also applicable to PP and PS.

• *Chloroform or 1,1,1-trichloromethane Extraction*

A portion of the PP sample (2-20 g) is weighed accurately into a 250 ml round-bottomed flask. To this is added 50 ml of chloroform (or 1,1,1-trichloromethane), which is then placed in the flask under a water-filled reflux condenser. The mixture is gently brought to the boil on a water bath and heated for 30 minutes. The solution is cooled and then decanted into a 100 ml volumetric flask after filtering through a No. 42 Whatman filter paper. Any polymer collected in the filter paper is transferred to the round-bottomed flask and 40 ml of chloroform is added. The extraction procedure is then repeated. The cooled solution is filtered into the volumetric flask containing the first extract. The residue is washed with a little more chloroform, filtered into the volumetric flask and diluted to the 100 ml mark with chloroform. The solution is shaken well. Alternatively, the sample can be ground in a Wiley Mill to pass through a 60 mesh screen. A 10-20 g portion of sample is extracted in a Soxhlet apparatus with heptane for a minimum of 6 hours. The extract is transferred to a 300 ml tall-form beaker, and evaporated to approximately 20 ml, and then diluted to 40 ml with chloroform.

• *Ethanol-Methanol Extraction System*

The sample to be analysed must be very thinly sheeted or powdered. A sample (1.000 ± 0.0005 g) is wrapped with an extraction cloth, which has been previously treated to remove sizing, and so on. The sample is placed in an Underwriter's extraction cup and extracted for 16 hours with 95% ethanol or methanol. The alcoholic extract is transferred to a 100 ml volumetric flask, cooled to room temperature and diluted to the mark with the extraction solvent.

Alternatively, the polymer compound containing the unknown stabiliser is cut or ground into small pieces, and about 5 grams is extracted by heating under reflux for 24 hours with 50 ml of ethanol. The extract is cooled to room temperature and the polymer is filtered off.

• *Cyclohexane Extraction*

A representative sample of PE is ground in the Apex Mill. The sample (1 g) is placed into a 100 ml round-bottomed flask and cyclohexane (20 ml) is added. A condenser is fitted to the flask and the cyclohexane is allowed to reflux on a water bath for 1 hour. The condenser is washed with 20 ml cyclohexane, the flask is removed from the bath, and then cooled to room temperature and shaken well. After filtering through a No. 802 filter paper into a 100 ml volumetric flask, the filtrate is diluted to the mark.

• *Diethyl Ether Extraction*

Polypropylene (2-5 g) is extracted with diethyl ether for 8 hours in a Soxhlet continuous extraction apparatus. The weight to be used will vary with the type and amount of additive expected. If these are not known take the maximum amount, if possible. The diethyl ether is removed by distillation on a water bath and ethanol (5 ml) is added to each flask. The flasks are left to stand for 10 minutes. If necessary, at the end of this time, the resulting solutions are filtered quantitatively to remove any precipitated polymer. If required, the contents of the flask are evaporated to dryness and the contents are then dissolved in a suitable solvent for further analysis of additives. The extracted polymer is left to air dry.

Alternatively, polymer (5 g) is weighed into an extraction thimble, the diethylether (130 ml) is added, followed by extraction for 3 hours. The system is cooled to room temperature and the solvent is drained into a 250 ml flat bottom flask. The extraction thimble and extraction apparatus are rinsed with 25-30 ml of extraction solvent and drained into a 250 ml flask (a turbid solution due to the precipitation of extracted polyolefin may be seen upon cooling, however, this is not uncommon nor should any special precautions be taken). The extraction solvent is removed by evaporation to leave a dry residue.

• *Heptane Extraction*

Samples of PP sheets (50 x 50 x 0.5 mm thick) are weighed and then refluxed in 50 ml of boiling heptane. The efficiency of extraction is better than 98% after 3 hours of extraction.

• *Acetonitrile Extraction*

The sample is cut into small shavings with a drill bit prior to extraction. The plastic shavings (1 g) are extracted overnight with 5 ml of acetonitrile. The extraction is performed at ambient temperature in a sealed amber vial with constant stirring. The additives are sufficiently soluble in the acetonitrile extracting solvent due to the small amounts of analyte present. The extract solutions are filtered prior to analysis.

• *Decalin Extraction*

Extraction with decalin for 30 ml at 110 °C has been used to extract antioxidants from PE and PP [7, 8].

2.2.2 Polystyrene

• *Toluene Extraction*

Sample (5.0 + 0.01 g) is weighed and transferred to a 250 ml Pyrex glass centrifuge bottle. Toluene (50 ml) is added into the bottle. A polythene coated magnetic stirrer rotor is dropped into the bottle which is stoppered with a cork (avoid rubber bungs). The bottle is placed on a magnetic stirrer and left for several hours until the sample has completely dissolved or dispersed in the solvent. Absolute alcohol (50 ml) is accurately pipetted into the gently stirred contents of the bottle to precipitate the polymer. The resulting solution is centrifuged to isolate the solvent phase from the polymer phase.

• *Methyl Ethyl Ketone*

Methyl ethyl ketone or propylene oxide, are alternative suitable solvents for PS. Dissolved polymer is reprecipitated by the addition of methyl alcohol or absolute ethanol (up to 300 ml) and the polymer is removed by filtration or centrifugation. The additive-containing extract is then be gently concentrated to dryness as described previously.

• *Diethyl Ether Extraction*

Sample (5 ± 0.1 g) is weighed and then transferred to a 50 ml beaker containing 25 ml diethyl ether. The beaker is covered with a watch glass and then left overnight. The ether is decanted carefully into a large beaker and the beads are washed with two further portions (10 ml) of ether, decanting each washing into the main extract. Using an air line and a warm water bath the ether is carefully evaporated off until about 1 ml of solution remains. The solution is transferred by a 1 ml pipette to a 2 ml volumetric flask. The walls of the beaker are rinsed with 5-10 ml of ether and concentrated to about 0.5 ml. This solution is transferred to the 2 ml volumetric flask and the flask contents are diluted to 2 ml with diethylether.

• *Ethanol or Methanol Extraction*

The sample to be analysed must be very thinly sheeted (or powdered by passing through a Wiley Mill). A sample (2.00 + 0.02 g) is accurately weighed and wrapped with an extraction cloth which has been previously extracted to remove sizing, and so on. The sample is placed in an Underwriter's extraction cup and extracted for 16 hours with 95% ethanol

or methanol. The alcohol extract is transferred to a 100 ml volumetric flask, cooled to room temperature and diluted to the mark with the extraction solvent.

2.2.3 Acrylic Polymers

A fractional reprecipitation procedure involving a solution of the polymer in acetone, followed by reprecipitation with light petroleum can be used to separate additives from acrylics. The acetone - light petroleum extract can be used for the determination of plasticisers and lubricants (**Figure 2.2**).

2.2.4 PVC

Diethyl ether is a favoured solvent for removing additives from this polymer. It has been used to extract stabilisers, lubricants and plasticisers from PVC. **Figure 2.3** shows a scheme involving ether extraction for the separation of additives from PVC [4-6, 9-10].

Table 2.3 gives the results of following four hours of extraction with ether by extraction with other solvents. It can be seen that extraction for four hours with carbon tetrachloride/methanol azeotrope gives better results than extraction for 15 hours with methanol.
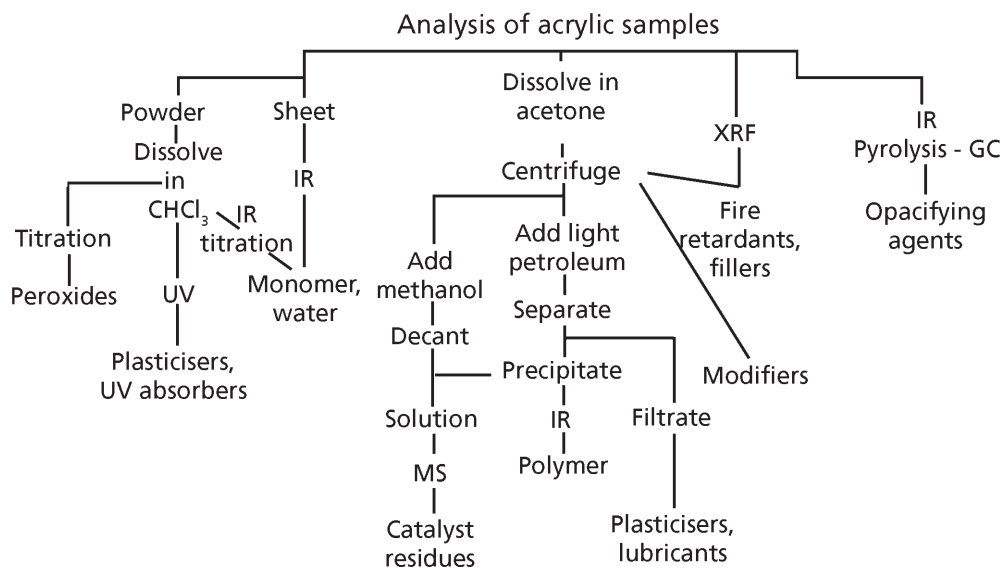
Figure 2.2 Analysis of acrylic samples. *Source: Author's own files*
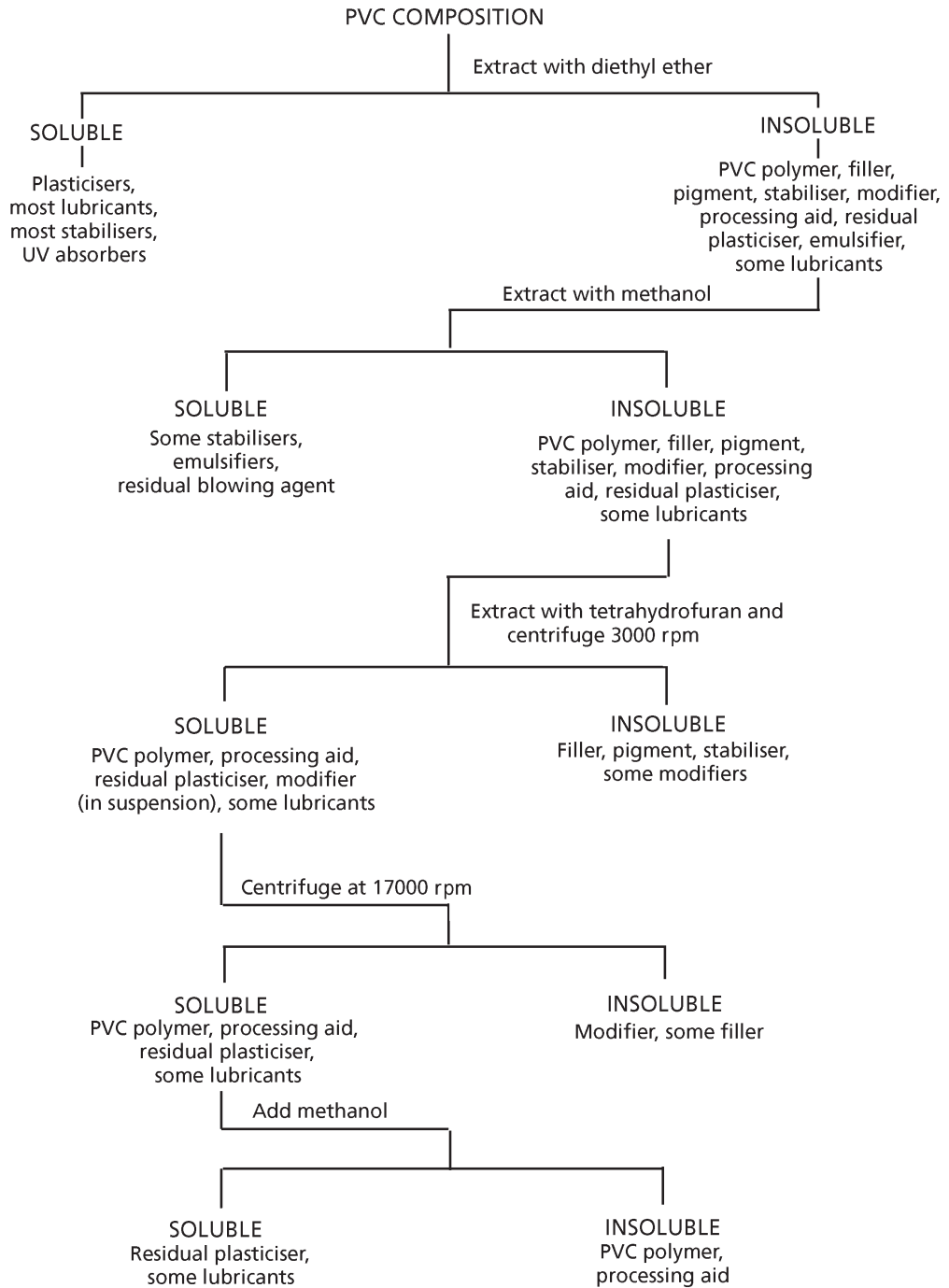
Figure 2.3 Analysis of PVC compositions. *Source: Author's own files*

Table 2.3 Multiple extraction			
Plasticiser	Concentration (%)	Extracts (%)	
		4 hour ether, 5 hour MeOH	4 hour ether, 4 hour CCl$_4$, MeOH
Bisoflex 791	28.5	27.7	28.7
Tritolyl phosphate	28.5	25.8	28.9
Mesamoll	28.5	25.5	28.1
Bisoflex 795	28.5	28.1	29.0
Reoplex 220	28.5	20.4	29.3
Hexaplas PPA	23.5	11.0	17.4
Reproduced with permission from J. Haslam and D.C.M. Squirrell, Analyst, *1955, 80, 957, 871 [14]*			

Haslam and Soppet [11] found that extraction of PVC with acetone, followed by precipitation of dissolved polymer with light petroleum, gave poor results - only 28.5% was recovered from a composition containing 31.8% tritolyl phosphate. Substitution of 1, 2-dichloroethane for acetone gave no improvement, but diethyl ether extracted 31.8% of the sample, and the extract contained a negligible amount of PVC. For routine extraction it was recommended by Haslam and Soppet that the sample be stood overnight in cold ether, then extracted for 6-7 hours in the apparatus. This procedure has also been described by Döhring [12], who specified that anhydrous ether should be used. Thinius [13] compared the rates of extraction of dioctyl phthalate by ether, carbon tetrachloride and petroleum, at room temperature. In 70 minutes the ether extract from a composition containing 40% plasticiser amounted to 39.7%. In the same time the carbon tetrachloride rate of extraction was 33.1% and the petroleum extract was 29.9%. Extraction with carbon tetrachloride for 64 hours gave only 35.6% extract. Thinius also found that mixtures of phthalate and phosphate esters could be completely removed by ether, but light petroleum gave only 65% of the expected yield. Toluene dissolved some PVC at room temperature, and very much more in a Soxhlet extraction.

For compositions containing polypropylene adipate, which is only partly extracted by ether, Haslam and Squirrell [14] used a 6 hour ether extraction, followed by an 18 hour methanol extraction. The ether extract was 34.5% from a composition containing 36.1% of a mixture of equal parts phthalate and tritolyl phosphate, but only 33.1% from a composition containing 45.7% of a mixture of equal parts of dioctyl phthalate, tritolyl phosphate and polypropylene adipate.

The combined ether and methanol extracts amounted to 34.7% and 44.3%, respectively. Wake [15] quotes the results of some unpublished work carried out at the laboratories of RAPRA - methanol extracted 40.5% and 36.8% from compositions containing 42.3% polypropylene sebacate and 36.4% polypropylene adipate, respectively. The extracts contained PVC equivalent to 0.6% and 0.9%, respectively. Clarke and Bazill [16] extracted with ether for 15 hours then with methanol for 8 hours. They state that ether removes plasticisers whose molecular weight is less than 1000.

Korn and Woggon [17] used methanol or diethyl ether to extract diphenylthiourea and 2-phenylindole dicyanamide from PVC.

The extraction of plasticisers from PVC compositions must involve diffusion processes, and the rate of extraction should depend, to some extent, on the initial plasticiser concentration. This was found to be true for the extraction of Mesamoll by ether [18]. Compositions made by ICI, Corvic D65/1, lead stearate (0.1%), and Mesamoll (10-50%) were extracted with ether for 1-8 hours, and the plasticiser contents m (% w/w), at times t (hours), were calculated from the weights of the extracts. **Figure 2.4** shows the curves obtained by plotting log (m/m_o) against t, for different values of m_o, the initial plasticiser content. In every case, except when $m_o = 10\%$, there is initially a very rapid loss of plasticiser, followed by a period when m/m_o decreases exponentially. When $m/m_o = 10\%$, the rate of decrease of m/m_o is very small at all stages of the extraction.

An approximate solution of the diffusion equation is:

dc/dt = div (D grad c)

This equation is appropriate to diffusion out of isotropic solids of arbitrary shape when D is constant. In this case the diffusion equation reduces to:

dc/dt = D∇^2c

and the proportion of the diffusing substance remaining in the solid after time t is given by:

$$\frac{c - c_s}{c_o - c_s} = \frac{\alpha}{\beta} \exp (-\beta^2 (S/V)^2 Dt) \tag{2.1}$$

where c_o is the concentration in the solid at $t = 0$, c_s is the surface concentration at $t > 0$, c is the average concentration in the solid at $t > 0$, α and β are shape constants, and S/V is the surface-to-volume ratio. It has been shown that it is applicable in all cases if $(S/V)^2 Dt$ is greater than 0.6. The samples used in the extraction experiments, performed by Robertson and Rowley [18], had a surface-to-volume ratio of about 50 cm^{-1}, so that for $t > 1$ hour and D $> 10^{-7}$ cm^2/s, equation (2.1) should be applicable to their results, if D is constant.
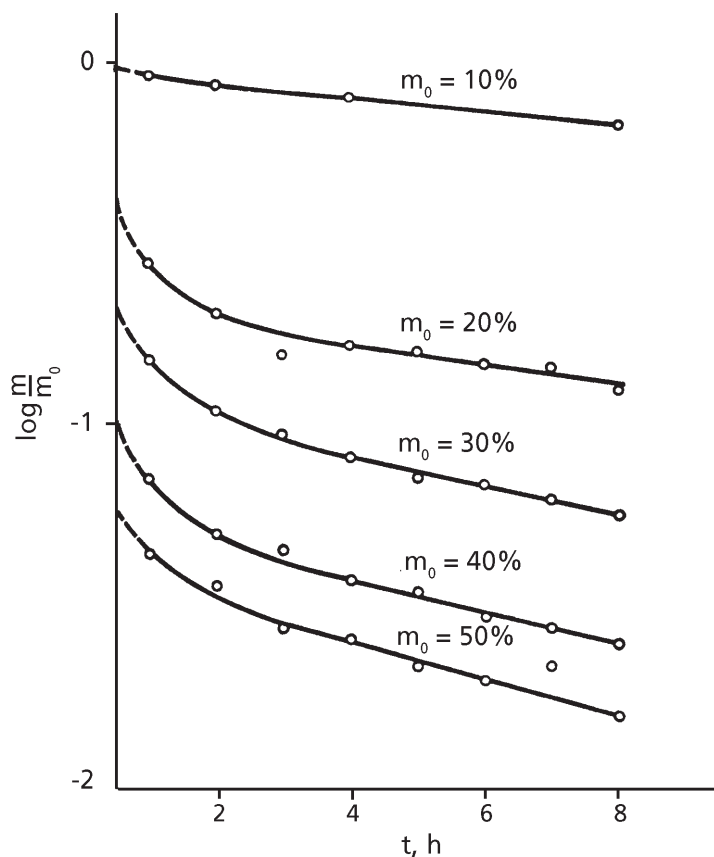
Figure 2.4 Effect of extraction time (t) and plasticiser concentration (m_o) on ether
extraction of Mesamoll from PVC
Reproduced from Robertson and Rowley, British Plastics [18]

Assuming that $o_s = 0$, S/V is constant, and $m/m_o = c/c_0$ (none of these assumptions can be
exactly true at all stages of the extraction, but should be nearly correct during the later
stages), Equation (2.1) can be written as:

$$\log (m/m_o) = A - \beta t \tag{2.2}$$

Where β is proportional to (S/V)Dt. It can be seen that after the first few hours the curves are
of the form given in Equation (2.2), which can therefore, be assumed to described adequately
the important later stages of the extraction process. In the earlier stages the departures from
linearity are probably due to the rapidity with which D decreases as m decreases.

Other solvent extraction procedures for the isolation of plasticisers in PVC are reviewed
in **Table 2.4.**

Table 2.4 Plasticisers in PVC		
Solvent Extraction Method		**Ref.**
Diocytylphthalate tritolylphthalate	Diethyl ether extraction, weighing	[11, 12]
Plasticisers	Solvent extraction, weighing	[18]
Polypropylene adipate Dioctylphthalate Tritolylphthalate	Diethyl ether then methanol extraction, weighing	[14]
Polypropylene sebacate Polypropylene adipate	Methanol extraction	[15]
Gas Chromatography		
Plasticisers	Solvent extraction, gas-liquid chromatography (GLC)	[19, 20]
Alkyl adipate Alkyl phthalate	Solvent extraction, GLC	[21, 22]
Benzylbutyl phthalates	Solvent extraction, GLC	[23]
Alkyl phthalate Fatty acid esters	Solvent extraction, GLC	[24, 25]
Dimethyl phthalate Dimethyl sebacate Triacetin Diacetin Diethyl phthalate	Dichloromethane extraction, GLC	[26]
Adipate and phthalate type	Mild pyrolysis - gas chromatography (Py-GC)	[27]
Plasticisers	Solvent extraction, gas chromatography (GC)	[28]
Plasticisers	Hydrolysis to alcohols, GC	[29]
Dibutyl phthalate Di-isobutyl phthalate Bis (2-ethylhexyl) phthalate Di-*n*-octyl phthalate	Py-GC	[30, 31]
Alkyl phthalate Alkyl adipates Alkyl azealates Alkyl citrates Alkyl sebacates Alkyl glycollates Alkyl phosphates	Tetrahydrofuran extraction, GLC (includes determination of alcohol degradation products)	[32]
Plasticisers	Py-GC of polymer	[33]

2.2.5 Rubbers

Various extraction solvents for rubbers are listed in **Table 2.5**.

	Type of additive	Extraction solvent	Extraction procedure	Ref.
Table 2.5 Extraction solvents from rubber				
Rubbers	Amine and phenolic antioxidants	Ethanol/HCl	Reflux, then steam distill amines from extract	[34]
Rubbers	Phenyl salicylate, resorcinol benzoate	Ether		[35]
Rubbers	Antioxidants	Acetone		[36]
Rubbers	Ketone-amine condensates, phenols, 2-mercaptobenzimidazole	Acetone		[37]
Source: Author's own files				

2.2.6 Polyacrylamide

A weighed quantity of polymer (1-10 g) is added to 50 ml of a methanol/water solution (80:20 *v/v*) in a glass bottle. A magnetic stirring bar coated with Teflon is added and the solution is stirred to extract the acrylamide monomer for at least 3 hours, preferably overnight.

2.2.7 Polyurethane

A weighed sample of polyurethane foam is covered with 75 ml of methanol in a 250 ml beaker and soaked for 5 minutes with occasional compression. The methanol is decanted, squeezing the foam as completely as possible to express the methanol. This is repeated twice with fresh methanol and the combined extracts are concentrated to 25 ml.

2.2.8 Vinyl Chloride, Butadiene, Acrylonitrile, Styrene, 2 Ethylhexyl Acrylate Copolymers

A weighed portion of the copolymer is placed in a septum vial containing measured amounts of *N*, *N*-dimethylacetamide. The vials are heated to 90 °C to aid dissolution of the polymer. When the dissolution is complete, the vials are cooled to room temperature.

A portion of distilled water is forcibly injected into each polymer solution. The vials are shaken briefly to assure complete mixing of the water with the organic phase and to prevent the precipitated polymer from forming a film on top of the solution.

Special care and specialist techniques are required when dealing with laminates and surface-coated films. For major components the separation is made quantitatively and the analysis is completed by various techniques. For volatile components, separation, identification and quantification can often be carried out in one analytical process.

2.2.9 Other Polymers

Steam-solvent distillation using diethyl ether has been used to remove and analyse for odour and taint from additives in food packaging films. Another technique that has been used is vacuum/thermal extraction. This procedure has been applied to polyamides and fluorocarbon polymers. The procedure is used for the direct isolation or release of volatile components from a polymeric matrix and may involve the combined use of vacuum and heat, as for example in the mass spectrometer direct insertion probe or during dry vacuum distillation. Alternatively, the volatiles may be swept from the heated sample by a flow of inert gas for concentration by freeze trapping and/or collection on to a solid adsorbent prior to thermal or solvent desorption for GC or mass spectrometric (MS) examination.

2.3 Fractional Precipitation

In this method a solution or dispersion of a plastic is stirred into at least 10 times its volume of a solvent, which acts as a precipitant for the dissolved plastic but which dissolves completely in the first solvent. The precipitated plastic is pulverised and repeatedly extracted with the precipitant/solvent or re-dissolved and precipitated.

Or a non-solvent is added to a solution of the plastic until the first faint turbidities appear due to the high polymer plastic components. The solvent is then reduced on a water bath or by vacuum distillation. The solvent and the non-solvent must be completely miscible and the solvent must have a lower boiling point than the non-solvent.

Or the plastic is dissolved in a solvent, which dissolves the plastic at higher temperatures - the plastic separates out on cooling while the additives remain in solution.

Or plastic dispersions can often be separated by stopping the action of the emulsifier and/or dispersing agent, i.e., breaking the emulsion. The following methods can be used according to the type of emulsifier:

1. Alteration of the solvent phase.

2. Precipitation of the emulsifier by the addition of acids or a interfacially active counterion.

3. Freezing the dispersion out with solid carbon dioxide.

4. Subjection of the dispersion to dialysis, whereby the water-soluble inorganic salts and relatively low molecular emulsifiers are diffused through cellophane membranes so that the protective colloid and the polymer can now be easily separated quantitatively by centrifugal action. This method is labour intensive but very effective and if it does not completely release any chemisorbed constituents from the polymer - filler matrix it will often leave them in a form very vulnerable to attack by the analytical reagent(s) finally used in the determination.

2.4 Fractional Extraction

Fractional extraction can be used in three ways, depending on the substance under examination:

(a) Finely shredded solid plastics are extracted one-by-one in a Soxhlet apparatus with solvents, of increasing solvent power.

(b) To ensure that the plastic particles are fine enough to allow the components to be extracted to diffuse sufficiently quickly, a solution or dispersion of the plastic is poured over an inert carrier, such as silica gel or Sterchamol, the solvent is allowed to evaporate and the carrier is then extracted in a heatable column with solvents of increasing solvent power.

(c) The components of a plastic are distributed between two non-miscible liquids in separating funnels or a distribution apparatus.

Most of these procedures can be carried out on material cut to a particle size of less than 2 mm diameter - it is often advantageous to produce material of a smaller size and with a large surface area to mass ratio. This is conveniently done by grinding at the temperature of liquid nitrogen using an efficient and easily cleaned cutter mill.

The extraction of additives strongly adsorbed or chemisorbed on the polymer - filler matrix must be carefully observed by the analyst, as a change of the method of manufacture of, for example, the filler or in the method of compounding the plastic formulation, can

also markedly alter the degree of adsorption being produced and hence invalidate an established quantitative extraction procedure. The use of 'stronger' extraction reagents can cause complications at the measurement stage and hence each system must be carefully screened and frequently checked.

In a modification of this procedure the polymer is refluxed with a reagent, which decomposes additives present to put them in a form, which is soluble in the solvent. Thus when PP on which is chemisorbed fatty acid amides or amines, is refluxed with a solution of ethylene dichloride and trichloroacetic acid then the amides are decomposed as follows:

$$RCONH_2R' + H_2O = R'NH_2$$
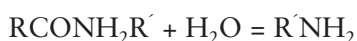
2.5 Separation by Diffusion Methods

The plastic is precipitated from a solution or dispersion in a glass vessel as a thin film on the inner wall; meanwhile a solvent, which is a non-solvent towards the plastic, is added in several stages. The solvent must be able to dissolve the additives. Additives or a second plastic can be isolated in a short time by diffusion alone if the mixture is left to stand in the solvent, occasionally shaken and the solvent is renewed four to six times.

2.6 Dialysis or Electrodialysis

This method has only been used for separating low-molecular weight salts and interfacially active substances from protective colloids and high polymer plastics and for fractionating pure plastics according to their molecular weight.

Some examples of these four separation procedures are shown in **Table 2.6**.

2.7 Vacuum Thermal Displacement Extraction Method

These procedures are used extensively for the direct isolation or release of volatile components from a polymeric matrix and may involve the combined use of vacuum and heat, as for example in the MS direct insertion probe or during dry vacuum distillation. Alternatively, the volatiles may be swept from the heated sample by a flow of inert gas for concentration by freeze trapping and/or collection on to a solid adsorbent prior to thermal or solvent desorption for GC or MS examination.

Table 2.6 Examples of separating procedures		
Plastic	Operation	Aim or separating procedure
(a) Fractional precipitation procedures (precipitation by addition of non-solvent for polymer to solvent solution of polymer).		
Polyvinyl chloride	Stirring of a concentrated solution of tetrahydrofuran into methanol	Plasticisers, emulsifiers remain in solution, PVC and its polymers are precipitated
Polyacrylate	Stirring the solution in acetone into 20 times the amount of water	Emulsifiers, water soluble resins and salts remain in solution, polymerisate is precipitated
(b) Fractional precipitation (titration of solvent solution of polymer with non-solvent for polymer).		
Polyacrylate	Water is added to the solution in acetone until faint turbidity occurs, acetone is then distilled off under vacuum	Emulsifiers, water soluble resins and salts remain in solution, polymerisate is precipitated
(c) Fractional precipitation (thermal precipitation of polymer from solution at low temperature).		
Polyethylene	Dissolve in enough benzene to make a clear solution appear when warmed then cooled	Polymerisate is precipitated, additives soluble in cold benzene, paraffin, waxes, resins remain in solution
(d) Emulsion breaking methods		
(1) Addition of solvent		
Polymethacrylate-dispersions	Dispersion is stirred into 20 times its amount of methanol or isopropanol	Polymerisate is precipitated, emulsifier and any protective colloid remain in solution
(2) Emulsifier precipitation by acid addition		
Rubber or butadiene *co*-polymers	Dispersion is broken by acidifying as long as soap is used as the emulsifier	After acidifying, fatty or resin acid is extractable with ether; latex is precipitated
(3) Freezing out dispersion by Cardice addition		
Polyvinyl acetate or silicone oil dispersions	Action of emulsifier destroyed by cold	Polymerisate is precipitated, can now be filtered off or centrifuged off
(4) Application of dialysis		
Polyvinyl acetate ester or polyacrylate dispersions	Salts and low molecular emulsifiers are dialysed	In the dialysate, salts and emulsifiers, in the dialysate residue, protective colloid polymerisate

Table 2.6 Continued		
Plastic	Operation	Aim or separating procedure
Fractional extraction procedures		
Solvent extraction of shredded plastic		
Polyvinyl chloride	Consecutive extractions with CCl_4, ether, benzene, CH_2CCl_2, tetrahydrofuran	Isolation of stabilisers and plasticisers, recognition of co-polymers or poly blends
Solution or dispersion of plastic passed over inert carrier on which plastic adsorbs, solvent evaporation from carrier, then desorbtion from carrier with strong solvents		
Polyethylene	Consecutive extraction of silica with gasoline, methanol, $CHC1_3$, water, methanol or acetone, then benzene or toluene (perhaps warm)	In the gasoline: waxes; in CH_3OH: emulsifiers; in $CHC1_3$: montan waxes in water: cellulose derivatives and polyvinyl alcohol; in benzene/toluene: polyethylene
Plastics components distributed between two non-miscible liquids		
Polyvinyl acetate	Extracted from aqueous methanol solutions or dispersions with pentane/ether mixtures	Isolation of plasticisers
Separation by diffusion		
Polyvinyl acetate	Polymer precipitated with Ligroin or ligroin/ether mixtures	Isolation of the plasticisers, can also be used
Separation by dialysis or electrodialysis		
Polyacrylate	See (4)	
Source: Author's own files		

2.7.1 Effects of Polymer Milling on Extraction

Schröder [38] warns that during solvent extraction techniques there may be complications, which can result in faulty interpretation of results due to stabiliser rearrangements or decompositions. However, although oxidation of the polymer additives during extraction may be avoidable, there exists the danger that crushing the polymer prior to extraction may lead to a sequence of reactions, which affect the chemical structure of the inhibitor. All polymers of longer chain length suffer from degradation when under mechanical stress which usually starts by a chain rupture in the centre of the macromolecule and results in the formation of macro radicals. This degradation is accelerated at low temperatures and even occurs when cutting with a knife. Pazonyi and co-workers [39] found a linear relationship between the radical concentration (determined by the consumption of diphenyl-picryl-

hydrazyl) and the surface (**Figure 2.5**) when cutting PE and plasticised PVC. They could prove that this could occur when the chemical bonds with polymers, which to some extent are present in the elastic state are cut by mechanical forces with 100% efficiency. In the presence of inhibitors reactions between macro radical and inhibitor may occur even in the absence of oxygen. As a consequence reaction products with the polymers themselves, but also deactivation products of the intermediately formed inhibitor radical are to be expected.

Workers at the National Bureau of Standards accept that an attachment of butyl residues of dibutyl-tin-diacetate to PVC radicals occurs in the presence of UV radiation:

$$R + (C_4H_9)_2Sn\ (CH_3COO)_2 \rightarrow R - C_4H_9 + C_4H_9Sn\ (CH_3COO)_2$$

which has been confirmed by examination of results obtained by Frye and co-workers [40] with ^{14}C butyl-labelled organotin compounds. In the presence of oxygen the probability of reaction of the macro radicals with the inhibitor system is increased considerably if phenolic or amine antioxidants are present.

Further losses on reaction induced decomposition products mainly occur when the extracts obtained are re-concentrated. Even the inherent volatility of some antioxidants - above all that of the phenols and aromatic amines (**Table 2.7**) is so high that it provides the basis of a direct determination in the polymer by vacuum sublimation as suggested by Yushkevichyute
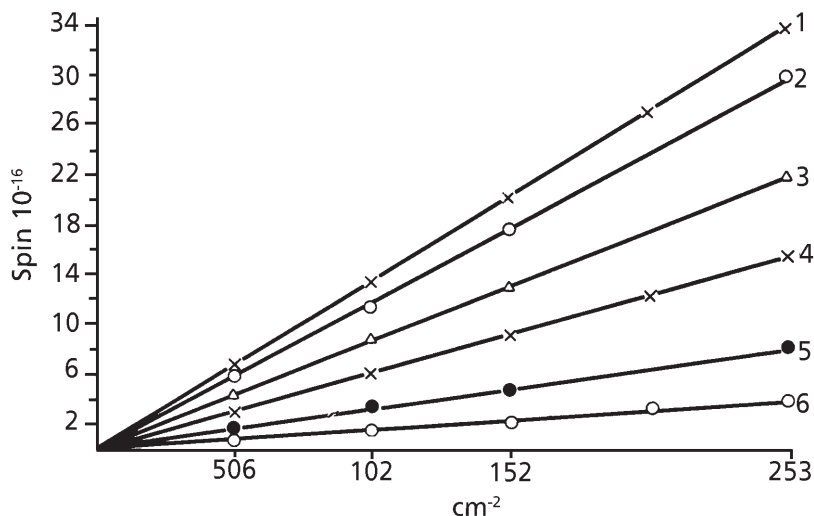
Figure 2.5 Consumption of diphenyl picrylhydrazyl radicals in relation to surface area of polyethylene and PVC
Reproduced from Schröder, Pure and Applied Chemistry [38]

Table 2.7 Volatility of antioxidants [40]		
Antioxidant	Vapour pressure (mm Hg)	Loss of weight (% at 150 °C)
2,6-Di-*t*-butyl-*p*-cresol	22.15	100
2-Benzyl-6-*t*-butyl-*p*-cresol	1.83	100
2,2′-Methylene-bis-6-*t*-butyl-*p*-cresol	0.169	19 ... 28
Diphenylamine	7.52	100
N-Iso-propyl-*N*′-phenyl-*p*-phenylene-diamine	0.59	40 ... 53
N-*N*′-Diphenyl-*p*-phenylenediamine	0.032	2 ... 3
Source: Author's own files		

[6] for the determination of antioxidants in PE and can also be applied to the explanation of the mechanism of action of phenolic and amine antioxidants in PE and PP.

Thus a separation by distillation of the 2,6-di-*t*-butyl-4-methylphenol from its dimer deactivation product at 100 °C was successful and provided evidence for the isomerisation of the phenoxy radicals formed primarily to oxybenzyl radicals and their recombination to dioxydiphenylethane:
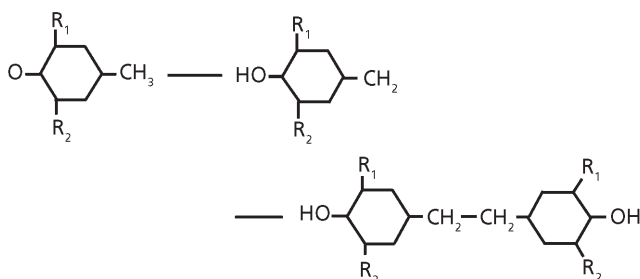
On the other hand the high volatility of additives occurring in the classic method of re-concentrating polymer extracts by distillation - even by evaporation of the solutions will result in considerable loss of substance as was found by Schröder [38] in the case of 2,6-di-*t*-butyl-4-methylphenol. He found an evaporation loss of 0.75% after 24 hours when storing Ionol with a large surface in stagnant air. This loss increased to 63% when the chloroform solution was evaporated in a fume cupboard.

Schröder [38] also points out that the distillation processes - even careful freeze-drying - should be avoided for quantitative work in systems of such high volatility as the stabilisers,

especially if the quantity and type of the decomposition products are also of interest. In such cases only an enrichment by chromatographic processes should be considered. From the point of view of separation from the polymer, gel-permeation chromatography is a possible method since the separation of molecules in the pores of the gels is mainly achieved according to particle size, and the large polymer molecules can be excluded from the separation process by suitable selection of the pore size distribution of the gels so that they leave the separation column together with the solvent. Such a separation of low molecular substances from polymer mixtures have been described for plasticisers [41], oils [42] and methylsilanols [43]. It is to be seen from the work of Coupek and co-workers [44] and others [45, 46] who deal systematically with this problem, as to how far the stabiliser mixture is separated subsequently.

The effects of mechanical degradation by polymer crushing on stabiliser structure, such as those discussed previously, are, of course, avoided in separation methods based on dissolving the polymer in a solvent, then precipitating the polymer, but not the stabiliser, with a non-solvent, providing a solvent extract which contains only the stabiliser. Again, however, this process needs a consideration of the solution-precipitant effects on the stability, especially of the reaction products of stabilisers or their fragments with the polymer. Such reaction products have been both determined and isolated with PVC, PE, PP and natural rubber.

Thus, Frye and co-workers [47] were able to provide evidence by infrared (IR) spectroscopy [46] and radiochemistry [48] of the insertion of ester groupings from barium, cadmium or zinc-carboxylates into PVC after heat treatment. Tin contents and organic residues of organotin stabilisers in heat-treated PVC are indicated by the same authors [47, 49]. Schlimper [50] and Schröder and co-workers [51] proved the direct reaction between PVC and nitrogen-containing organic stabilisers by elemental analytical examinations and infrared and UV spectrometry. Phenolic antioxidants or their decomposition products in part were re-found in PP after oxidative degradation. With rubber vulcanisates hydrochloric acid-resistant amine-rubber compounds have been reported after thermal oxidation in the presence of aromatic amines [52].

2.8 Solvent Extraction – Infrared Spectrometry

Udris [53] has described two schemes, based on chromatography and infrared spectroscopy, for the identification, in PVC extracts of:

i) dialkyltin dialkylthioglycollates:

      R SCH$_2$ COOR´

       Sn

      R SCH$_2$ COOR˝
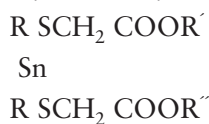
dialkyltin dilauryl mercaptides:

R SCH$_2$ (CH$_2$)$_{10}$ CH$_3$

  Sn

R SCH$_2$ (CH$_2$)$_{10}$ CH$_3$

R, R´, R˝ = alkyl stabilisers in which the dialkyltin group is combined with both thiol and carboxyl groups.

ii) dialkyltin maleates

R OO CCH

  Sn

R OO CCH

dialkyltin dialkyl maleates

R OO CCH = CH COOR´

  Sn

R OO CCH = CH COOR˝

dialkyltin dilaurates

R OOC (CH$_2$)$_{10}$ CH$_3$

  Sn

R OOC (CH$_2$)$_{10}$ CH$_3$
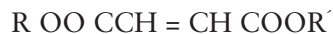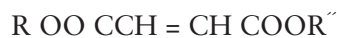
It is first of all necessary to prepare an extract of the PVC in which the organotin stabiliser is quantitatively recovered.

For the extraction of the first set of compounds, i) the polymer is refluxed with acetone and the silver salts precipitated by the addition of aqueous silver nitrate. After drying the residue is examined by infrared spectroscopy to identify alcohols, thioacids, thiols, and alkyl groups attached to tin. For the extraction of the second set of compounds ii) the polymer is refluxed with 10% aqueous sodium hydroxide prior to the identification of alcohols by gas chromatography then the alkyl groups attached to tin and carboxylic acids are identified.

Udris [53] examined methods for the recovery and identification of tin stabilisers in excess plasticiser (90 to 95%). The plasticisers included diisooctyl phthalate and mixtures of diisooctyl phthalate and tritolyl phosphate in various proportions.

Good samples of dialkyltin dichlorides were isolated by this method from mixtures of tin stabilisers with diisooctyl phthalate and tritolyl phosphate; the dialkyltin groups have been identified in dibutyl tin dinonylmaleate, dioctyltin dilaurate, dibutyltin dinonylthioglycollate and dioctyltin thioglycollate.

Renier and co-workers [54] give details of a method for the infrared spectral analysis of Methacrol 2138 (polydiisopropylaminoethylmethacrylate-*co*-decylmethacrylate) and Santowhite (4,4´ butylidene bis (6-*tert*-butyl-*m*-cresol) in extracts of polyethyl urethane urea (PEUU) biomedical implantable material.

The extraction was carried out *in vitro* using methanol.

Figure 2.6 a-c provides a quantitive comparison of the infrared spectra of polyether urethane urea and Santowhite. The extract spectrum differed from that of the bulk of the polymer by the presence of bands from Santowhite in the 1630-1150 cm^{-1} region and by the increased intensity and breadth of the 3324 cm^{-1} (ν (N-H)) and 1711 cm^{-1} ν (C=O) hydrogen bonded bands of the urethane group.

Table 2.8 gives the IR bands in the extract of polyether urethane urea that are attributed to the extracted Methacrol 2138 and Santowhite. Quantitative determination of Santowhite in the extracts was made with the band at 1386 cm^{-1}, a δ(C-H) methylene band of Santowhite and a normalising band ν_s(CH$_2$ – O) at 2797 cm^{-1} which was assigned to the ether functionality of the PEUU.

Patticini [55] has described an IR method for the determination of 1 to 8% of mineral oil in PS. In this method the PS sample is dissolved in carbon tetrachloride, together with known mineral oil standards. The solutions are evaluated by measurements made between 3,100 and 3,000 cm^{-1} using a spectral subtraction technique.

Table 2.8 New major FT-IR bands in polyether urethane urea extracts				
Bands (cm^{-1})	**Assignment[a]**	**Extract**		
		B	C	D
2998	ν_A(CH$_3$)	SW	-	SW
1730	ν (C=O)	-	MT	MT
1598	ν (C=C) aromatic	SW	-	SW
1490-1358	δ + ω(C-H) aliphatic + δ(C-CH$_3$) and δ(O-H)	SW	-	SW
1413	δ(C=C) aromatic	SW	-	SW
1272	ν(C-O) + δ(O-H)	SW	-	SW
1035	ν(C-O) or δ(C-H) aromatic	SW	-	SW
a: ν stretch; δ: bend; ω: wag *Reproduced with permission from M. Renier, J.M. Anderson, A. Hiltner, G.A. Lodoen and C.R. Payert, Journal of Biomaterials Science – Polymer Edition, 1993, 5, 3, 231 [54]*				
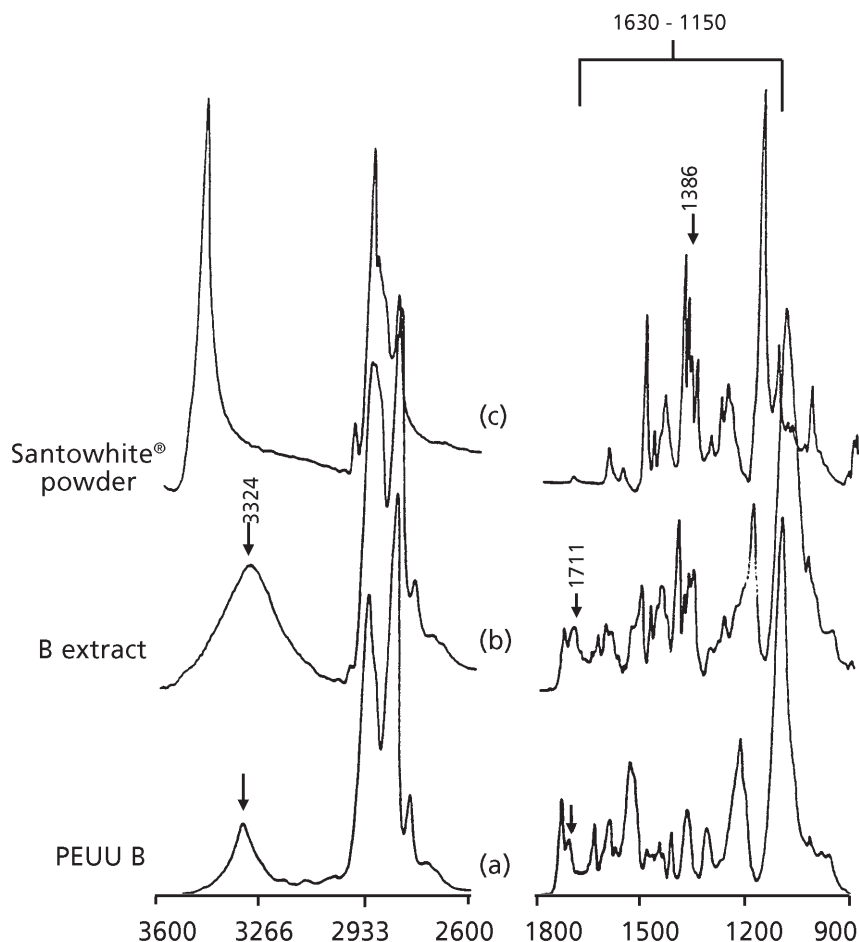
Figure 2.6 Qualitative comparisons of the infrared spectra. (a) PEUU B, (b) B extract, and (c) Santowhite powder showing the influence of Santowhite powder on the B extract spectrum in the 1630-1150 cm^{-1} region and the increased intensities of the υ(N-H) band at 3324 cm^{-1} and the υ(C=O) hydrogen bonded carbonyl band at 711 cm^{-1} from the PEUU urethane group

Reproduced with permission from M. Renier, J.M. Anderson, A. Hiltner, G.A. Lodoen and C.R. Payet, Journal of Biomaterials Science – Polymer Edition, 1993, 5, 3, 231 [54]

Supercritical fluid chromatography (SFC) coupled with Fourier transform infrared spectroscopy has been used to determine polymeric surfactants in various polymers [56, 57].

Spell and Eddy [58] have described IR spectroscopic procedures for the determination of up to 500 ppm of various additives in PE pellets following solvent extraction of additives at room temperature. They showed that Ionol (2,6-di-*t*-butyl-*p*-cresol) and Santonox R

(4,4′-thio-bis-(6-*t*-butyl-*m*-cresol) are extracted quantitatively from PE pellets by carbon disulfide in 2-3 hours and by iso-octane in 50-75 hours. The carbon disulfide extract is suitable for scanning in the infrared region between 7.8 and 9.3 nm, whilst the iso-octane extract is suitable for scanning between 250 and 350 nm.

Robertson and Rowley [18] studied the extraction of plasticisers from PVC using different solvents prior to analysis by IR spectroscopy.

Table 2.9 gives the results of following 4 hour extractions with ether, by extractions with other solvents. It can be seen that extraction for 4 hours with carbon tetrachloride/methanol azeotrope gives better results than extraction for 15 hours with methanol.

If a composition containing a polyester plasticiser and a monomeric plasticiser is extracted first with ether, then with methanol or carbon tetrachloride/methanol, the ether extract

Table 2.9 Multiple extractions			
Plasticiser	Concentration, %	Extracts, %	
		4 h ether, 5 h MeOH	4 h ether, 4 h CCl$_4$MeOH
Bisoflex 791	28.5	27.7	28.7
Tritolyl phosphate	28.5	25.8	28.9
Mesamoll	28.5	25.5	28.1
Bisoflex 79S	28.5	28.1	29.0
Reoplex 220	28.5	20.4	29.3
Hexaplas PPA	23.5	11.0	17.4
*Reproduced with permission from M.W. Robertson and R.M. Rowley, British Plastics, 1960, **33**, 1, ?? [18]*			

Table 2.10 Extraction of mixed plasticisers			
Solvent	Time (h)	Extract (%)	
Diethyl ether	8	28.6	
Carbon tetrachloride	4	33.4	
Diethyl ether	4	27.3	27.8
Methanol	15	0.5	
Diethyl ether	4	27.2	33.2
Carbon tetrachloride/methanol	4	6	
*Reproduced with permission from M.W. Robertson and R.M. Rowley, British Plastics, 1960, **33**, 1, ?? [18]*			

will contain nearly all the monomeric plasticiser, and some of the polyester, and the second extract will contain almost pure polyester. **Table 2.10** gives the results of extracting a composition containing Reoplex 220 (19.0%), Bisoflex 791 (7.5%), and Bisoflex 79S (7.0%), using various procedures, and **Figure 2.7** shows the IR spectra of the extracts and the original plasticisers.
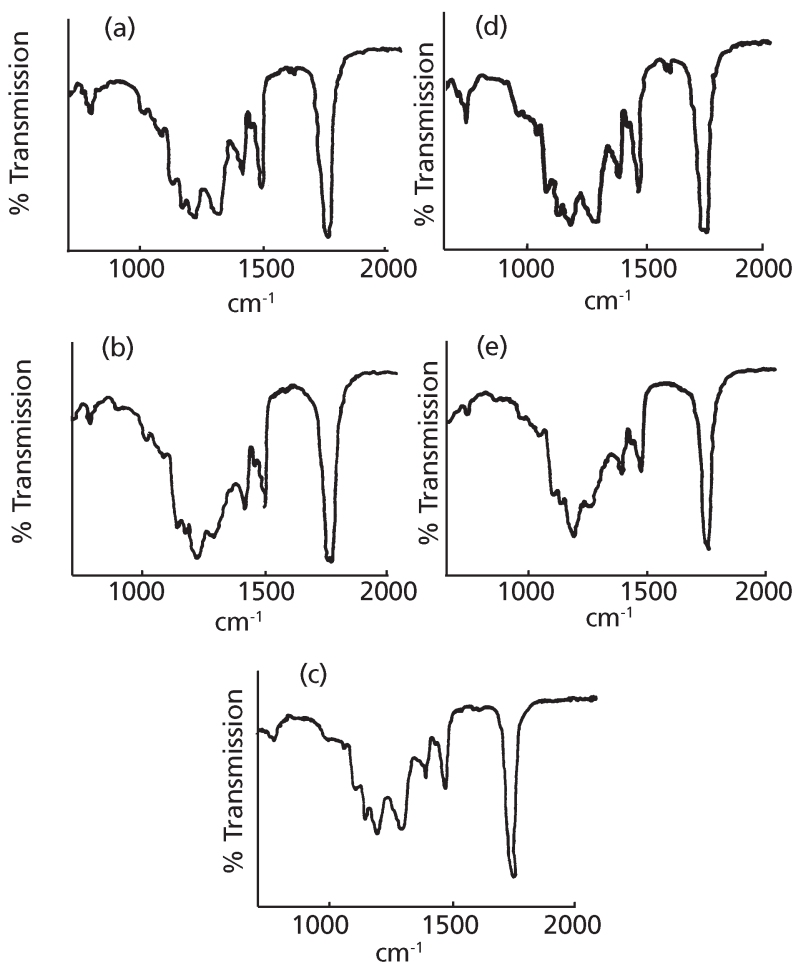
Figure 2.7 IR spectra of PVC plasticisers and extracts (a) mixture of Reoplex 220 (5607%), Bisoflex 791 (22.4%), (b) Reoplex 220, (c) carbon tetrachloride extract, (d) ether extract, (e) carbon tetrachloride-methanol extract
Reproduced from Robertson and Rowley, British Plastics [18]

2.9 Solvent Extraction – Ultraviolet Spectroscopy

Straightforward UV spectroscopy is liable to be in error because of interference by other highly absorbing impurities that may be present in the sample [59-62]. Interference by such impurities in direct UV spectroscopy has been overcome or minimised by selective solvent extraction or by chromatography [60]. However, within prescribed limits UV spectroscopy is of use and, as an example, procedures are described next for the determination of Ionol (2,6-di-*tert*-butyl-*p*-cresol) and of Santonox R (4,4´-thio-bis-6-*tert*-butyl-*m*-cresol) in polyolefins [63-66].

Certain additives, e.g., calcium stearate and thiodipropionate, do not interfere in the determination. Other phenolic antioxidants, e.g., Ionox 330, Topanol CA and Santonox R, do interfere.

2.9.1 Ionol in Polyolefins

A polymer sample (20 g) was weighed into a 250 ml round-bottomed flask and 50 ml of chloroform was added. A water-cooled condenser was connected and the flask was placed on the electric heating mantle and brought gently to boiling point. The solution was refluxed for 30 minutes at a moderate rate. After cooling, the chloroform solution was carefully decanted into a 100 ml volumetric flask (using a filter if necessary) and stoppered immediately. A further 40 ml of chloroform was added to the contents of the round-bottomed flask and a second extraction of the polymer was carried out. When cool, the contents were filtered into the volumetric flask containing the first extract. The residue was washed with sufficient chloroform to dilute it to the mark. The flask was shaken to ensure homogeneity. The UV spectrum of the chloroform extract against a chloroform blank was recorded from 250 to 310 nm using 1 cm cells.

The absorbance of the Ionol absorption peak was measured at 278 nm (see **Figure 2.8**). The concentration of Ionol CP present in the extract was determined by reference to the prepared calibration curve.

2.9.2 Santonox R In Polyolefins

A representative sample was ground in the Apex Mill. About 1 gram of the sample was weighed into a 100 ml round-bottomed flask and cyclohexane (20 ml) was added. A condenser was fitted to the flask and the cyclohexane was allowed to reflux on a water bath for 1 hour. The condenser was washed with 20 ml cyclohexane, the flask was removed from the bath, cooled to room temperature and then shaken well. The solution was filtered through a No. 802 filter paper into a 100 ml separating funnel. The filter

paper was washed with a further 10 ml cyclohexane. Freshly prepared sodium hydroxide solution (25 ml) was added and then the solution was shaken for 3 minutes then allowed to settle. The caustic layer was run into a 100 ml standard flask. The extraction was repeated with another 2 x 25 ml portions of alkali. The extract was made using 1 cm silica cells and sodium hydroxide solution as a blank. The base line absorbance stated in the calibration procedure was calculated as follows and the concentrations of Santonox R read from the graph:

$$A_{BL} = A_{266} - A_{335} - 0.684 \, (A_{236} - A_{335})$$

where A_{BL} = base line absorbance, A_{335}, A_{266}, A_{236}, = absorbance at 335, 266, 236 nm, respectively.

The base line absorbance was plotted against the concentration of Santonox R in mg/100 ml.

Ruddle and Wilson [66] have described a UV spectroscopic method for the characterisation of phenolic stabilisers in solvent extracts of polymer compositions.
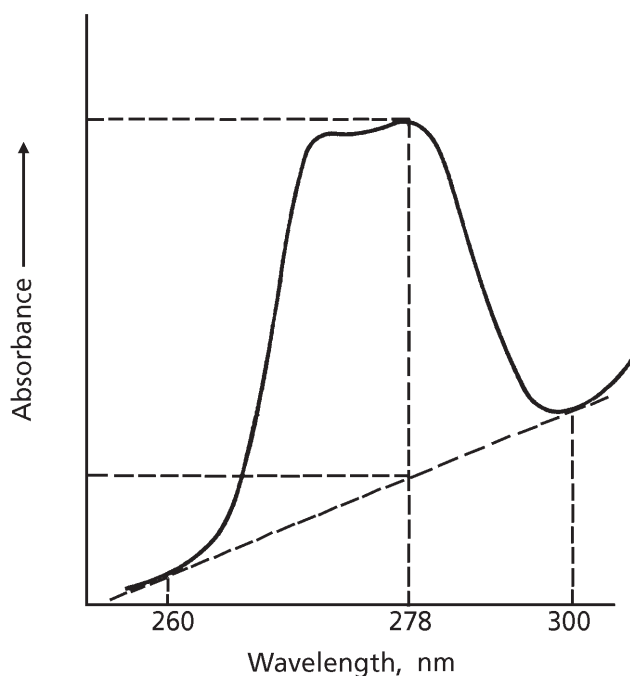
Figure 2.8 Determination of Ionel CP in polyolefins by UV spectroscopy. *Source: Author's own files*

Table 2.11 Wavelengths of maximum absorption in ethanol, ethanol-potassium hydroxide, ethanol-nickel peroxide and ethanol-nickel peroxide – potassium hydroxide

Trade name	Chemical constitution	Ethanolic solution λ_{max} (nm)	Alkaline ethanolic solution λ_{max} (nm)	Nickel peroxide reaction product λ_{max} (nm)	Absorption change after nickel peroxide reaction	Alkaline reaction product λ_{max} (nm)
Topanol OC	2,6-Di-*t*-butyl-4-methylphenol	277	303, 274, 257	340, 286	x8	Absorption supressed
Binox M	Bis-(3,5-di-*t*-butyl-4-hydroxy-phenyl)methyl	277	303, 225	428	x30	578
Ionox 330	1,3,5-Trimethyl-2,4,6 tris-(3,5-di-*t*-butyl-4-hydroxy-benzyl) benzene	277	303, 274	336, 304	x8	No change

Reproduced with permission from L.H. Ruddle and J.R. Wilson, Analyst, 1969, 94, 1115, 105 [66]

These workers point out that usually the additive must be separated in a pure state from co-extracted additives usually by thin-layer chromatography (TLC) and then identified by measurement of the UV, IR, nuclear magnetic resonance (NMR) and mass spectra of the compound. This full treatment is required only for new stabilisers - for a characterisation of well known compounds the simplest method is by direct comparison of the UV absorption spectra with those of a series of known stabilisers. For some compounds this will probably be sufficient, but many substituted phenols have similar spectra, and for three of the most frequently used antioxidants the UV spectra are identical. Topanol OC, Ionox 330 and Binox M (see **Table 2.11** for their chemical constitution) in ethanolic solution all have λ_{max} = 277 nm, with a shoulder at 282 nm. To extend this procedure Ruddle and Wilson [66] prepared the spectra of alkaline solutions of the phenols, which were then measured either directly against a solvent blank or as 'difference spectra' measured against the neutral solution. This still gives almost identical spectra for the three compounds mentioned previously.

Ruddle and Wilson [66] developed two further stages in this procedure for extending the use of UV spectrophotometry in the characterisation of these compounds. They consist of (a) measuring the UV absorption spectrum of the stabiliser solution after reaction with solid nickel peroxide and (b) re-measuring it after making the reaction products alkaline. Cook [67] obtained the substituted stilbene quinone after

reaction of 2,6-di-*t*-butyl-4-methylphenol with lead dioxide, and Braithwaite and Penketh [68] have used lead dioxide for the determination of Topanol OC in liquid paraffin. They obtained an absorption peak with λ_{max} = 420 nm. Stafford [69] used air for the oxidation and obtained a product with λ_{max} = 365 nm.

Kharasch and Joshi [70] have reported on the oxidation of bis-(3,5-di-*t*-butyl-4-hydroxy-phenol) methane, carried out by pumping oxygen into an alkaline ethanolic solution of the phenol. They obtained a dark purple solution produced by the anion of
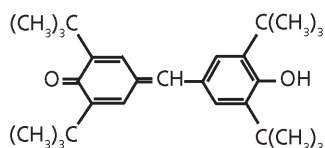
The reaction at room temperature of dilute solutions of antioxidant (about 1 mg/100 ml), with nickel peroxide is complete within 2 minutes and, if continued for longer periods, the absorbance of the strongest band at 286 nm begins to diminish.

The sets of spectra for Topanol OC, Binox M and Ionox 330, are shown in **Figure 2.9** (**a, b** and **c**). **Table 2.11** gives the wavelengths of maximum absorption for each procedure, and also some indication of the absorbance change, i.e., the dilution required, after nickel peroxide reaction. The initial concentration of the stabilisers was 10 mg/100 ml of ethanol.

In an attempt to overcome the difficulty of interference effects by other polymer additives in the UV spectroscopic determination of phenolic antioxidants, Wexler [71] makes use of the bathochromic shift exhibited by phenols on changing from a neutral or acidic medium to an alkaline one. This shift is due to the change of absorbing species because of solute-solvent interaction. Using a double-beam recording spectrophotometer, he measured a difference spectrum by placing an alkaline solution of the polymer extract in the sample beam, and an identical concentration of sample in acid solution in the reference beam. The resulting difference spectrum is a characteristic and useful indication of the concentration and chemical identity of the phenolic substance. Possible interferences due to non-ionising, non-phenolic species are usually cancelled out in the difference spectrum which should make the technique of interest to the polymer analyst. Typical spectra obtained for an antioxidant are shown in **Figure 2.10**. These spectra exhibit two maxima and two minima. Close adherence to Beer's law is usually obeyed by the difference peak spectra.

Soucek and Jelinkova [72] have used differential UV spectra run in acid and alkaline solutions to determine 2,6-di-*tert*-butyl-4-methylphenol and 4 substituted 2,6-xylenol in PP. These two substances have virtually identical spectra in the absence of alkali. In alkaline medium 4 substituted 2,6-xylenol forms a phenolate readily, thus allowing use of the bathochromic shift for its determination.
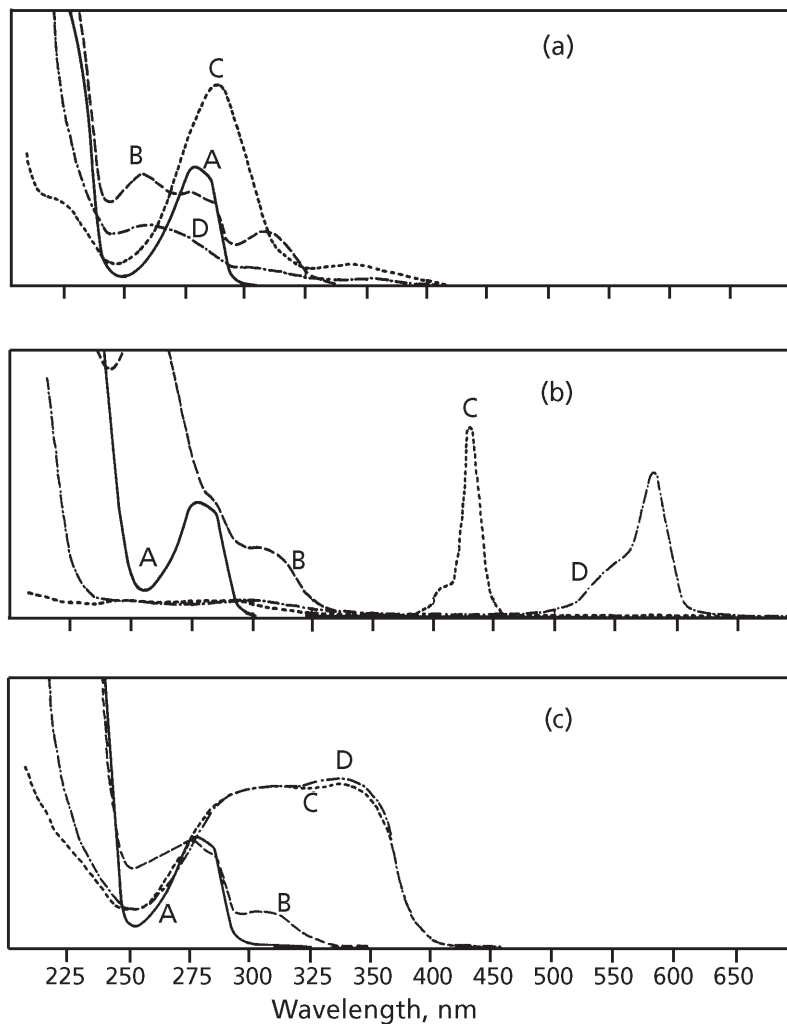
Figure 2.9 UV spectra for (a) Topanol CA, (b) Binox M, and (c) Ionox 330. Curve A: ethanolic solution, curve B: alkaline ethanolic solution (10 ml of ethanolic solution plus 1 ml of water, plus 2 ml of ethanolic potassium hydroxide solution), curve C: ethanolic solution after reaction with nickel peroxide, and curve D: nickel peroxide reaction product made alkaline with two drops of ethanolic potassium hydroxide solution
Reproduced from Kharash and Joshi, Journal of Organic Chemistry [70]
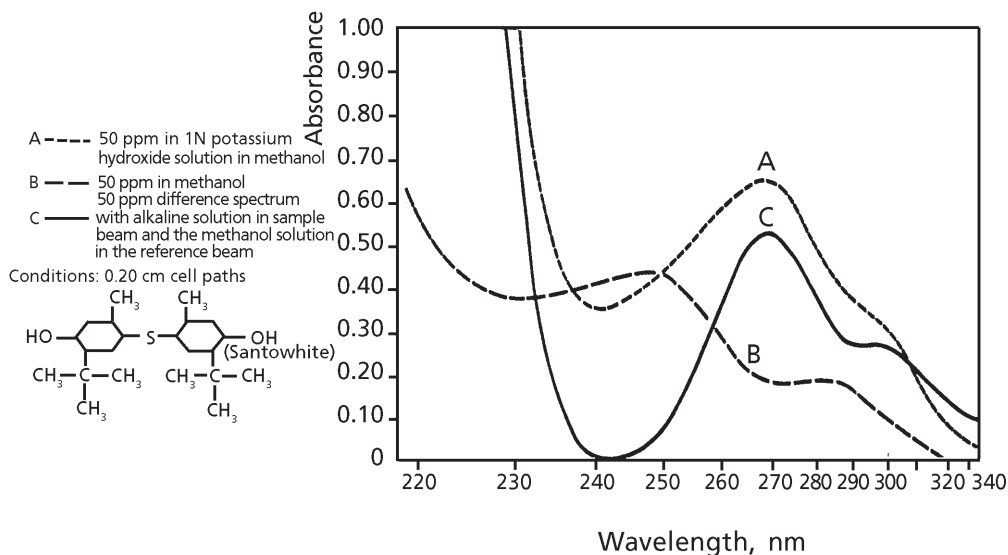
Figure 2.10 UV spectra of 4,4′-thiobis-(6-*tert*-butyl-*m*-cresol) exhibiting bathochromic shift in alkaline medium
Reproduced from Wexler, ACS [71]

Scheele and co-workers [73, 74] have found extensive agreement between conductiometric and UV spectroscopic methods of quantitative antioxidant analysis.

Crompton [75] in a method for the determination of Nonox CI (*N*,*N*-di-β-napththyl-*p*-phenylenediamine) in HDPE describes a 1½ hour toluene extraction of the polymer under reflux, performed under a nitrogen blanket and mentions that, under these conditions no oxidation of the antioxidant occurs. In this way he was able to distinguish between true Nonox CI oxidation occurring during polymer manufacture and 'accidental' oxidation occurring during the preliminary solvent extraction stage of analysis. He also mentions that, under these conditions, some 5% of the additive remains unextracted in the polymer, but that this is allowed for in the method of calibration which involves refluxing known quantities of Nonox CI with virgin PE, as in the sample extraction procedure.

2.9.3 Styrene Monomer

Crompton and co-authors [76] have described a UV spectroscopy method for the determination of styrene monomer in chloroform.

In this method the PS sample (0.5 g) is dissolved in 50 ml of chloroform or another suitable spectroscopic solvent and the UV spectrum recorded in the region 280-310 nm against polymer-free solvent in the reference cell. If the polymer is incompletely soluble in the solvent (e.g., due to the presence of gel or pigments), it is dissolved in 30 ml of solvent and the suspension filtered rapidly under light vacuum through an asbestos pad to remove insolubles.

Conventional and high-impact polystyrene (HIPS) contains various non-polymer additives (e.g., lubricants) which result in widely different and unknown background absorptions at the wavelength maximum at which styrene monomer is evaluated (292 nm). The influence of the background absorptions on the evaluation of the optical density due to styrene monomer is overcome by the use of an appropriate baseline technique, claimed to make the method virtually independent of absorptions due to polymer additives. In this technique a straight line is drawn on the recorded spectrum across the absorption peak at 292 nm in such a way that the baseline is tangential to the absorption curve at a point close to the absorption minima occurring at 288 nm and 295-300 nm (**Figure 2.11**). A vertical line is drawn from the tip of the styrene absorption peak at 292 nm to intersect the baseline and the height of this line is then a measure of the optical density due to the true styrene monomer content of the test solution.

This baseline correction technique can obviously be applied to the determination of styrene monomer in PS only if any other UV absorbing constituents in the polymer extract (e.g., lubricant, antioxidants) absorb linearly in the wavelength range 288-300 nm. If the polymer extract contains polymer constituents other than styrene with non-linear absorptions in this region, then incorrect styrene monomer contents will be obtained. An obvious technique for removing such non-volatile UV absorbing compounds is by distillation of the extract followed by UV spectroscopic analysis of the distillate for styrene monomer as described next.

The PS sample (0.5 g) is dissolved in chloroform or ethylene dichloride (20 ml) in a stoppered flask and the solution is poured into an excess of methyl alcohol (110 ml) to reprecipitate dissolved polymer. The polymer is filtered off and washed with methanol (120 ml) and the combined filtrate and washings gently distilled to provide 200 ml of distillate containing only styrene monomer and any other distillable component of the original polystyrene sample. Non-volatile polymer components (namely stabilisers, lubricants and low molecular weight polymer) remain in the distillation residue. The optical density of the distillate is measured either at 292 nm or by the baseline method against the distillate obtained in a polymer-free blank distillation. Calibration is performed by applying the distillation procedure to solutions of known weights of pure styrene monomer in the appropriate quantities of methyl alcohol and the chlorinated solvent.

Table 2.12 shows results obtained for styrene monomer determinations carried out on two samples of pigmented polystyrene by the direct ultraviolet method and by the distillation
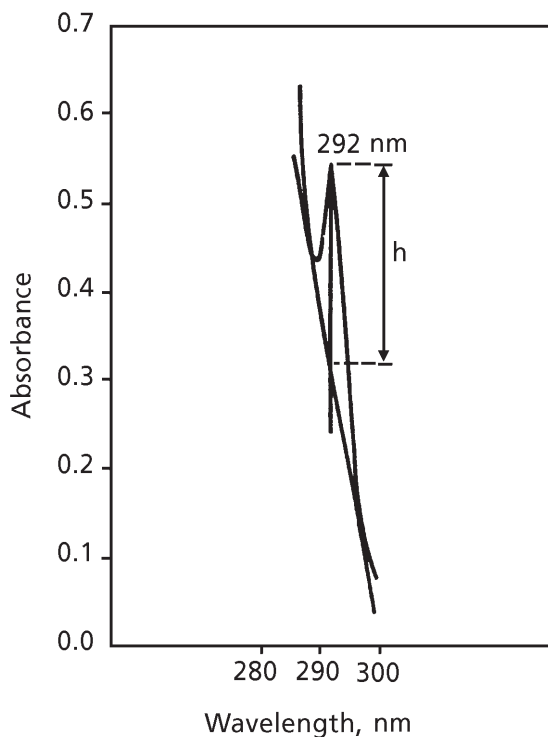
Figure 2.11 Typical UV absorption curve of a PS containing styrene monomer
Reproduced from Crompton and co-workers, British Plastics [76]

Method	Solvent	Styrene monomer (% *w/w*) Polystyrene sample	
		No. 1	No. 2
Direct UV	Chloroform	<0.05	0.13
	Carbon tetrachloride	<0.05	0.13, 0.14
	Ethyl acetate	<0.05	0.16, 0.18
			0.14, 0.12
			0.14, 0.14
			0.15
Distillation/ UV method	Ethylene dichloride/ methanol	0.16, 0.18 0.16, 0.18 0.20	0.27, 0.29 0.26, 0.29 0.29

Table 2.12 Comparison of direct UV and distillation/UV methods for the determination of styrene monomer

Reproduced with permission from T.R. Crompton, L.W. Myers and D. Blair, British Plastics, *1965, 38, 12, 740 [76]*

modification of this method. It is seen that the distillation method gives results that are consistently some 0.1% higher than those obtained by direct spectroscopy, indicating that additives present in the polystyrene are interfering in the latter method of analysis.

Both polystyrene samples contained an ester and a mineral oil type of lubricant together with a phenolic antioxidant. The lubricants have little absorption in the 280-300 nm region and do not interfere in either method of analysis at the 5-10% concentrations at which they are used in polystyrene formulations. The absorption spectrum of the phenolic antioxidant, however, shows a sharply decreasing non-linear absorbance in the 280-300 nm region and contributes significantly to the background absorption of the test solution in the direct UV spectroscopic method. This invalidates the baseline correction procedure and leads to erroneous styrene monomer values. In the distillation procedure, however, the test solution used for spectroscopy does not contain the phenolic antioxidant and there is no interference in the determination of styrene monomer.

2.10 Solvent Extraction – Visible Spectroscopy

2.10.1 Phenol Antioxidants

A very popular method of estimating antioxidants in polymer extracts is by coupling or oxidising them to form coloured products and measuring the resulting absorbance in the visible region of the spectrum. This technique is not particularly specific for individual antioxidants, but is specific for phenolic antioxidants in general (also amine antioxidants), and hence can often be applied without interference from other types of polymer additives.

Meyer [77] described a quantitative method for estimating hydroxy toluene (BHT) involving a colour-forming reaction with 2,6-dichloro-*p*-benzoquinone-4-chloramine. Glavind [78] and Blois [79] have devised methods for estimating total antioxidants, irrespective of type, by coupling them with the free radical α, α´-diphenyl-β-picrylhydrazyl. The decrease in absorption of the reagent solution upon mixing with the polymer extract is related to the amount of antioxidant present.

Stafford [69] has described a procedure for the determination of Ionol (2,6-di-*tert*-butyl-*p*-cresol), in polyolefins, involving refluxing the polymer with cyclohexane for 30 minutes followed by oxidation in potassium hydroxide-saturated isopropanol to produce a colour which is evaluated spectroscopically.

An early British Standard method for estimating the total phenolic antioxidant content of PE involves a preliminary extraction of the polymer with hot toluene to extract the additive,

followed by addition of ethanol to precipitate any dissolved polymer, then coupling the extract with diazotised sulfanilic acid to produce a colour which can be compared with standards by visible spectrophotometry. Dicresylol propane and Santonox R (4,4′-thio-bis-(3-methyl-6-*tert*-butylphenol)), in particular, are mentioned as additives that can be determined by this technique.

Metcalfe and Tomlinson [5] have described a very useful general colorimetric procedure for the determination of phenolic and other types of antioxidant in PE. This procedure involves oxidation of the antioxidant (A) under controlled conditions with an absolute ethanol solution of ferric chloride:

$$A_{reduced} + Fe_3^+ = A_{oxidised} + Fe^{2+}$$
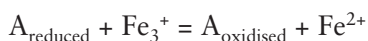
The oxidation is followed by reaction of the ferrous iron produced, with 2, 2′-dipyridyl to form a coloured complex, the intensity of which is proportional to the concentration of antioxidant present. The procedure has been applied to various phenolic and amine type antioxidants, namely, Succanox 18, BHT, Ionol (2,6-di-*tert*-butyl-*p*-cresol), and Nonox CI (*N-N*-di-β-napthyl-*p*-phenylenediamine). A typical application of the procedure is given next, namely to the determination of down to 0.01% of Santonox R in PE. As the Metcalfe and Tomlinson [5] procedure determines Santonox R only in its reduced form, it does not include any Santonox R which may be present in the oxidised form in the original polymer, for example produced by atmospheric oxidation of the additive during polymer processing at elevated temperatures. Total reduced plus oxidised Santonox R can be determined by UV spectroscopic procedures.

In 1960 Hilton [80] published a method for the determination of phenolic antioxidants in polymers based on the preparation of a methanol or ethanol extract of the polymer, followed by coupling the extracted phenol with diazotised *p*-nitroaniline in strongly acidic medium. The solution is then made alkaline and the visible absorption spectrum determined. Many of the antioxidants studied have an absorption maximum at a characteristic wavelength. Hence, in some instances, it is possible to both identify and determine the antioxidant, provided a pure specimen of the compound in question is available for calibration purposes. **Table 2.13** shows absorptivity and wavelength maxima data taken from Hilton's paper. The methods are summarised next.

Figure 2.12 shows absorption spectra in the 400-700 nm region of solvent extracts of five PS obtained by coupling with diazotised *p*-nitroaniline.

Only polystyrene D shows clear evidence for the presence of a phenolic antioxidant - as is shown by the formation of a blue-violet coloration upon addition of the reagent.

Szalkowski and Garber [81] and Hilton [63] and Burchfield [64] have also discussed diazotisation methods for the determination of phenolic antioxidants.

Table 2.13 Composition and absorptivity data for phenolic antioxidants after Hilton			
Antioxidant	Composition	Absorptivity Amax – A700	Wavelength, max (nm)
AgeRite Alba	Hydroquinone monobenzyl ether	31.48	565
AgeRite Spar	Styrenated phenol	44.06	548
AgeRite Superlite	A polyalkyl polyphenol	23.40	560
Antioxidant 5	Not disclosed	18.81	585
Antioxidant 425	2,2′-Methylene-bis-(6-*t*-butyl-4-phenol)	22.30	585
Antioxidant 2246	2,2′-Methylene-bis-(6-*t*-butyl-4-methyl phenol)	20.60	578
Deenax	2,6-Di-*t*-butyl-*p*-cresol	Does not couple	
Ionol	2,6-Di-*t*-butyl-*p*-cresol	Does not couple	
1-Naphthol	1-Naphthol	120.2	598
2-Naphthol	2-Naphthol	115.1	540
Naugawhite	Alkylated phenol	8.20	580
Nevastain A	Hindered phenolic compound	12.44	550
Nevastain B	Hindered phenolic compound	6.62	550
Nonyl phenol	Nonyl phenol	36.25	538
p-Phenyl-phenol	*p*-Phenyl-phenol	80.80	548
Polygard	Tris (nonylated phenyl) phosphite	Must be hydrolysed before it will couple	
Santovar A	2,5-Di-*tert*-amyl-hydroquinone	Colour too weak	
Santovar O	2,5-Di-*tert*-amyl-hydroquinone	Colour too weak	
Santowhite Crystals	4,4′-Thio-bis (6-*tert*-butyl-2-methylphenol	78.84	565
Santowhite MK	Reaction product of 6-*tert*-butyl-*m*-cresol and SCl_2	66.94	560
Santowhite Powder	4,4′-Butylidene-bis (3-methyl-6-*tert*-butylphenol)	Colour too weak	
Solux	*N*-*p*-Hydroxyphenyl-morpholine	Colour too weak	
Stabilite white powder	Not disclosed	Colour too weak	
Styphen 1	Styrenated phenol	22.61	558
Wingstay S	Styrenated phenol	50.82	545
Wingstay T	A hindered phenol	10.27	590
Source: Author's own files			
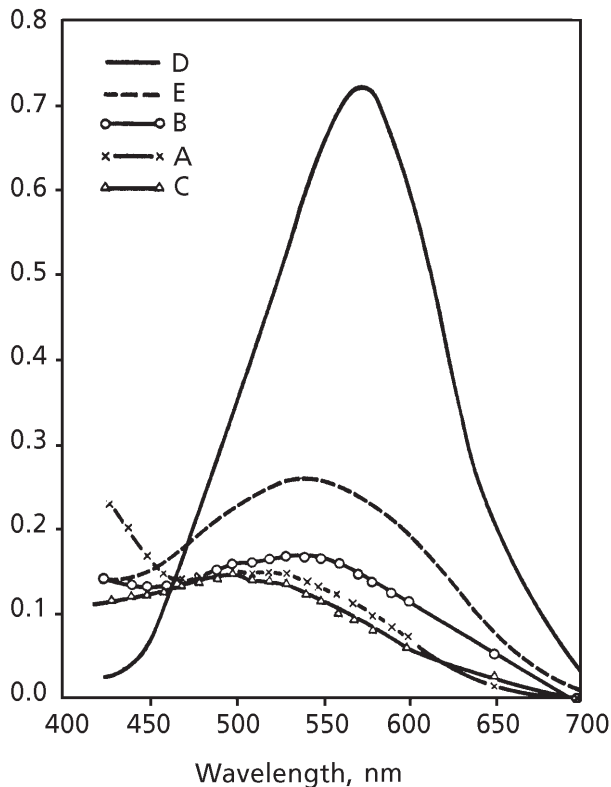
Figure 2.12 Comparison of absorption spectra of diazotised *p*-nitroaniline coupled with extracts from 0.3 g HIPS [80]. *Source: Author's own files*

2.10.2 Amine Antioxidants

Hilton [63] has reported an excellent procedure, described next, for the colorimetric determination of amine antioxidants.

The sample to be analysed must be very thinly sheeted or powdered. Sample (1.000 ± 0.0005 g) is wrapped with an extraction cloth which has been previously extracted to remove sizing, etc. The sample is placed in an Underwriter's extraction cup and extracted for 16 hours with 95% ethanol or methanol. The alcohol extract is transferred to a 100 ml volumetric flask. The extract is cooled to room temperature and diluted to the mark with the extraction solvent. A portion (10 ml) is transferred to a 100 ml volumetric flask and 15 ml of methanol-hydrochloric acid solution and 1 ml of a coupling agent

comprising *p*-nitroaniline sodium nitrite is added. The flask is placed in the dark for l.5 hours and then diluted to the mark with methanol-hydrochloric acid. The absorption spectrum is determined from 700 nm to 350 nm using a Cary spectrophotometer or other spectrophotometer (see **Figure 2.13**).

If a red colour is formed immediately upon coupling and the colour then fades to an amber or brown, it is likely that one of antioxidants containing phenyl-beta-napthylamine is present. In this case an alternate procedure 'B' must be used.

Hilton [82] described a colorimetric method 'B' for determining amine antioxidants (*p*-phenylenediamine derivatives) based on the reaction of an ethanol extract of the polymer with cupric acetate in an hydrochloric acid/potassium chloride buffered medium. Kabota [83] made coloured derivatives of amines with benzothiazoline-2-one hydrazone hydrochloride and ferric chloride, and evaluated the colours obtained, spectroscopically.

Figure 2.13 Visible spectra of amine antioxidants, using the diazotised *p*-nitroaniline method
Reproduced from Hilton, Rubber Age [63]

An early British standard procedure described a method for the determination of Nonox CI (*N,N′*-di-2-naphthyl-*p*-phenylenediamine) in low-density polyethylene (LDPE). In this method the antioxidant is separated from the polymer by bringing the LDPE into solution in toluene, followed by precipitation of the polymer with ethanol. The mixture is then filtered to remove the po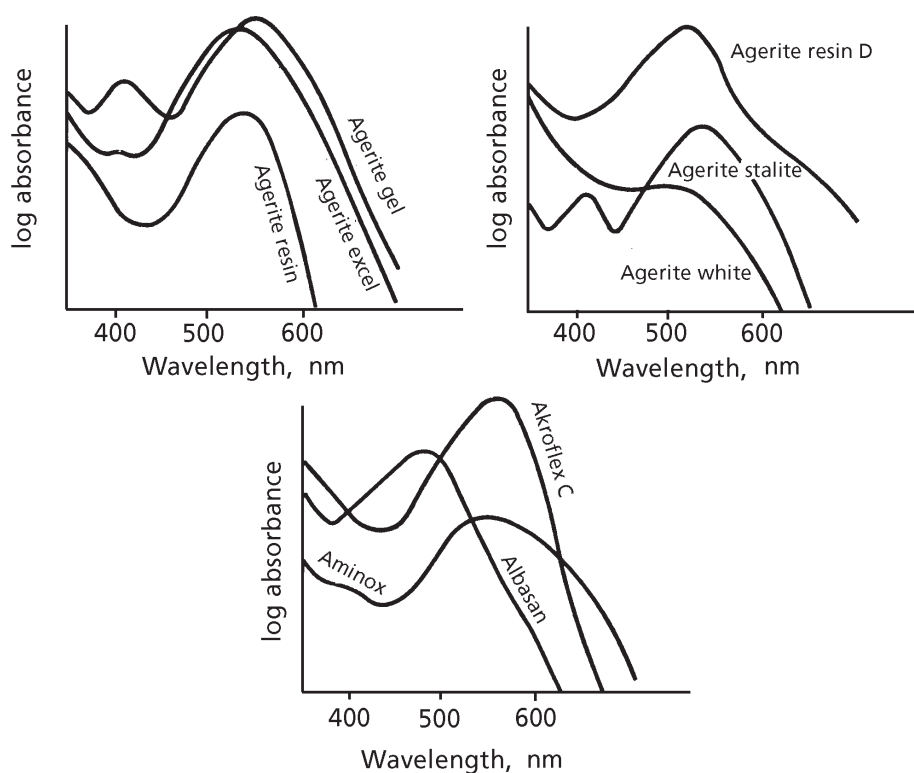lymer, the antioxidant remaining in the filtrate. The antioxidant content of the filtrate is determined colorimetrically by oxidation with hydrogen peroxide, in the presence of sulfuric acid. This reagent produces a green colour with Nonox CI, which gradually reaches a maximum intensity. The colour is evaluated at 430 nm when the maximum depth of colour is reached. Crompton [75] has described a modification to this procedure for the determination of Nonox CI in HDPE which, compared to LDPE, has only a small solubility in toluene. He has also extended the procedure to the determination of oxidised Nonox CI, and a further product which he calls degraded Nonox CI. This latter material is produced only in polymers containing acidic forms of carbon black and is believed to be produced by decomposition of oxidised Nonox CI by carbon black acidity. He applied these procedures to a study of the effect of 12 different acidic and alkaline carbon blacks on Nonox CI degradation, occurring during PE extrusion.

2.10.3 Tris Nonyl (Phenylated Phenyl) Phosphite

The widely used method for the determination of this stabiliser is based on the determination of phosphorus. This involves a tedious preliminary digestion with nitric and perchloric acids. Kellum [84] has described a colorimetric method for determining Polygard based on hydrolysis to nonyl phenol, followed by coupling with *p*-nitro benzene-diazonium fluoroborate and colorimetric estimation at 550 nm:
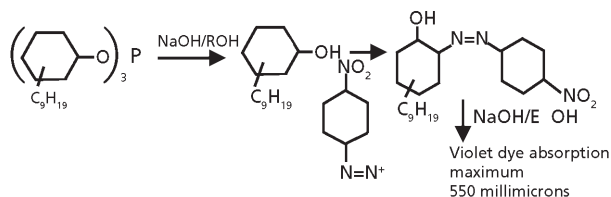
Various other phenolic antioxidants produced dyes under these conditions, namely, Wingstay S, Agerite Superlite and Nevastain A. The procedure was applied to the determination of Polygard in dry rubber and latexes and the results obtained showed good precision. Good agreement was obtained between this procedure and direct determinations of phosphorus by elemental analysis.

Brandt [85] has described an alternate method for the determination of Polygard in styrene-butadiene rubber which utilises the bathochromic shift in the spectrum of phenols resulting from the formation of phenolate ions in alkaline solution.

Polygard in iso-octane has a UV spectrum with a peak at 273 nm in neutral solution. By adding a strong base (tetrabutylammonium hydroxide) the Polygard is hydrolysed and the peak is shifted to 296 nm. The difference in absorbance at 299 nm between the neutral and alkaline solutions is directly proportional to the amount of Polygard present. By use of this bathochromic shift, interference of nonphenolic impurities is eliminated and a background correction factor is not required.

2.11 Solvent Extraction Spectrofluorimetry

Fluorescence spectrometers are equivalent in their performance to single beam UV-visible spectrometers in that the spectra they produce are affected by solvent background and the optical characterises of the instrument. These effects can be overcome by using software built into the Perkin-Elmer LS-5B instrument or by using application software for use with the Perkin-Elmer models 3700 and 7700 computers.

2.11.1 Perkin-Elmer LS-2B Microfilter Fluorimeter

The model LS-2B is a low-cost, easy to operate, filter fluorimeter that scans emission spectra over the wavelength range 390-700 nm (scanning) or 220-650 nm (individual interference filters).

In a filter fluorimeter the following are necessary:

- A source of UV/visible energy (pulsed Xenon),

- A method of isolating the excitation wavelength,

- A means of discriminating between fluorescence and excitation energy, and

- A sensitive detector and a digital display of the fluorescence intensity.

The model LS-2B has all these features arranged to optimise sensitivity for microsamples. It can also be connected to a highly sensitive 7 µl liquid chromatographic detector for detecting the constituents in the column effluent. It has the capability of measuring fluorescence, time-resolved fluorescence, and bio- and chemiluminescence signals. A 40-portion autosampler is provided. An excitation filter kit containing six filters - 310, 340, 375, 400, 450 and 480 nm is available.

In many cases visible fluorescence techniques are less subject to interference by other polymer additives present in a polymer extract than are UV methods of analysis. Therefore,

in some cases visible fluorimetry offers a method of determining a polymer constituent without interference from other constituents, when this would not be possible by UV spectroscopy. Apart from specificity, fluorescence techniques are more sensitive than absorption spectroscopic techniques.

Aromatic amines and phenols are among the few classes of compounds in which a large proportion of their members exhibit sensible fluorescence; other types of visible fluorescing compounds include some benzoquinones, hydroxyl methoxy benzophenones, coumarin derivatives and UV absorbing polymer additives.

2.11.2 Antioxidants

Kirkbright and co-workers [86] carried out a study of the general feasibility of the fluorimetric or phosphorimetric determination of stabiliser compounds after their extraction from polymers with organic solvents. They examined the fluorescence and phosphorescence characteristics of 29 common antioxidants and UV absorbers in an organic solvent medium at room temperature and –200 ºC, respectively, and they report the fluorescence and phosphorescence spectral characteristics in a mixture of diethylether, isopentane, ethanol and chloroform and the calibration data phosphorescence detection limits and phosphorescence life-times.

The solvent used for nearly all measurements was a mixture of diethyl ether, isopentane, ethanol and chloroform prepared from analytical reagent grade solvents in the volume ratio of 75:75:30:20. Stock 1000 ppm solutions of these compounds were prepared by direct dissolution in the solvent mixture, or by dissolution in chloroform followed by dilution with ether, isopentane and ethanol. Nonox CI was dissolved in diethylamine to prepare a 1000 ppm solution - 1 ml was then diluted to 10 ml with a mixture of ether, isopentane and ethanol.

The room temperature fluorescence excitation and emission spectra were recorded for the 1000 ppm solutions of the compounds. The same solutions were then transferred to the thick-walled sample tubes aligned in the quartz Dewar flask containing liquid nitrogen. The low temperature luminescence excitation and emission spectra were then recorded. The phosphorescence spectra at –196 °C were then obtained after the phosphoroscope rotating can had been fitted. The phosphorescence life-time was determined by observation of the decay curve of the phosphorescence on the X-Y recorder or with the oscilloscope.

Working curves for both low temperature luminescence intensity (phosphorescence plus fluorescence) and phosphorescence intensity *versus* concentration in parts per million of the compound in the solvent mixture were obtained for each of the stabiliser compounds which exhibited appreciable luminescence. The wavelengths of maximum excitation and

emission were set on the spectrophosphorimeter, and the relative intensity readings from the photomultiplier microphotometer were recorded for a series of standard solutions containing 0.001-1000 ppm of each compound.

Figure 2.14 shows the excitation and emission spectra obtained for Nonox CI.

These are typical of the results obtained for the other compounds whose spectra are not shown. The shapes of the spectra are influenced by the particular instrument used, because they are uncorrected for variations in detector sensitivity, xenon arc lamp emission or grating transmission with wavelength.

Most of the fluorescence signals recorded by Kirkbright and co-workers [86] at room temperature for the compounds examined were of low intensity. Thus, while it was
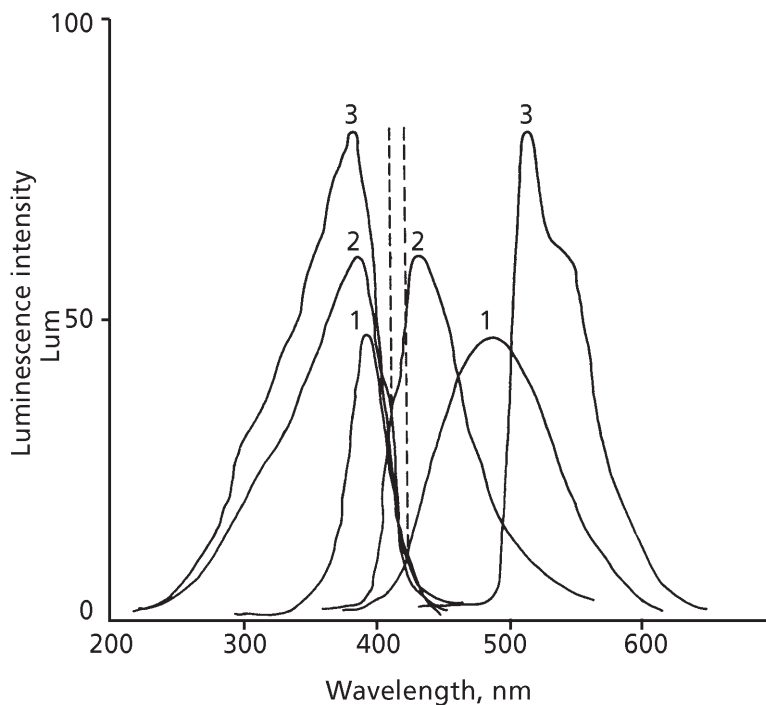
Figure 2.14 Spectral characteristics of luminescence observed for Nonox CI. (1) Excitation and emission spectra at room temperature, sensitivity scale 0.01, (2) excitation and emission spectra at −196 °C for total luminescence, sensitivity scale 0.01, (3) excitation and emission spectra at −196 °C for phosphorescence, sensitivity scale 0.01
Reproduced from Kirkbright and co-workers, Elsevier [86]

detectable at the high concentration (1000 ppm) used for study of the spectra characteristics, the room-temperature fluorescence of most of the compounds was of little practical value in trace analysis. Three compounds did, however, show quite intense room temperature fluorescence - these were Nonox CI, Tenox BHA and Agerite Superlite. Room temperature fluorescence calibration graphs for these compounds at their wavelengths of maximum excitation and emission are shown in **Figure 2.15**. The low-temperature luminescence observed for most of the compounds examined was usually much more intense than the room temperature fluorescence emission, but largely consisted of phosphorescence. This was borne out by the almost exactly similar spectral characteristics of the low-temperature luminescence and phosphorescence and the similarity of the IR calibration graphs. Only two compounds (Nonox CI and Tinuvin P) showed low temperature luminescence characteristics from their phosphorescence. Irganox 1010 exhibited an apparent low temperature fluorescence of different spectra characteristics to the weak
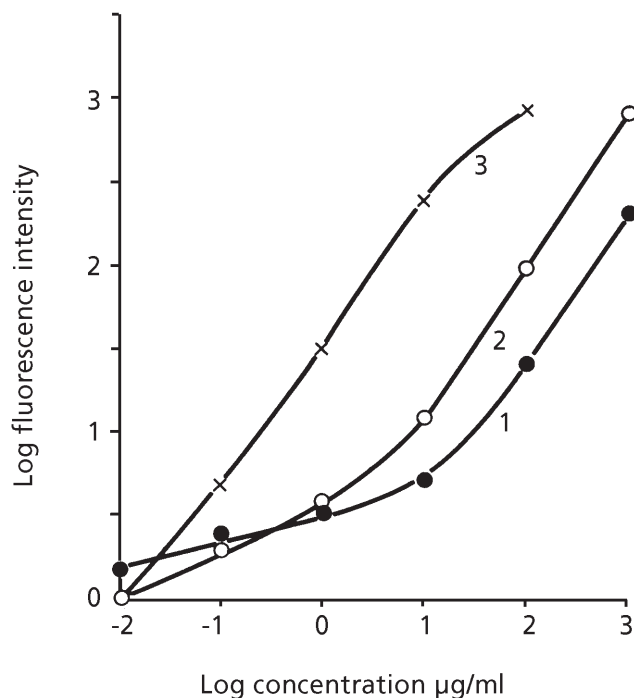
Figure 2.15 Working curves for room temperature fluorescence: (1) butylated hydroxyl anisole (●), (2) Agerite Superlite (O), (3) Nonox CI (x)
Reproduced from Kirkbright and co-workers, Elsevier [86]

113

room temperature emission, but which did not show detectable phosphorescence. The low temperature luminescence observed for Irganox 1010 may, however, be short life-time phosphorescence which was undetectable with the rotating can phosphoroscope. Four compounds (Topanol OC, Ionox 330, Irganox 1076 and Irganox 1093) showed relatively weak room temperature emissions in the ether-isopentane-ethanol mixture but no low-temperature fluorescence or phosphorescence was detectable. Four compounds (Tinuvin 326, DLTDP, Uvinol 400 and Binox M) exhibited no luminescence under any conditions, while the phosphorescences of Voidox 100%, Salol, Cyasorb UV 531 and Cyasorb UV 24 were too weak to permit its examination in dilute solutions or accurate measurement of the phosphorescence life-times.

Kirkbright and co-workers [86] conclude that measurement of the phosphorescence characteristics of samples obtained after extraction of polymers with organic solvents yields useful information regarding the nature and concentration of the stabiliser compounds present. It should be possible to obtain good selectivity, with a sensitivity which compares favourably with that of UV absorption spectrophotometry, in the determination of two or more stabiliser compounds simultaneously by correct choice of excitation and emission wavelengths and phosphorescence speeds.

2.12 Solvent Extraction – Mass Spectrometry

Mass spectrometry is used as a fingerprint technique to identify components of additive systems extracted from polymers [87, 88].

The strengths of this technique are high sensitivity and the ability to distinguish between closely related compounds of differing relative molar masses e.g., the different alkyl thio-di-propionates used as synergistic stabilisers in polyolefin and the UV absorbing benzotriazole derivatives. Often, it is not necessary to separate the components before examination as some separation may be achieved by careful variation of the sample probe temperature to produce in effect, a fractional distillation of the components. The presence, however of large amounts of low relative molecular weight polymer such as PE and PP may cause interference by producing a high hydrocarbon background extending to several hundred relative atomic units. In such cases, a TLC separation can be used.

Hurtubise and Latz [89] have also studied the fluorimetric, determination of butylated hydroxy anisole in waxed cardboard. The antioxidant is isolated from an ethyl ether extract of the sample by TLC on Silica Gel G prior to fluorimetry. This method could, doubtlessly, be applied with minor modifications to the analysis of polymers.

Parker and Barnes [90] found that in solvent extracts of rubbers, the strong absorption by pine-tar and other constituents masks the absorption spectra of phenyl naphthylamines,

whereas the fluorescence spectra of these amines are sufficiently unaffected for them to be determined directly in the unmodified extract by the fluorescence method. Parker has also discussed the possibility of using phosphorescence techniques for determining phenyl naphthylamines.

2.12.1 Ultraviolet Absorbers

UV absorbers are used to protect the plastic material as well as the foodstuff packaging from the actinic action of UV radiation. Actinic effects may cause discoloration of both the plastic material and the foodstuff, and may also occasion changes in taste and loss of vitamins in the food.

The UV absorbers can be divided into different groups:

(a) Benzophenone derivatives

(b) Salicylic acid esters

(c) Resorcinol esters

(d) Benzotriazole compounds

(e) Coumarone derivatives

By their nature, many of these types of compounds are easily analysed by fluorimetry, thus Uvitex OB has an intense UV absorption at a wavelength of 378 nm, which is high enough to be outside the region where many potentially interfering substances present in the polymer extract would be excited to fluoresce. This is illustrated in the following fluorimetric procedure for the determination of down to 10 ppm Uvitex OB in PS. Antioxidants such as Ionol CP (2,6-di-*tert*-butyl-*p*-cresol), Ionox 330 (1,3,5-tri-methyl-2,4,6-tri(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene), Polygard (tris-(nonylated phenyl) phosphite), Wingstay T (described as a butylated cresol), and Wingstay W and many others, do not interfere in this procedure.

In a typical method, 0.2 g of the PS sample was shaken with chloroform to achieve a solution. The sample was excited by UV radiation of wavelength 370 nm from a mercury vapour lamp and the fluorescence spectrum of the sample recorded over the range 400-440 nm. The reading from the fluorimeter was noted and the Uvitex OB concentration in the PS determined by reference to a prepared calibration graph.

A clean-up MALDI time of flight mass spectrometry [91] used in conjunction with SFC extraction has been used to determine UV stabiliser and antioxidants

The mass spectrum of the UV stabilisers, Tinuvin 622 LD and Chimassorb 944 LD showed that oligomeric compounds were present. The antioxidants Irgonox 1076, Irgapas 168 and Irgonox 1010 were all detected in the MALDI time of flight spectrum from LDPE. Vargo and Olson [92] used absorbance and mass spectrometry to detect antioxidants and UV stabilisers exiting from an high-performance liquid chromatography (HPLC) column in acetonitrile extracts of PP. Up to 18 antioxidants and UV stabilisers were determined in ether extracts of polyolefins by laser desorption Fourier transform ion cyclotron resonance MS [93].

Juo and co-workers [94] have demonstrated that ammonia desorption chemical ionisation was a better ionisation technique than fast atom bombardment (FAB) for the determination of additives in PE extracts.

2.13 Solvent Extracts – Electrochemical Methods

2.13.1 Acrylamide

Betso and McLean [95] have described a differential pulse polarographic (DPP) method for carrying out this determination of the acrylamide. A measurement of the electrochemical reduction peak current is used to quantitate the acrylamide concentration. The DPP technique also yields a well-defined acrylamide reduction peak at approximately -2.0 V *versus* a standard calomel electrode (SCE), suitable for qualitatively detecting the presence of acrylamide. The procedure involves an extraction of the acrylamide monomer from the polyacrylamide, a treatment of the extraction solution on mixed resin to remove interfering cationic and anionic species and polarographic reduction in an 80/20 (*v/v*) methanol/water solvent with *tert-n*-butylammonium hydroxide as the supporting electrolyte. Acrylic acid is polarographically distinguishable from acrylamide in a neutral medium. Ethyl acrylate is an interference in the analysis. Acrylonitrile is removed, from interfering substances by treatment on mixed resin. The detection limit of acrylamide monomer by this technique is less than 1 ppm.

The acrylamide reduction peak is well-defined and well-resolved from the background, no difficulty is encountered in either the detection or measurement of this peak. The DPP acrylamide reduction current is directly proportional to concentration. The polarographic detection limit for acrylamide in a clean system is less then 1 pg/ml acrylamide. Even at this low concentration, the acrylamide reduction peak is well-defined and resolved from the background.

Some other applications of polarography to the determination of polymer additives and catalyst remnants are reviewed in **Table 2.14**.

Table 2.14 Applications of polarography		
Polymer	Determined	Reference
Polystyrene	Ionol 4,4-isopropylidene-diphenol	[96, 97]
Polyolefins	Antioxidants	[98, 99]
Rubbers	Accelerators Phenolic antioxidants Amine antioxidants	[98, 100-115]
Adapted with permission, from T.R. Crompton, Polymer Reference Book, *Rapra Technology, Shrewsbury, Shropshire, UK, Table 7.4*		

2.13.2 Antioxidants

Electrochemical methods have been investigated but in general are only to be recommended where a simpler method is not available. Mocker [105, 112, 113] and Mocker and Old [116] have explored the use of polarography and find the technique to be more applicable to rubber accelerators than to antioxidants. They included both phenolic and amine types of antioxidants in their study. Difficulties arise because the dropping mercury electrode cannot be used at potentials more positive than +0.4 V with respect to the SCE, and since many aromatic phenols (and amines) can only be oxidised at electrodes, positive voltages have to be applied in their analysis. Nevertheless, the polarography of some amines and phenols has been studied [107, 117, 118] and whilst no electrode is as suitable for polarography as the dropping mercury electrode, antioxidants have also been studied with other types of electrodes, notably the graphite [100, 101] and platinum [98, 99, 101, 102, 119, 120] electrodes, e.g., determination of Ionol (2,6 di-*tert*-butyl-*p*-cresol) [108].

In addition, at least two commercially available antioxidants have been shown by differential cathode-ray polarography to exhibit reduction waves: Santonox R gives a poorly shaped wave at -0.6 V in an electrolyte consisting of ammonia and ammonium chloride in methanol-water [98] and 3, 5-di-*t*-butyl-hydroxytoluene gives a wave at -0.65 V in aqueous sodium or lithium hydroxide [99]. In both cases, 40 ppm of analyte gave a current which was adequate for quantitative analysis.

Other procedures which have been described include the conversion of an antioxidant into a polarographically reducible form [120] and a general method for antioxidants which involved measuring a decrease in the height of the wave, due to the reduction of dissolved oxygen by antioxidants [102].
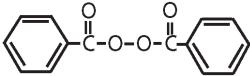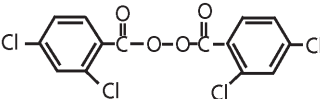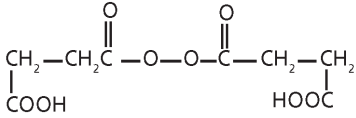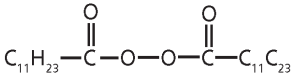
2.13.3 Organic Peroxides
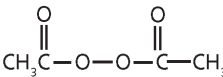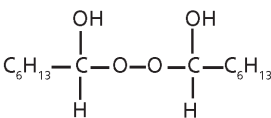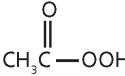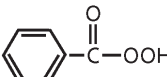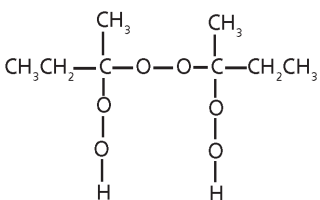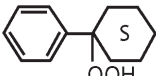
Organic peroxides can occur in small amounts in some types of polymers such as PS as a result of the fact that a peroxide has been used as a polymerisation catalyst in polymer manufacture. Also, stable organic peroxides such as dicumyl peroxide have been used as synergists, in conjunction with bromine and or phosphorus-containing additives, to impart fire resistance to cellular expanded PS and other types of plastics.

Kuta and Quackenbush [121] have studied the polarography of 23 commercially available organic peroxides. Polarograms were recorded, using a Sargent Model XXI polarograph on solutions of these compounds in an electrolyte consisting of 0.3 M lithium chloride dissolved in benzene methanol (1:1), using ethylcellulose as a maximum suppressor. Half-wave potentials for some of the peroxides they examined are shown in **Table 2.15**.

The compounds fell into six different groups, based on their structure and behaviour in the polarographic cell. The first group of eight compounds, shown in **Table 2.15** had reduction waves at or near zero voltage. Included were diaroyl and diacyl peroxides and peroxy acids. The diaroyl peroxides (benzoyl and 2,4-dichlorobenzoyl peroxides) showed linear relationships between diffusion current and concentration in the range 9×10^{-2} to 4×10^{-4} M, and the diacyl peroxides (acetyl, lauroyl, and succinic acid peroxides) between 1×10^{-2} and 1×10^{-4} M. The succinic acid peroxide showed a second reduction wave, at -1.44 V, which was attributed to the free acid group - a polarogram of succinic acid showed a reduction wave at approximately the same potentials.

Peroxyacetic and peroxybenzoic acids gave reduction waves at 0.00 voltage in the presence of ethylcellulose and methylene blue, but they did not demonstrate a linear relationship between diffusion current and concentration. The acids evidently reacted slowly with the methanol in the solvent, as a continuous decrease in diffusion current was observed with increased time of contact. Peroxyacetic acid showed an additional wave at a half-wave potential of -1.41 V, probably because of the presence of acetic acid, whose half-wave potential was observed to be 1.44 V. Bis(1-hydroxyheptyl)peroxide gave two reduction waves at 0.00 and -1.20 V. A linear relationship existed between the concentration (1×10^{-2} to 1.3×10^{-4} M) and diffusion current at half-wave potential of -1.20 V, but not at 0.00 voltage.

In the second group in **Table 2.15**, two reduction waves were obtained for each of the three peroxides, the first at -0.60 to -0.70 V, the second at -1.0 to -1.26 V. Methyl ethyl ketone peroxide in dimethyl phthalate showed three half-wave potentials, one of which (-1.82 V) was attributed to the phthalate ester, the first reduction wave (0.60 V) was observed only when the concentration of peroxide was below 0.01 M, and the relationship between diffusion current and concentration was nonlinear, since the diffusion current showed a maximum at a concentration of 2.1×10^{-3} M. The second reduction wave (half-

Table 2.15 Polarographic behaviour of organic peroxide compounds			
Compounds	Peroxide Structure	Peroxide content (%)	Half-wave potential, (volts)
Group 1			
Benzoyl peroxide		97.9	0.00
2,4-Dichloro-benzoyl peroxide		99.6	0.00
Succinic acid peroxide		96.8	0.00
Lauryl peroxide		99.3	−0.15
Acetyl peroxide		48.4	−0.28
Bis(1-hydroxyl-heptyl)peroxide		94.2	−0.00 −1.20
Peroxyacetic acid		23.6	−0.00
Peroxybenzoic acid		-	−0.00
Group 2			
Methyl ethyl ketone peroxide		49.3	−0.60 −1.26
Phenylcyclohexane hydroperoxide		97.8	−0.66 −1.08
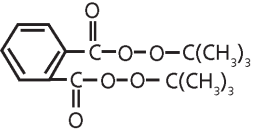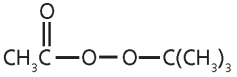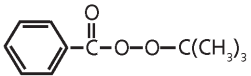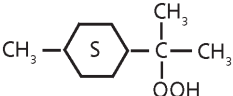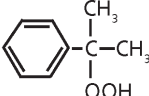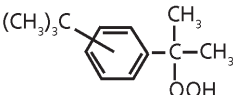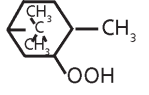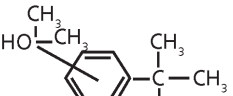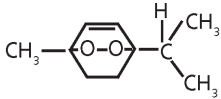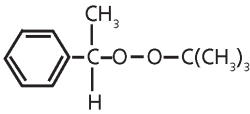
Table 2.15 Continued...			
Compounds	Peroxide Structure	Peroxide content (%)	Half-wave potential, (volts)
Di-*tert*-butyl perphthalate		49.8	−0.70 −1.05
Group 3			
Tert-butyl peracetate		98.8	−1.02
Tert-butyl perbenzoate		92.6	−0.95
Group 4			
p-Menthane hydroperoxide		44.1	−1.06
Cumene hydroperoxide		96.5	−1.08
Tert-butyl-isopropyl-phenylhydroperoxide		26.9	−1.06
Pinane hydroperoxide		90.3	−1.08
Diisopropylphenyl-hydroperoxides		97.7	−1.10
Tert-butyl hydroperoxide	$(CH_3)_3-C-O-O-H$	56.8	−1.15
Hydrogen peroxide	$H-O-O-H$	22.8	−1.16

Table 2.15 Continued…			
Compounds	Peroxide Structure	Peroxide content (%)	Half-wave potential, (volts)
Group 5			
Ascaridole		-	−1.22
Group 6			
Di-*tert*-butylphenyl oxide	$(CH_3)_3$—C—O—O—C$(CH_3)_3$	-	Not reduced
1-Phenylmethane-*tert*-butyl-peroxide		-	Not reduced
Source: Author's own files			

wave potential, -1.26 V) demonstrated a linear relationship between diffusion current and the previous concentrations. The samples of phenylcyclohexane hydroperoxide and di-*tert*-butyl perphthalate showed, for both reduction waves, a linear relationship between diffusion current and concentration in the range of 10^{-2} to 10^{-4} M.

Group three consisted of two peroxy esters (*tert*-butyl perbenzoate and terbutyl peracetate) which gave a single reduction wave at about -1.0 V. Both compounds showed a linear relationship between diffusion current and concentration in the range of 10^{-2} to 10^{-4} M.

The fourth group of seven hydroperoxides also showed a single reduction wave, and at a slightly more negative potential than the third group. The group consisted of di-isopropylphenyl, *tert*-butyl-isopropylphenyl, *p*-menthane, cumene, pinane, and *tert*-butyl hydroperoxides, and hydrogen peroxide. Five of the more complex members of the group reduced in the range of -1.02 ± 0.02 V. All gave a linear relationship between diffusion current and concentration in the range 10^{-2} to 10^{-4} M.

In a class by itself (Group 5) was the transannular peroxide ascaridole, which reduced at -1.22 V. It showed a linear relationship between diffusion current and concentration in the range 9.2 x 10^{-2} to 1.6 x 10^{-3} M.

Two peroxides, di-*tert*-butyl peroxide and 1-phenylmethyl-*tert*-butyl peroxide, were not reduced in the voltage span of 0.00 to -2.00 V.

The procedure of Kuta and Quackenbush [121] can be modified for the determination of relatively simple organic peroxides such as benzoyl peroxide, *para-tert*-butyl perbenzoate and lauroyl peroxide in PS, and would no doubt be suitable for the determination of other types of peroxides. In these procedures a suitable weight of polymer is dissolved in toluene and then an equal volume of 0.6 M lithium chloride in methanol is added. Precipitated polymer is removed by centrifuging and peroxides in the filtrate are determined by cathode-ray polarography. Polymerisation additives, styrene monomer or antioxidants in the polymer do not interfere in the polarographic procedure. A procedure for the determination of down to 20 ppm *para-tert*-butyl perbenzoate in PS is given next.

Procedure

Sample (5.0 ± 0.01 g) is transferred to a 250 ml Pyrex glass centrifuge bottle, and toluene (50 ml) is added. A polythene coated magnetic stirrer rotor is placed into the bottle which is stoppered with a cork (avoid rubber bungs). The bottle is placed on a magnetic stirrer and left for several hours until the sample has completely dissolved or dispersed in the solvent. Into the gently stirred contents of the bottle 50 ml of 0.6 M lithium chloride reagent is accurately pipetted.

The bottle is placed in a centrifuge and spun at 700-900 *g* until the insolubles have completely settled to the bottom of the bottle leaving an absolutely clear upper phase containing all the peroxide present in the original sample.

Toluene (50 ml) was diluted with lithium chloride solution (50 ml) to act as a blank. Sample solution (5 ml) and the blank solution (5 ml) were pipetted into two polarographic cells and these were immersed in the constant temperature tank of the cathode-ray polarograph (thermostatted at 25 °C). Degassing operations were carried out as described next. The sample and the blank solutions were degassed immediately before carrying out all polarographic measurements.

A supply of oxygen-free nitrogen was connected to the polarographic cell. The dropping mercury electrode system was lowered over this cell, so that the outer glass sleeve of the electrode dipped 1-2 mm into the water tank (providing a water seal to prevent the ingress of atmospheric oxygen). The anode connection was immersed in the side arm of the polarographic cell. Nitrogen was passed for 15 minutes to completely displace oxygen from the cell solution, and then switched off. The glass sleeve was left in position to prevent re-entry of atmospheric oxygen into the cell solution and the polarographic measurements described next were carried out within 1 to 3 minutes of stopping the gas purge.

The analytical conditions used with the Southern Analytical Davis Differential A1660 cathode-ray polarograph (with single cell operation) are:

Cathode	dropping mercury
Reference anode	mercury pool
Circuit	forward sweep (with derivative units control switch off)
Sensitivity control	select a suitable current scale-factor and keep this constant throughout the analysis. Alter the instrument sensitivity by means of the shunt scale-factor control.
Start potential	-0.7 V

By means of the 'Y' shift control, the light spot is adjusted to the origin of the axes on the left-hand side of the graticule on the cathode-ray tube. This operation is repeated at different shunt scale factor settings, until the polarographic wave is visible on the graticule.

The analytical conditions used with the Southern Analytical K1000 polarograph are:

Cathode	dropping mercury
Reference anode	mercury pool
Circuit	cathodic direct
Start potential	-0.7 V

The polarograph is adjusted to its maximum sensitivity setting. The 'X'-shift control and the 'Y'-shift controls are adjusted until the light spot commences its sweep at the origin of axes at the left-hand side of the graticule on the cathode-ray tube. This operation is repeated at different sensitivity settings until the polarographic wave is visible on the graticule.

The readings are taken on the freshly degassed solutions as follows. The polarograph is adjusted to the *para-tert*-butyl perbenzoate start potential (-0.7 V) and the wave is obtained as described previously for the PS sample solution. The maximum height of the peak, (at about -0.9 V), is read off from the graticule. The dropping mercury electrode is raised from the cell and a suitable 'standard addition' of a toluene solution of *para-tert*-butyl perbenzoate (ensure that the weight of peroxide present in the 'standard addition' is similar to that already present in the cell solution) is delivered as quickly as possible into the sample solution by means of a horizontally held Agla syringe. The volume of 'standard addition' solution is limited to less than 0.05 ml in order to avoid dilution errors. The electrode is lowered into the sample cell and nitrogen is again passed for 2 minutes. The new peak height at -0.9 V is read immediately. The peak height at -0.9 V on the degassed PS-free reagent blank solution is determined in a similar way.

Calculations

Para-tert-butyl perbenzoate (ppm *w/w*)

$$= \frac{100 \times M \times 10^6}{5 \times W} \times \frac{(h_1 s_1 - h_3 s_3)}{(h_2 s_2 - h_1 s_1)}$$

where

W = weight (g) of PS sample taken for analysis (assuming a 5 ml portion taken for polarography),

h_1 = peak height (graticule divisions) of sample solution before standard addition,

h_2 = peak height (graticule divisions) of sample solution after standard addition,

h_3 = peak height (graticule divisions) of polymer-free reagent blank solution,

s_1, s_2 and s_3 are the corresponding instrument sensitivity settings (the product of h and s are known as peak currents in μA).

M = weight (g) of *para-tert*-butyl perbenzoate in volume of 'standard addition' solution added to cell solution.

2.13.4 Acrylonitrile

Residual amounts of styrene and acrylonitrile monomers usually remain in manufactured batches of styrene-acrylonitrile copolymers. As these copolymers have a potential use in the food packaging field, it is necessary to ensure that the content of both of these monomers in the finished copolymer is below a stipulated level.

Claver and Murphy have reported a polarographic method [122] for determining down to 30 ppm of residual acrylonitrile in styrene-acrylonitrile copolymers.

Crompton and Buckley [123] modified this procedure, improving its sensitivity to a lower detection limit of 2 ppm acrylonitrile in polymer. They also found that it was possible, using the same base electrolyte, to determine styrene monomer in amounts down to 20 ppm in styrene-acrylonitrile co-polymers.

Methacrylonitrile can also be determined if acrylonitrile is absent. Both styrene and acrylonitrile can also be determined in acrylonitrile-butadiene-styrene terpolymers, using the same procedure. Tetrabutylammonium iodide (0.1 M; TBAI) in aqueous dimethylformamide (DMF) was used as the base electrolyte and polarography was carried out using a differential cathode ray polarograph.

Figures 2.16a and **2.16b** show polarograms of single solutions of acrylontrile and styrene monomers in the base electrolyte, and of a mixture of the two monomers. It is seen that the waves for the two monomers are well resolved from each other.

Procedure

The stock bottle of DMF is purged with oxygen-free nitrogen or hydrogen for 30 to 40 minutes to sweep out dissolved oxygen. The bottle is kept well stoppered and repurged each time it is opened. Freshly purged DMF solvent is used throughout the analysis.

Styrene-acrylonitrile sample (1.25 ± 0.01 g) is weighed into a 50 ml calibrated flask. Anhydrous DMF (25 ml) is transferred by pipette into a flask. The flask is stoppered and swirled to dissolve the polymer. The solution is diluted to the mark with TBAI reagent (0.2 M) and is mixed well. For the blank solution, DMF (25 ml) and the 0.2 M TBAI reagent (25 ml) are transferred by pipette to a 50 ml calibrated flask and then mixed well. The sample solution (5 ml) and 5 ml of the blank solution are transferred by pipette into
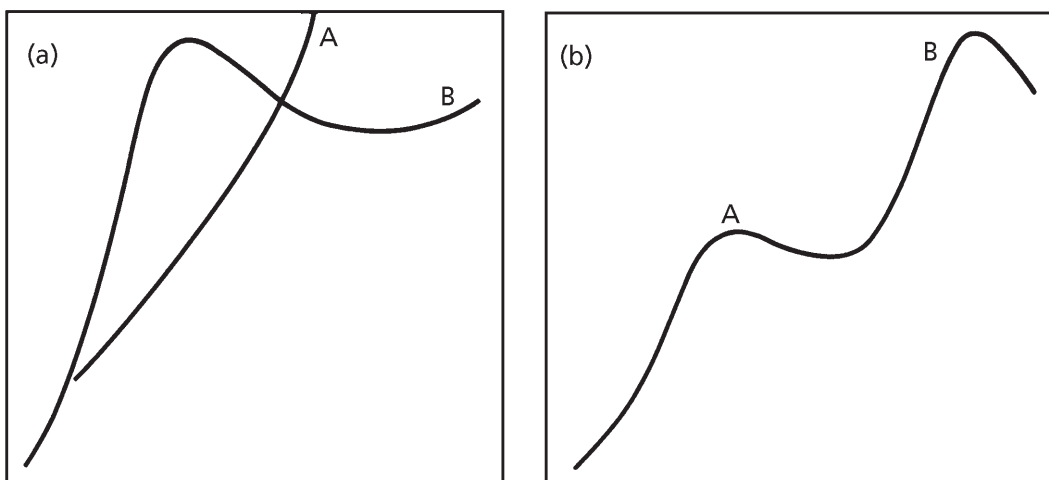
Figure 2.16 (a) Cathode ray polarogram of a synthetic solution of acrylonitrile in TBAI-DMF base electrolyte. Curve A: base electrolyte blank solution, Curve B: 4 ppm of acrylonitrile in base electrolyte, start potential = -1.7 V. (b) Cathode ray polarogram of a synthetic solution of 11.2 ppm of styrene and 9.3 ppm of acrylonitrile monomer in TBAI-DMF base electrolyte. Wave A: acrylonitrile wave, wave B: styrene wave, start potential = -1.7 V
Reproduced from Crompton and Buckley, RSC [123]

two polarographic cells and these are immersed in the constant temperature bath of the polarograph. Purging of the cell with hydrogen or nitrogen is performed immediately before any polarographic measurements are made.

2.13.5 Determination of Styrene

The readings of the freshly degassed sample solutions are taken as described next.

The polarograph is adjusted to the styrene start potential (-2.0 V) and the styrene wave is obtained as described previously. The maximum height of the styrene peak is read off from the graticule and the voltage, V_{STY}, at which this maximum polarographic reading occurs is noted. The electrode is raised from the cell and a suitable 'standard solution' of a solution of styrene in a DMF-water (95 + 5 *v/v*) mixture is delivered into the sample solution by means of a horizontally held Agla syringe. The volume of standard addition solution is limited to less than 0.05 ml in order to avoid dilution errors. The electrode is lowered into the sample cell and hydrogen or nitrogen is again passed for 5 minutes. The new height of the styrene wave corresponding to V_{STY} volts is noted.

2.13.6 Determination of Acrylonitrile

The readings indicated next are taken on the same sample solution as used to determine styrene.

The polarograph is adjusted to the acrylonitrile start potential (-1.7 V). To determine acrylonitrile, the operations described previously for styrene are repeated by using a solution of acrylonitrile in a DMF-water (95 + 5 *v/v*) mixture to make the 'standard solution' of acrylonitrile. The voltage, V_{ACN} at which the maximum polarographic reading occurs is noted.

2.13.7 Organometallic Stabilisers

Other types of organometallic stabilisers have been used in the formulation of PVC. Mal'kova and co-workers [124] described an alternating current polarographic method for the determination of cadmium, zinc and barium stearates or laurates in PVC. The samples are prepared for analysis by being ashed in a muffle-furnace at 500 °C, a solution of the ash in hydrochloric acid being made molar in lithium chloride and adjusted to pH 4.0 ± 0.2. Alternatively, the sample solution can be prepared by boiling with 2 M hydrochloric acid for 3 minutes, cooling and adjusting the pH of a portion of the solution to 4 with 2 M lithium hydroxide. The solution obtained in either instance is de-aerated by passage

of argon and the polarogram is recorded. Cadmium, zinc and barium give sharp peaks at -0.65, -1.01 and -1.90 V, respectively, *versus* the mercury-pool anode. The first digestion procedure is recommended if the sample, contains esters of phosphorus acid.

Other techniques that have been used for the examination of organometallic stabilisers extracted from PVC include column chromatography (barium, cadmium and zinc salts of fatty acids [125]), paper chromatography (cadmium, lead and salts of fatty acids [126]), polarography (cadmium, lead and zinc salts [127]), spectroscopy (cadmium, lead and zinc salts [128]) chemoluminescence techniques and flame photometry (sodium, potassium, barium, cadmium and lead salts [129]).

2.14 Chronopotentiometry

Ward [119] has discussed in some detail the determination of phenolic and amine types of antioxidant and antiozonant in polymers by the chronopotentiometric technique, using a paraffin wax impregnated graphite indicating electrode and solutions of lithium chloride and lithium perchlorate and acetonitrile in 95% ethanol as supporting electrolytes. The precision obtainable for repeated chronopotentiometric runs in acetonitrile was found to be better than ± 1.0% in cases in which electrode fouling did not occur, and ± 1.7% when the electrode was fouled by electrolysis products.

Table 2.16 shows data obtained by Ward [119] in a chronopotentiometric study of several commercially available antioxidants.

Although $ir^{1/2}/C$ always increased as antioxidant concentration (C) was decreased, plots of ir% *versus* (C) gave a nearly straight line suitable for use as an analytical working curve (**Table 2.16**).

At a given concentration of electroactive species, the product $ir^{1/2}$ was constant as i, and thus r were varied over a 2- to 3-fold range.

The range of transition times measured was limited to not less than 5 or not more than 30 seconds. The lower limit was imposed by the accuracy with which it was possible to measure r with the recorder used. The upper limit results from disturbance of the diffusion layer by such effects as vibration, convection, etc. Within these limits, the precision with which transition times could be reproduced was ± 1.0%, even when the electrode was removed from the solution between runs and dried before being replaced. This increase in reproducibility appears to rise from the ability of the solvent to wet the electrode and suggests an important advantage to be gained by the use of non-aqueous solvents with carbon electrodes.

Table 2.16 Chronopotentiometry of various commercial antioxidants in 95% ethanol		
c (µm/l)	ir1/2/C	Supporting electrolyte
A 2,6-Di-*t*-butylcresol		
10.10	124.0	LiClO$_4$
6.06	126.0	
3.03	136.0	
1.01	152.0	
B Age-Rite Alba: Hydroquinone monobenzyl ether		
10.10	111.0	LiCl
6.04	112.0	
3.02	122.0	
1.01	136.0	
C Flexone 6H: *N*′-phenyl-*N*′-cyclohexyl phenylenediamine		
9.38	84.2	LiCl
5.90	88.3	
2.95	89.8	
0.98	105.0	
D Age-rite Stalite: heptylated diphenylamine		
10.00	73.2	LiCl
6.02	74.6	
3.01	80.3	
1.00	93.0	
E Santovar A: 2,5-Di-*t*-amylhydroquinone		
10.10	91.1	LiCl
6.06	94.0	
3.03	98.0	
1.01	107.0	
F Flexone 3C: *N*-isopropyl-*N*′-phenyl phenylenediamine		
10.30	96.3	LiCl
6.17	99.4	
3.09	110.6	
1.03	119.3	

c (μm/l)	ir1/2/C	Supporting electrolyte
Table 2.16 Continued...		
G Age-Rite powder: *N*-phenyl-β-naphthylamine		
10.30	159.0	LiCl
6.21	157.0	
3.11	160.0	
1.03	186.0	
H Antioxidant 2246: 2,2′-methylene-bis-(6-*t*-butyl-4-ethylphenol)		
10.00	237.0	LiClO$_4$
6.00	229.0	
3.00	231.0	
1.00	243.0	
I Santowhite powder refined: 4,4′-butylidene-bis-(3-methyl-6-*t*-butylphenol)		
11.20	323.0	LiClO$_4$
6.73	316.0	
3.36	348.0	
1.12	410.0	
Reproduced with permission from G.A. Ward, Talanta, *1963*, **10**, *3, 261 [119]*		

2.15 Anodic Voltammetry

Budyina and Marinin [130] have described methods based on anodic voltammetry for the determination of Ionol (2,6-di-*t*-butyl-*p*-cresol) and quinol in polyester acrylates. To determine Ionol the sample is dissolved in 25 ml of acetone and a portion (10 ml) is treated with 2.5 ml of acetone and 5 ml of methanol and diluted to 25 ml with a solution 0.1 M in lithium chloride and 0.02 M in sodium tetraborate. A polarogram is recorded with a graphite-rod indicator electrode. To determine quinol, the sample (1 to 3 g) is dissolved in 80 ml of methanol or methanol:acetone (1:1) and the solution is diluted to 100 ml with the lithium chloride - sodium tetraborate solution. A polarogram is recorded under the same conditions. Concentrations are determined by the addition method. The values (*versus* the SCE) are 0.25 V for Ionol and 0.16 V for quinol.

2.16 Solvent Extraction – Nuclear Magnetic Resonance Spectroscopy (NMR)

HPLC followed by ^{13}C NMR spectroscopy has been used to determine PS oligomers in the molecular weight range up to 4800 in PS [131]; *n*-hexane-tetrahydrofuran or *n*-hexane-methylene dichloride were used as eluting solvents.

Carlson and co-workers [132] have discussed the identification of antioxidants in acetonitrile extracts of rubber vulcanisates. The sample is finely ground in a Wiley mill and the ground material (10 g) is shaken with 50 ml of acetonitrile for 30 minutes. The mixture is filtered, and the filtrate is evaporated to 20 ml at 60 °C and then cooled at –20 °C for 2 to 3 hours. The supernatant liquid is decanted from residual oil and evaporated to dryness at 60 °C, and the residue of antioxidant used for identification by MS, IR and NMR analysis (see **Figure 2.17**).
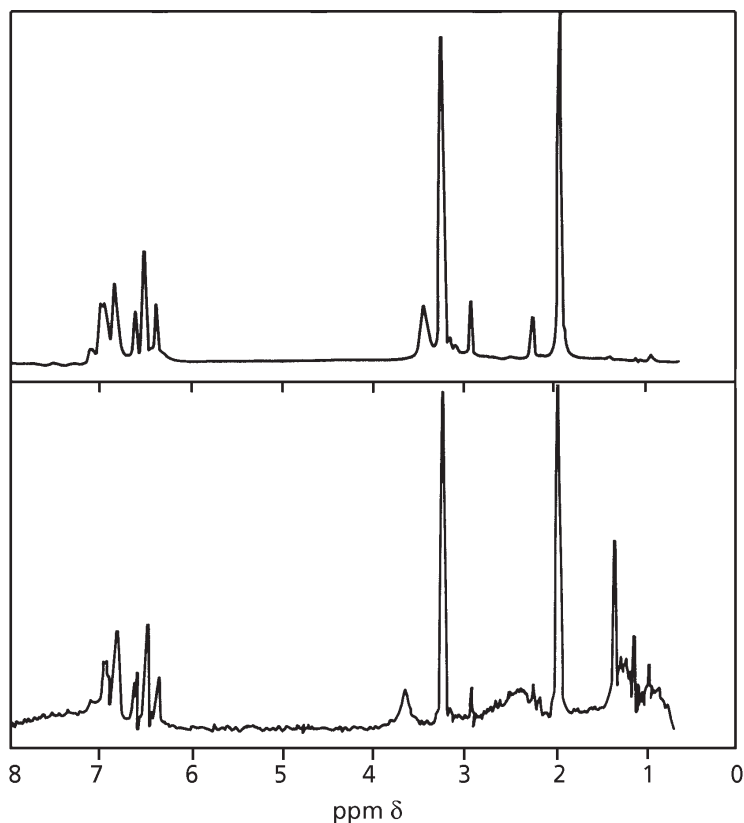
Figure 2.17 NMR spectra of Stabilite Alba (upper spectrum) and acetonitrile extract of a vulcanisate containing Stabilite Alba (lower spectrum). *From Carlson and co-workers, ACS [132]*

The choice of solvent for NMR analysis is important. Carbon disulfide and deuterated acetonitrile were used by Carlson and co-workers [132]. If the acetonitrile extract contained more than one antioxidant, the improper choice of solvent may lead to selective dissolution of the antioxidants. Comparison of the unknown and reference NMR spectra should only be done if both spectra were obtained using the same solvent. The NMR spectra of antioxidants will change in different solvents.

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3 Liquid Chromatography

3.1 Introduction

Theoretical investigations into this technique have shown that it is capable of achieving the resolving power of gas chromatography (GC). Liquid chromatography (LC) has undergone tremendous developments in recent years. The resolving power in chromatography in general depends on three factors: the number of theoretical plates (N), the relative selectivity $\Delta K/K$ and the relationship between the migration rate of the corresponding zone and that of the liquid phase (R):

$$Rs = (N/16)^{1/2} \, (\Delta K/K) \, (1 - R)$$

(K is a thermodynamic member and corresponds to the median distribution coefficient of two neighbouring coefficients). Assuming almost equal selectivities in the gas and liquid phases and a uniform R value of 0.5 with GC and LC which is common in practice, LC approaches the efficiency of GC, as far as comparable N values or heights of equivalent theoretical plates (HETP) which are closely related to this.

The new high-efficiency carrier materials for column chromatography are mainly particles with a solid core and a thin porous envelope with particle diameters in the micro range. Majors [1] tested the commercial carrier materials in an automatic high-performance liquid chromatograph (HPLC) system with antioxidants. He separated a four-component mixture of aromatic amines at HETP values of < 1 mm within 10 minutes and with good reproducibility on Corasil I (glass bead with a single layer of porous silica gel) loaded with β,β′-oxydipropionitrile. He also achieved separations of phenolic antioxidants as well as quantitative determinations in extracts of polyacetals the results of which are much superior to those of the infrared (IR)-spectrometric determination due to the high resolution with liquid-solid column chromatography (LSCC).

A diagram of an HPLC system is shown in **Figure 3.1**.

The unit employed a micro-regulating, high pressure feed pump equipped with an 11 mm plunger, capable of a maximum flow rate of 7.3 litres per hour and output pressure of
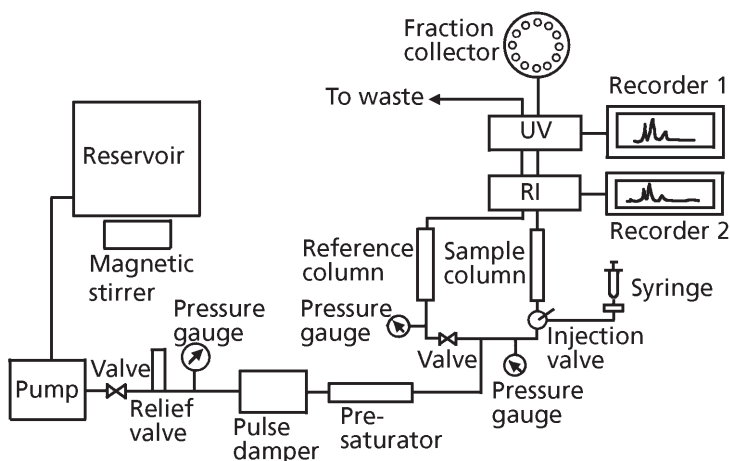
Figure 3.1 Diagram of HPLC system. RI: Refractive index detector, UV: ultraviolet detector
Source: Author's own files

34 MPa. The solvent reservoir was placed a few feet above the pump since a slightly positive inlet pressure was required for operation. The degassed solvent was slowly stirred by means of a magnetic stirrer and was heated externally to slightly above room temperature to keep the solvent degassed. A stock valve was placed on the high pressure side of the pump to aid in priming the pump or to shut off the solvent flow when required. A Circle Seal (Circle Seal Co., Anaheim, California USA) adjustable relief valve set at 34 MPa was placed on the high pressure side of the pump for safety in case a blockage occurred upstream. A Hellicoid Free Aura Gauge 0-34 MPa was used to monitor the output pressure. Downstream from the pressure gauge, the entire system was connected with 1 mm id, 1.6 mm od, stainless steel tubing to insure a minimal dead-volume in the system which is particularly desirable when changing solvents or solvent programming. For most experiments up to 17 MPa output pressure, an ALC-100 LC pulse damper (Waters Associates, Framingham, MA, USA) was used. In certain cases when extremely high inlet pressures were required, a Greer Olaer Accumulator (Greer Olaer Products, Los Angeles, California, USA), which can be charged with gas under pressure, has been used to minimise pulses.

Figure 3.2 shows high speed chromatograms obtained with mixtures of *N,N*-diethylaniline, *N*-ethylaniline, diphenylamine and *N*-phenyl-2-naphthylamine amine antioxidants used in rubber manufacture.

Figure 3.3 shows the separation achieved by Majors [1] of three plasticisers used in 1% isopropanol in hexane extracts of polyvinyl chloride (PVC). The plasticisers cannot be
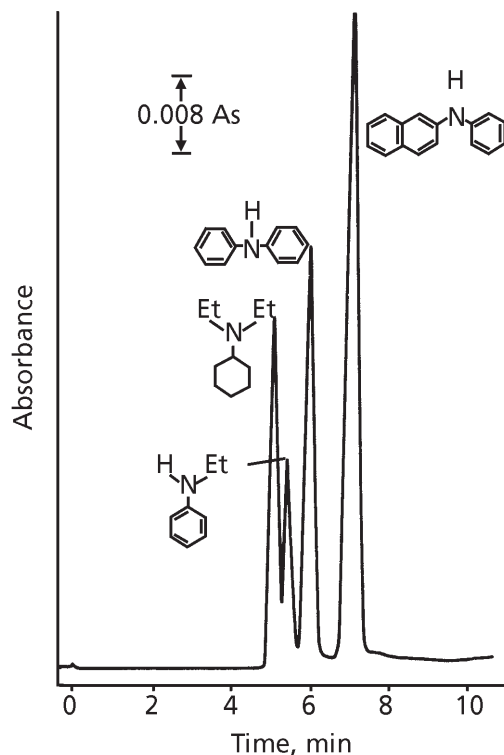
Figure 3.2 Separation of aromatic amine antioxidants using Zipax. Column: 1000 mm x 2.1 mm id, packing: 0.5% β,β´-oxydipropionitrile on 20-37 μm Zipax support, carrier gas: iso-octane, flow rate: 0.31 ml/min, sample: 10.6 μl of a mixture of 9.5 μg/ml each of *N,N*-diethylaniline and *N*-ethylaniline, 29 μg/ml of diphenylamine and 52 μg/ml of *N*-phenyl-naphthylamine in iso-octane
Source: Author's own files

directly determined by GC but must first be saponified. The separation of all three was obtained in less than eight minutes on Zipax with HETP.

Majors [1] also studied the separation of an hindered phenolic antioxidant by high speed liquid-solid column chromatography (**Figure 3.4**).

Campbell and Wise [2] applied column chromatography to the determination of known phenolic antioxidants in polyethylene (PE). This method is applicable to the analysis of mixtures of Santowhite powder (4, 4´-butylidene-bis-(6-*tert*-butyl-*m*-cresol) with BHT (2,6-di-*tert*-butyl-*p*-cresol) and mixtures of Santonox R (4, 4´-thio-bis-(6-*tert*-butyl-*m*-
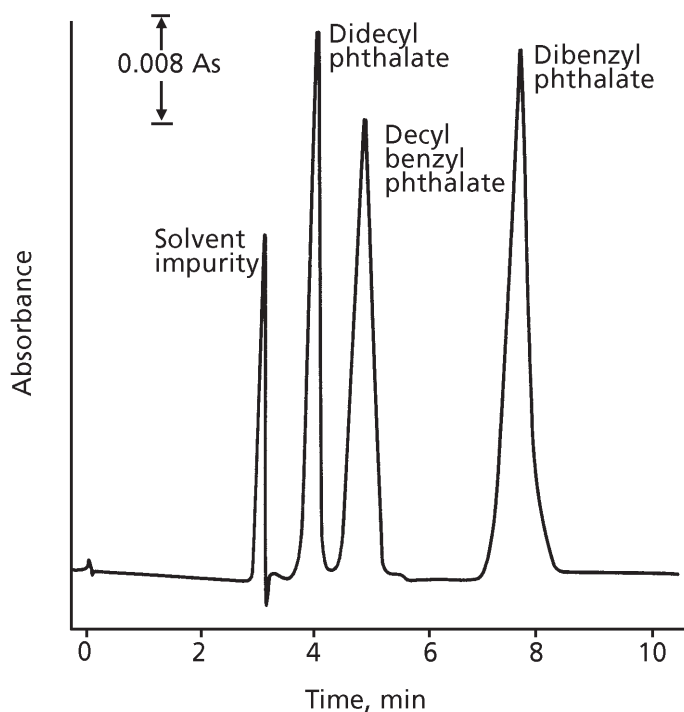
Figure 3.3 Separation of phthalate plasticisers using Zipax support. Column and carrier - same as Figure 3.2; flow rate: 0.50 ml/min, sample: 10.6 μl of a mixture of 0.40 μl/ml each of didecyl phthalate and decyl benzyl phthalate and 0.35 mg/ml of dibenzyl phthalate in heptane *Reproduced from Majors, Journal of Chromatographic Science [1]*

cresol) with BHT in the concentration range 0.01-0.3%. This method should be equally applicable to other types of polyolefins.

Total additives are first removed from the PE sample by extraction with warm chloroform. The chloroform extract is then transferred to a column comprising a slurry of aluminium oxide in the same solvent.

Elution with chloroform removes BHT only as the first fraction. Continued elution of the column with solutions of 10% water in methanol removes Santowhite powder or Santonox R as a separate pure fraction, free from BHT. Additives can then be determined in the respective extracts after they have been diluted to a standard volume with solvent by ultraviolet (UV) spectroscopy.
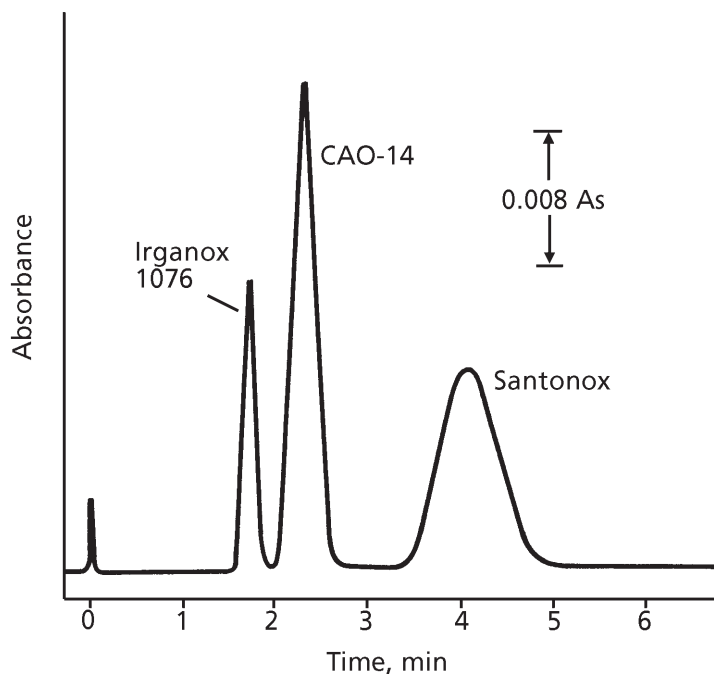
Figure 3.4 Liquid-solid column chromatographic separation of hindered phenolic antioxidants using Corasil II. Column: 1000 mm x 2.1 mm id; packing: 37-50 nm Corasil II (activated at 110 °C), carrier: 1% (*v/v*) iso-propanol in hexane; flow rate: 0.95 ml/min; Sample: 10.6 µl of a mixture of 0.54 mg/ml Irganox 1076, 0.81 mg/ml CAO-14, and 1.4 mg/ml Santonox R dissolved in carrier
Reproduced from Majors, Journal of Chromatography [1]

Typical elution chromatograms which show the separation of mixtures of BHT –Santonox R, are shown in **Figure 3.5**. It is noted that the water-methanol effluent front elutes the bulk of the Santonox R. A large error would result if some of the first part of the aqueous methanol fraction were discarded.

Campbell and Wise [2] verified their procedure by analysing PE samples containing known amounts of antioxidants. The analytical results are given in **Table 3.1**.

Modern HPLC has been developed to a very high level of performance by the introduction of selective stationary phases of small particle sizes, resulting in efficient columns with large plate numbers per litre.
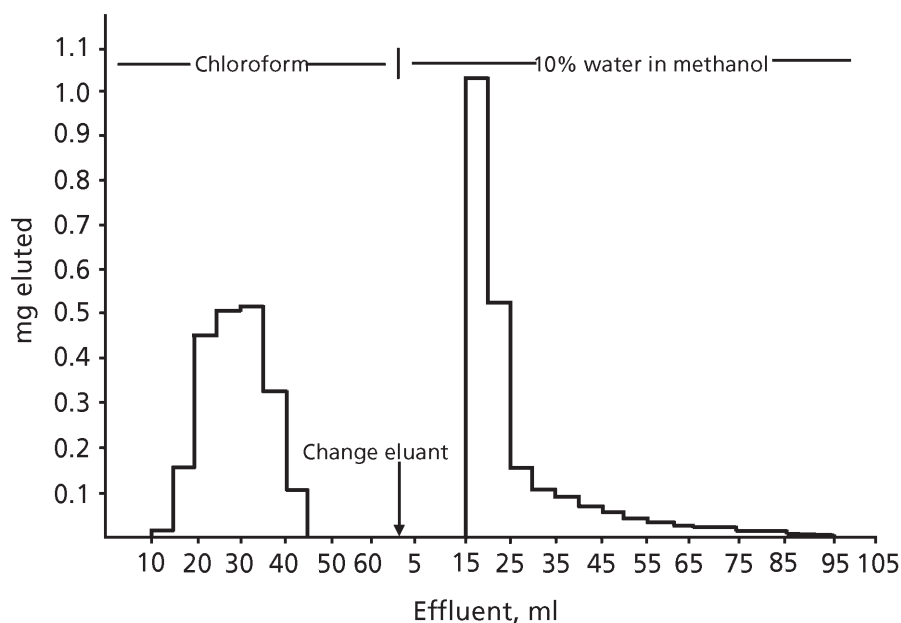
Figure 3.5 Elution chromatogram of butylated hydroxy toluene and Santonox
Reproduced from Campbell and Wise, Journal of Chromatography [2]

Table 3.1 Analysis of some standard polyethylene samples by combined column chromatography/UV spectroscopy								
BHT			**Santowhite Powder**			**Santonox R**		
% added	**% found**	**% recovered**	**% added**	**% found**	**% recovered**	**% added**	**% found**	**% recovered**
0.270	0.265	98.0	0.260	0.264	101.3	-	-	-
0.263	0.260	98.8	-	-	-	0.257	0.248	96.5
0.0513	0.0508	99.2	0.253	0.249	98.4	-	-	-
0.0535	0.0534	99.8	-	-	-	0.251	0.245	97.5
Reproduced from Campbell and Wise, Journal of Chromatography *[2]*								

The Zipax material used as a column packing has been reported to have a relatively inert surface [3-5] whereas the Corasil support is also recommended for liquid-solid column chromatography [3-5]. Little has been reported on the use of these solid-core silicaceous backboned Corasil supports with a polar liquid-coating in liquid-liquid chromatography.

Kirkland [6] has studied the support in some detail for several model systems, and has reported much improved performance for this material in liquid-liquid chromatography when compared to coated glass beads or diatomaceous earth. A number of separations have been described using Durapak type supports and by Majors [1] using various solid core supports operating at 34 MPa.

There are several types of chromatographic columns used in HPLC. The most commonly used chromatograph mode in HPLC is reversed-phase chromatography. Reversed-phase chromatography is used for the analysis of a wide range of neutral and polar organic compounds. Most common reversed phase chromatography is performed using bonded silica-based columns, thus inherently limiting the operating pH range to 2.0-7.5. The wide pH range (0-14) of some columns (e.g., Dionex IonPac NSI and NS 1-5 nm columns) removes this limitation, consequently they are ideally suited for ion-pairing and ion-suppression reversed-phase chromatography: the two techniques which have helped extend reverse-phase chromatography to ionisable compounds.

Typically, reversed-phase ion-pairing chromatography is carried out using the same stationary phase as reversed-phase chromatography. A hydrophobic ion of opposite charge to the solute of interest is added to the mobile phase. Samples which are analysed by reverse-phase ion-packing chromatography are ionic and thus capable of forming an ion pair with the added counter ion. This form of reversed-phase chromatography can be used for anion and cation separations and for the separation of surfactants and other ionic types of organic molecules.

Ion suppression is a technique used to suppress the ionisation of compounds (such as carboxylic acids) so they will be retained exclusively by the reversed-phase retention mechanism and chromatographed as the neutral species.

Four basic types of elution are used in HPLC. These are described in Sections 3.1.1, 3.1.2, 3.1.3, and 3.1.4.

3.1.1 The Isocratic System

This consists of a solvent delivery for isocratic reversed phase and gel filtration chromatography.

This isocratic system provides an economic first step into HPLC techniques. The system is built around a high-performance, dual-piston, pulse-free pump providing precision flow from 0.01 to 5 ml/min.

Any of the following detectors can be used with this system:

- fixed wavelength UV detector,

- variable UV visible,

- wavelength monitor,

- rapid diode array spectral detector (discussed later),

- refractive index detector,

- electrochemical detector,

- wavescan EG software.

3.1.2 Basic Gradient System

This is a simple upgrade of the isocratic system with the facility for gradient elution techniques and greater functionality. The basic system provides for manual operating gradient techniques such as reversed-phase, ion-exchange and hydrophobic interaction chromatography. Any of the detectors listed in the isocratic system section can be used.

3.1.3 Advanced Gradient System

For optimum functionality in automated systems designed primarily for reversed-phase chromatography and other gradient techniques, an advanced-gradient system is recommended. Key features include:

- A configuration that provides the highest possible reproducibility of results.

- A two-pump system for highly precise and accurate gradient formation for separation of complex samples.

- Full system control and advanced method developments provided from a LC controller.

- Precise and accurate flows ranging from 0.01 to 5 ml/min.

3.1.4 The Inert System

By a combination of the use of inert materials (glass, titanium, and inert polymers) this system offers totally inert fluidics. Primary features of the system include the following:

- The ability to perform isocratic or gradient elution by manual means,

- Full system control from a liquid chromatography controller, and

- Precise and accurate flows from 0.01-5 ml/min.

This is the method of choice when corrosive buffers, e.g., those containing chloride or aggressive solvents, are used.

3.2 Chromatographic Detectors

Details concerning the types of detectors used in HPLC are given in **Table 3.2**. The most commonly used detectors are those based on spectrophotometry in the region 185-400 nm, visible UV spectroscopy in the region 185-900 nm, post-column derivatisation with fluorescence detection (see Section 3.2.1), conductivity and those based on multiple wavelength UV detectors using a diode array system detector (see Section 3.2.2). Other types of detectors available are those based on electrochemical principles, refractive index, differential viscosity and mass detection.

3.2.1 Post-Column Derivatisation - Fluorescence Detectors

Modern column LC has been developed to a very high level by the introduction of selective stationary phases of small particle sizes, resulting in efficient columns with large plate numbers per metre. The development of HPLC equipment has been built upon the achievements in column technology, but the weakest part is still the detection system. UV/vis and fluorescence detectors offer tremendous possibilities, but because of their specificity it is possible to detect components only at very low concentrations when using a specific chromophore or fluorophore.

The lack of a sensitive all-purpose detector in LC like the flame ionisation detector in GC, is still disadvantageous for LC for the detection of important groups of compounds. Consequently, chemical methods are increasingly used to enhance sensitivity of detection. On-line post column derivatisation started with the classic work of Spackman [8] and has found increasing interest and use (Frei and Lawrence [9, 10], Krull [11], Engelhardt and Neue [12], Engelhardt and Lillig [13], Engelhardt and co-workers [14], and Uihlein and Schwab [15]).

With on-line post-column detection the complexity of the chromatographic equipment increases. An additional pump is required for the pulseless and constant delivery of the reagent.

Table 3.2 Detectors used in HPLC

Type of detector		Supplier	Detection Part No.	HPLC Instrument Part No.
Spectrophotometric (variable wavelength)	190-390 nm	Perkin Elmer	LC90	-
	195-350 nm	Konotron	735 LC	Series 400
	195-350 nm	Shimadzu	SPD-7A	LC-7A
	195-350 nm	Shimadzu Shimadzu	SPD-6A	LC-8A
	195-350 nm	LKB	SPD-6A	LC-6A
	206-405 nm (fixed wavelength choice of 7 wavelengths between 206 and 405 nm)		2510 Uvicord SD	
	190-370 nm)	Cecil Instruments		
	190-400 nm)			
Variable wavelength UV - visible	190-600 nm	Varian	2550	2500
	190-600 nm	LKB	2151	Uvicord SD
	190-700 nm	Konotron	432	Series 400
	190-800 nm	Konotron	430	Series 400
	185-900 nm	Konotron	720 LC	Series 400
	200-570 nm	Konotron	740 LC	Series 400
	190-800 nm	Dionex	VDM II	Series 400
	190-750 nm	Isco	V4	Microbo system
	214-660 nm (18 preset wavelengths)	Isco	UAS and 228	
	195-700 nm	Shimadzu	SPD-7A	LC-7A
	195-700 nm	Shimadzu	SPD-6AV	LC-8A
	195-700 nm	Shimadzu	SPD-6AV	LC-6A
	193-350 nm	Shimadzu	SPD-6A and SPDM-6A	LC-9A
			SPD-6AV	LC-9A
	196-700 nm	Shimadzu	-	LC-10A
	190-900 nm	Shimadzu	LC Star System	Star 9060
	190-900 nm	Varian	System for biomolecules	-
	190-900 nm	Pharmacia	-	LC/1210/1205

Table 3.2 Continued...

Type of detector		Supplier	Detection Part No.	HPLC Instrument Part No.
Variable wavelength UV - visible (continued...)	190-900 nm	ICI	Programmably variable wavelength detector	9050 series
	190-600 nm	Hewlett Packard	CE 1200	Series 1000
	380-600 nm	Cecil Instruments	750/16 and 5750/11	
	190-800 nm	Applied Chromatography Systems		
Conductivity	-	Dionex	CDM 11	4500 i
		Roth Scientific	-	Chrom-A-Scope
		Shimadzu	CDD-6A	LC-9A
Electrochemical detector	-	Dionex	PAD-11	4500 i
		LKB	2143	Wavescan EG
		Roth Scientific	-	Chrom-A-Scope
		Cecil Instruments	CE 1500	-
		PSA Inc	5100A	-
		Applied Chromatography Systems	650/350/06	-
		Shimadzu	L-ECD-6A	LC-9A
Refractive index detector	-	LKB	2142	Wavescan EG
		Roth Scientific	-	Chrom-A-Scope
		Cecil Instruments	CE 1400	Series 1000
		Shimadzu	RID-6A	LC-9A
			-	LC-1240
Fluorescence	220-900	Shimadzu	RF-551	LC-9A
	-	Shimadzu	FLD-6A	LC-9A
	220-650	Shimadzu	RF 335	LC-9A

Table 3.2 Continued...

Type of detector	Supplier	Detection Part No.	HPLC Instrument Part No.
Differential viscosity mass detection (evaporative)	Roth Scientific Applied Chromatography Systems	- 750/14	Chrom-A-Scope -
Diode array	Varian Perkin Elmer LKB Hewlett Packard	9065 LC 135, LC 235 and LC 480 2140 Multiple wavelength detector	2000L and 5001 5500 Series - - 1050 Series

Reproduced with permission from T.R. Crompton, The Polymer Reference Book, Rapra Technology, Shrewsbury, UK, 2006, Table 7.2. [7]

3.2.2 Diode Array Detectors

With the aid of a high-resolution UV diode array detector, the eluting components in a chromatogram can be characterised on the basis of their UV spectra. The detector features high spectral resolution (comparable to that of a high-performance UV spectrophotometer) and high spectral sensitivity. The high spectral sensitivity permits the identification of spectra near the detection limit, i.e., within the sub-milliabsorbance range.

Several manufactures (Varian, Perkin-Elmer, LKB and Hewlett Packard, see **Table 3.2**) have developed diode array systems. In the polychromator incorporated in the Perkin-Elmer LC 480 diode array system the light beam is dispersed within the range 190-430 nm onto a diode array consisting of 240 light-sensitive elements. This effects a digital resolution of 1 nm, which satisfies the spectral resolution determined by the entrance slit.

3.2.3 Electrochemical Detectors

These are available from several suppliers (**Table 3.2**). ESA supply the model PS 100A Coulochem multi-electrode electrochemical detector. Organics, anions and cations can be detected by electrochemical means.

3.3 Antioxidants

Figure 3.6 shows a chromatogram of a mixture of additives found by chromatography of a mixture of additives, solvent extracted with methyl chloride from a sample of polypropylene (PP). The mobile phase was water (channel A) and acetonitrile (channel B). The analysis performed on a Hewlett Packard Model HP109 Series M LC equipped with a diode array detector, shows the presence of methylated hydroxy toluene, methylated hydroxyethyl benzene, Amide E (erucamide), Irganox 1010 and Irganox 1076 (both sterically hindered phenols).

A similar separation of a methylene chloride extract of PE was achieved by HPLC [16]. The solvent programmer is set to 90% from 100% heptane to 100% methylene chloride in 5 minutes. The total flow rate is 3 ml/min. The Model 450 UV detector is set at 0.2 or 0.4 absorbance unit sensitivity and the recorder chart speed is 1 cm/min. Duplicate injections of 100 µl of each of the standard and sample solutions are made. The mobile phase gradient is started at the point of injection.
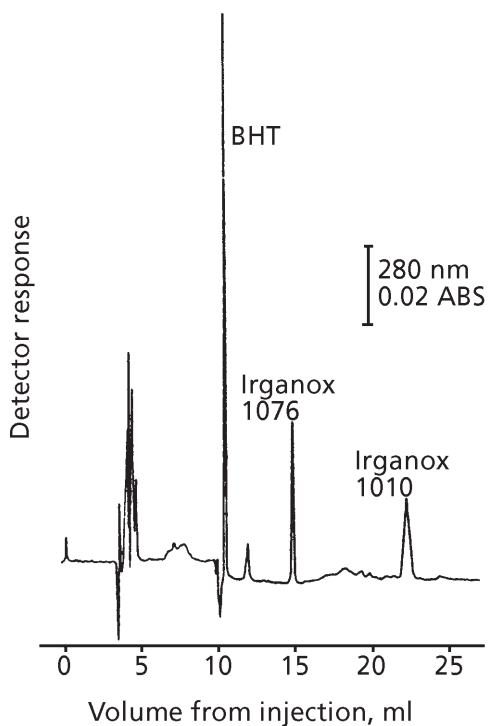

Figure 3.6 Chromatogram of 100 µl extract from 2.076 g PE
Source: Author's own files

Thilén and Shishoo [17] optimised experimental parameters for the quantification of polymer additives (Irganox 1010 and Irgafos 168) using supercritical fluid extraction combined with HPLC.

The experimental parameters of temperature pressure and modifiers were varied to find the best extraction conditions. The optimum pressure for extraction of these PP additives were found to be 12 MPa or 38 MPa, with methanol as the modifier. The quantitative extractions were significantly faster than those reported previously in the literature.

HPLC of polymer extracts has been used to determine dilauryl dithiopropionate, Irganox 1076 and distearyl-dithiopropionate in polyolefins [18], amine antioxidants and antiozonates in rubbers [16], Irganox 1076, Irganox 1010 and BHT in PE [19] and miscellaneous antioxidants, light stabilisers in polyolefins [20, 21] and Santonox R, Ethanox 736, CAO-5, Irganox 1035, Irganox 259 and Topanol [22] in polyolefins and also the determination of antioxidants and accelerators in vulcanised rubber formulations [23-25].

When HPLC is used in conjunction with other techniques such as mass spectroscopy (MS) and IR spectroscopy then identification and quantitation of polymer additives becomes more certain.

One of the limitations of GC and consequently of GC-MS is that in many cases polymer additives are insufficiently volatile to be separated on GC columns operating at even the maximum of their temperature range. As a consequence of this, there has, in recent years, been a growing interest in applying HPLC which is not subject to this temperature limitation, to the analysis of polymer extracts.

3.3.1 Instrumentation

Hewlett Packard, for example, supply the HP 5988A and HP 5987A mass-selective detectors for use with LC (see Appendix 1). This particle beam LC-MS uses the same switchable electron impact chemical ionisation source and the same software and data systems that are used for a GC-MS system. Adding a GC creates a versatile particle-beam LC-GC-MS system that can be switched from LC-MS to GC-MS in an instant.

Electron impact spectra from the system are reproducible and can be searched against standard or custom libraries for positive compound identification. Chemical ionisation spectra can also be produced.

The particle beam system is a simple transport device, very similar to a two-stage jet separator. The solvent vapour is pumped away, while the analyte particles are concentrated in a beam and allowed to enter the MS source. Here they are vaporised and ionised by electron impact.

The different ways a particle beam LC-MS can be configured reflect the versatility of the system in accommodating both the application and the availability of existing instrumentation. The system consists of these elements:

- Particle beam interface mounted on the Hewlett Packard 5988A or 5987A MS.

- LC (either the integrated Hewlett Packard 1090 or modular Hewlett Packard 1050).

- Data system (either HP 59970C Chem Station for single instrument operation or the Hewlett Packard 100 RTE A-series for multi-instrument or multi-tasking, multi-user operation).

3.3.2 Applications

Like other forms of molecular spectroscopy, MS may be used as a 'fingerprint' technique to identify the components of additive systems extracted from polymer compositions. The strengths of MS are high sensitivity and the ability to distinguish between closely related compounds of differing relative molecular mass, e.g., the various alkyl thiodipropionates used as synergistic stabilisers in polyolefins and the UV absorbing benzotrizole derivatives. Often it is not necessary to separate the components before examination as some separation may be achieved by careful variation of the sample probe temperatures to produce in effect, a fractional distillation of the components. The presence, however, of large amounts of low relative molecular weight polymers such as PE and PP can cause interference by producing a high hydrocarbon background extending to several hundred relative atomic mass units. In such instances thin-layer chromatographic separation can be used as a clean-up procedure.

Yu and co-workers [26] discussed LC interfaces for bench-top single quadruple LC-MS. The two most popular interfaces are particle beam and atmospheric pressure ionisation types. The system was applied to the analysis of additives in PP. Dilts [27] used a photodiode array detector coupled with particle beam LC-MS to characterise degradation of Irganox 1010, Irganox 1076 and Irgafos 16S in polyolefins.

Vargo and Olson [28] used MS detection in series with absorbance detection to identify or characterise antioxidants and UV light stabilising additives in acetonitrile extracts of PP, which were separated by LC.

Nanogram quantities of additives could be detected. The procedure was used to characterise additives in PP samples of unknown composition. BHT and Irganox 1076 were identified in the extract of an automotive component moulding. In addition, several other additives were identified (palmitic acid, dioctylphthalate, stearic acid and octadecanol).

Sidwell [29] examined extractables from plastic and rubber components of medical products by LC-MS and GC-MS.

3.4 Oligomers

Oligomers are very low molecular weight polymers. Thus PS usually contains low concentrations of monomer, dimer, trimer and tetramer of the general formula:

$$(C_6H_5 - CH = CH_2)_n, \text{ where n = 1 to 4}$$
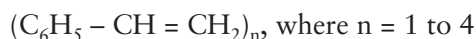
Methods for the determination of polymers in extracts of PS and polystyrene copolymers are based on particle beam LC-MS. Molecular cores were observed up to n = 18 oligomers at *m/z* 1930 [30, 31].

Petro and co-workers [31] used a moulded monolithic rod of macroporous PS-divinyl benzene copolymer as a separation medium for the HPLC of styrene oligomers and copolymers, e.g., styrene-2-naphthyl-methacrylate. On column precipitation redissolution chromatography is an alternative to size-exclusion chromatography (SEC). The solvent gradient used comprises a poor solvent (water, methanol, acetonitrile) and increasing amounts of a good solvent such as tetrahydrofuran.

Okada [32, 33] separated polyoxyethylenes (POE) on a K^+ loaded cation exchange resin with indirect conductiometry.

The detection is based on a difference in mobility between bare K^+ and a POE-K^+ complex. The effects of K^+ concentration in mobile phases and the complexation ability of POE on peak size are quantitatively evaluated. On the basis of theoretical considerations, the quantification scheme, where one monodisperse POE is used as a standard material for determination of all oligomers detected, is also presented. This scheme was applied to POE without chromophores, such as polyethylene glycols (PEG) and polyoxyethylene dodecyl ethers.

Tables 3.3 and **3.4** show the results of the determination of oligomers contained in 0.5 mg/ml sample solutions of PEG 400 and POE(9)D, respectively. Both analyses were carried out in purely methanolic mobile phases. PEG and POE were selected as standards for corresponding oligomer mixtures. K_f values for the POE(*n*)D series are listed in **Table 3.4** together with analytical results. Since K_f values generally included approximately 5% relative errors, the concentrations listed in tables show more ambiguity.

Figure 3.7 shows an example of an oligomer separation achieved by this method for various POE-HPLC has also been applied to the determination of oligomers in polyesters [34], alkylphenyl formaldehyde resins [35, 36] and polyethylene terephthalate [37, 38].

	Table 3.3 Data for the quantifiation of oligomers in PEG 400[a]				
n[b]	K_f (σ[c]), M^{-1}		Relative peak area	Concentration ratio	Concentration, mM
	Methanol	Acetone-methanol			
6[d]	219 (10)	227 (15)	1	1	0.53
7	487 (29)	433 (25)	3.16	1.42	0.76
8	579 (12)	527 (30)	5.65	2.14	1.13
9	884 (17)	639 (36)	6.90	1.71	0.91
10	1050 (33)	790 (43)	7.40	1.54	0.82
11	1200 (37)	928 (51)	6.24	1.14	0.60
12	1590 (65)	1130 (64)	4.36	0.60	0.32
13	1960 (98)	1370 (82)	2.69	0.30	0.16
14	2230 (170)	1550 (105)	1.51	0.15	0.08
15	2530 (198)	1680 (96)	0.67	0.06	0.03

[a]: *Sample concentration was 0.5 mg/l*   [b]: *Number of repeating oxyethylenes*
[c]: *Standard deviation*   [d]: *Standard compound*
Reproduced with permission from T. Okada, Analytical Chemistry, *1990,* **62**, *734, ACS* [32]

	Table 3.4 Data for the quantification of oligomers in POE(9)D[a]				
n[b]	Kf, M-1	σ[c]	Relative peak area	Concentration ratio	Concentration, 10^{-5} M
7	381	9	0.75	1.30	9.9
8[d]	660	8	1	1	7.6
9	848	36	1.34	1.04	7.9
10	1050	23	1.62	1.02	7.8
11	1280	36	1.81	0.93	7.1
12	1490	44	1.79	0.79	6.0
13	1860	86	1.5	0.62	4.7
14	2080	139	1.70	0.54	4.1
15	2160	53	1.55	0.47	3.6
16	2270	94	1.26	0.37	2.8

[a]: *Sample concentration was 0.5 mg/l*   [b]: *Number of repeating oxyethylenes*
[c]: *Standard deviation*   [d]: *Standard compound*
Reproduced with permission from T. Okada, Analytical Chemistry, *1990,* **62**, *734, ACS* [33]
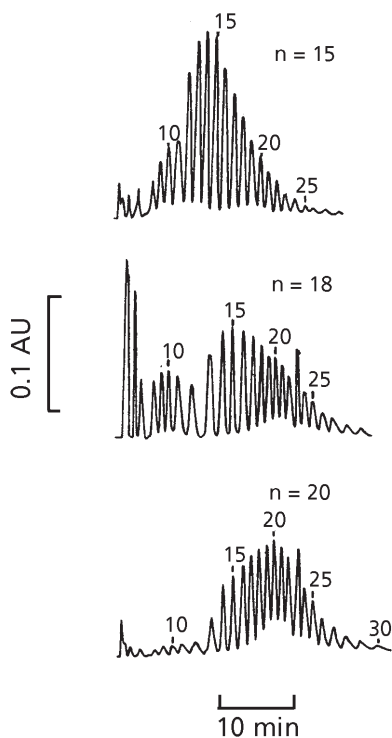
Figure 3.7 Oligomer separation of POE(15)NP, POE(18)NP, and POE(20)NP. Detection: UV (280 nm); sample concentration: 0.5 mg/ml. Linear gradient condition was as follows: methanol (1-10 min) → methanol containing 5 mM KCl (25 min) for POE(18)NP and POE(20)NP
Reproduced from Okada, American Chemical Society [33]

3.5 Acrylic Acid Monomer

Brown [39] has described an HPLC method for the determination of acrylic acid monomer in polyacrylate in which a known mass of polymer (500 mg) is added to 50 ml of a methanol:distilled water mixture (1 + 1) and allowed to stand overnight to complete the extraction of the monomer from the polymer. Various mixtures of methanol and distilled water (range 1 + 99 to 99 + 1; 50 ml) are added to the polymer for 1, 2, 8 or 24 hours.

A portion (12 μl) of the sample is injected into the liquid chromatograph's Rheodyne valve and chromatographed under the following conditions - column: Whatman PXS 10/25

nm PAC (250 x 4 mm id); mobile phase: 0.01% *v/v* orthophosphoric acid in distilled water; flow rate: 4 ml/min; pressure: 14 MPa; detector wavelength: 195 nm; chart speed: 0.5 cm/min; and absorbance scale: 0.02. According to the sensitivity required, duplicate portions of the sample (1-100 µl) are injected. The concentration of acrylic acid is found by comparison with a previously prepared calibration graph of total absorbance *versus* original acrylic acid concentration.

3.6 Acrylamide Monomer

HPLC using the reverse phase mode, has been used to determine acrylamide mononer and related compounds, including methacrylonitrile in polyacrylamide. Water soluble compounds such as acrylamide and methacrylamide have sufficient lipophilic character that they can be retained and separated on HPLC reverse-phase columns using water as the eluent. By employing a low wavelength UV detector, these compounds can be measured with high sensitivity. The relative precision of the 95% confidence level for acrylamide is ± 7.5%.

In this procedure the polymer is extracted for 4 hours with methanol/water (80 + 20) and the extract injected on to a Partisil-10 OD-2, 4 x 250 mm reverse phase column. These extracts can also be examined by ion exclusion liquid chromatography [40].

3.7 Amines

Winkler and co-workers [41] determined free primary amines in polymeric amine hardness by reversed phase liquid chromatography.

3.8 Plasticisers

Mukoyama and Mori [42] investigated the elution behaviour of alkylbenzenes, phthalate esters, oligostyrenes and prepolymers of epoxy resins and methylated melamine-formaldehyde resins on a column packed with hydrophilic poly-6-hydroxy-ethyl-methacrylate.

Criddle [43] has described a column chromatographic procedure for the identification and semi-quantitative determination of plasticisers in PVC. In this procedure the plasticiser is first Soxhlet extracted from 1 to 2 gram of PVC sample using anhydrous diethyl ether. Ether is then evaporated from the extract and residual traces of PVC precipitated by the addition of 2 ml of absolute ethanol. Following filtration of any polymer, the ethanol is finally evaporated off to provide a PVC free plasticiser extract.

Other plasticiser determinations in PVC include dibutylphthalates, di-2-ethylhexylphthalate, di-iso-decyl phthalate and tricresyl phosphate [18] and di-decylphthalate, di-decyl benzyl phthalate and dibenzyl phthalate [1].

3.9 Additive Mixtures

HPLC is very useful in additive studies on polymer extracts. The technique can be used for both reverse phase and absorption columns and isocratic and gradient elution [44-48].

Floyd [49] used two-dimensional SEC/reversed phase liquid chromatography in the analysis of additives in cellulose acetate.

3.10 High Performance Liquid Chromatography – Infrared Spectroscopy

In the work discussed so far in this chapter, IR spectroscopy (or UV spectroscopy) has been merely used by scanning the column effluent at a simple appropriate wavelength in order to detect particular compounds as they are eluted in the column effluent.

Fiorenza and co-workers [50] have described a technique based on column chromatography on neutral alumina for the separation of antioxidants, plasticisers, and so on, in rubber extracts (**Figure 3.8**). They detected the separated compounds by monitoring the effluent with a LKB 254 nm UV detector (**Figure 3.9**). In this procedure a carbon tetrachloride solution of the sample is applied to an alumina column wetted with the same solvent and the column is successively eluted with carbon tetrachloride, mixtures of carbon tetrachloride and benzene, benzene, mixtures of benzene and absolute ethanol, and finally, ethanol. Separations were carried out on a scale to provide enough of each separated compound for the preparation of IR and UV spectra.

Dwyer [51] used a combination of chromatography and IR spectroscopy to provide a versatile tool for characterisation of polymers. HPLC-Fourier-transform IR spectroscopy interface systems deposit the output of a chromatograph on an IR optical medium, which is then scanned to provide data as a time-ordered set of spectra of the chromatogram. Polymer analysis applications described include the identification of polymer additives, the determination of composition/molecular weight distributions in copolymers, the mapping of components of polymer alloys and blends, molecular configuration changes in polymers, and component identification in complex systems.

Jansen [52] developed an on-line LC-IR system for the analysis of additives in polymer extracts.

Ultraviolet spectra of individual pure components of mixture
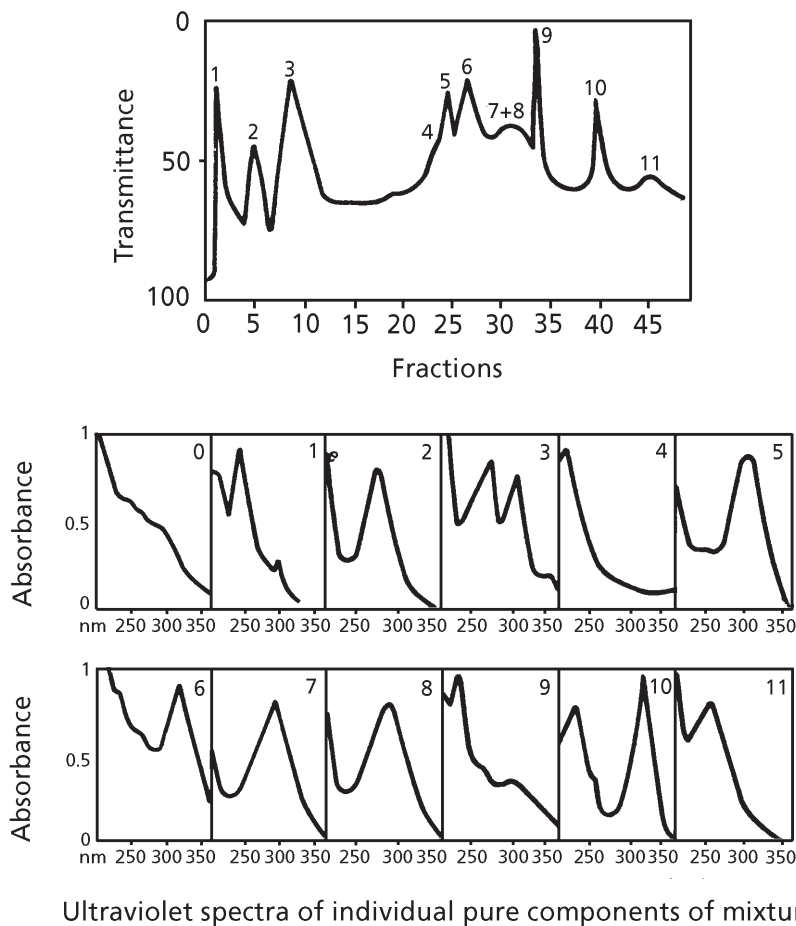
Figure 3.8 Column chromatography on alumina of antioxidants, accelerators and plasticisers in rubber extracts and UV spectra of separated compounds
Reproduced from Fiorenza and co-workers, Materie Plastiche ed Elastomerie [50]

3.11 Gel Permeation Chromatography

This technique has found limited applications in polymer additive analysis in plastics and rubbers. These include aromatic amines and antiozonants in rubber extracts [2, 50-62], and di-laurylthiodipropionate in polymer extracts [56].

Protivova and Pospisil [19] have reported on the behaviour of some amine antioxidants and antiozonants and some model substances (phenols, aromatic hydrocarbons and amines)
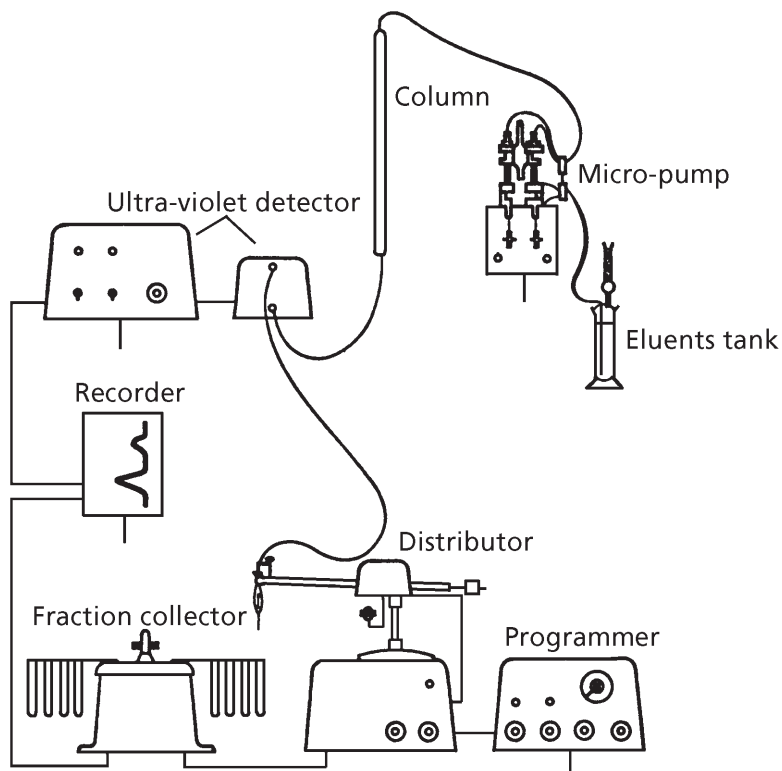
Figure 3.9 Experimental system employed in column chromatography of rubber extracts. *From Fiorenza and co-workers, Materie Plastiche ed Elastomerie [50]*

during gel permeation chromatography and have applied this technique, to the analysis of rubber extracts. Coupek and co-workers [53-56] and Protivova [57] have discussed the application of gel permeation chromatography to stabilisers of various types but have not discussed the use of this technique in quantitative analysis.

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4 Gas Chromatography

Measuring trace amounts of residual monomers in a synthetic polymer by gas-liquid chromatography (GLC) has been used for over a quarter century [1-3]. A recent review of gas chromatography (GC) polymer analysis has shown it to be useful for monitoring devolatilisation of unreacted monomers and solvent residues, particularly when they are an environmental hazard. Other reasons for analysis include: establishing the experimental conditions for polymer formation, and overall control of odour [4].

There are several injection methods currently used in GC monomer determinations. However, all of these techniques fall into two categories: direct injection and injection of the vapour above the polymer, i.e., headspace analysis or polymer solution. Direct injection of a polymer, or its precipitates, is perhaps the most common method. This technique requires both an inert material in the injection port to trap the polymer, and a narrow 'window of acceptance' on the injection port temperature. High temperatures lead to polymer decomposition while low temperatures prevent fast volatilisation of the monomer. In addition, the sample viscosity must be low enough to allow handling with a syringe.

There has been a great amount of recent interest in GLC separation of monomers in polymeric matrices. A direct injection approach has been reported, in which a copolymer was precipitated with concentrated acids and subsequently extracted with an organic solvent. This method avoids polymerisation of the monomer in the injection port, as well as permitting use of low-viscosity (aqueous) solvents. Other approaches include extractive distillation prior to separation, using either packed column [2] or capillary GLC [3].

The application of GC to the determination of various types of additives and adventitious organic compounds in plastics and rubbers is reviewed next.

4.1 Antioxidants

A gas chromatographic method for the determination of antioxidants and ultraviolet stabilisers in low-density polyethylene was developed which involved a binary solvent

extraction technique and temperature programmed mega-bore capillary GC with flame ionisation detection. Use of a mega-bore column gave a higher dynamic detection range. Additives were recovered at greater than 99% with a precision of 3-5% relative standard deviation (RSD).

Gaeta and co-workers [4] have described a gas chromatographic method for determining a number of commercial antioxidants such as, alkylated cresols, amines and substituted *p*-phenylene-diamines (2,6 di-*tert*-butyl *p*-cresol, *N*-phenyl-2-naphthylamine, *N*, *N′ sec*-heptyl phenyl-phenylendiamine) in oil-extended synthetic polymers such as polybutadiene or styrene-butadiene rubber. This involves extracting the antioxidant from the polymer with ethanol, taking up the concentrated extract with the appropriate solvent and analysing the resulting solution by GC. They found by the use of standard solutions of the antioxidants in carbon tetrachloride, acetone or carbon disulfide and the careful choice of chromatographic conditions that the elution of these materials had little or no interference from the extending-oil present. In addition, the oil was completely soluble in the solvent and all but the heaviest fractions eluted prior to that of the antioxidant.

To circumvent interference from the extending oil, no internal chromatographic standard was used to check response. Polymer standards were prepared. These were made by incorporating the oil and antioxidant into unstabilised polybutadiene or styrene-butadiene resin cement at typical levels of concentration. These preparations were then air-dried to a dry polymer condition. For analytical purposes, 10.0 ± 0.01 gram of polymer were ethanol extracted in a Soxhlet apparatus using 165 ml of solvent for 16 hours. The extract solution was then concentrated to about 10 ml volume and taken up in the appropriate solvent to a 50 ml volume and used for chromatographic analysis of the antioxidant.

Figure 4.1 shows a chromatogram of a polymer extract solution containing 2, 6-di-*tert*-butyl-*p*-cresol in carbon tetrachloride at 150 °C. It is evident that neither the oil nor the polymer system interferes with the elution of the antioxidant. It is worth noting that a highly aromatic oil, which was soluble in the solvent, was used in the polymer formulation.

In **Figure 4.2** the chromatogram of Agerite Superlite from a polymer extract solution in carbon disulfide at 165 °C is shown. The ratio of the areas of these two peaks is 1 to 1.19 which agrees reasonably well with the ratio of 1 to 1.12 obtained on a neat sample of Agerite Superlite. Thus measurement of these peaks for the quantitative estimation of this antioxidant in polymer is valid.

Lappin and Zannucci [5] concerned themselves with polypropylene additives such as hindered phenols and ultraviolet stabilisers which are stable at 350 °C. They used a gas chromatograph equipped with a flame ionisation detector. Copper columns, 6.4 mm x 1.5 m, packed with 10% SE-30 on 40- to 60-mesh Chromsorb V were used (the column may require silylation). The injection port and detector oven were held at a constant
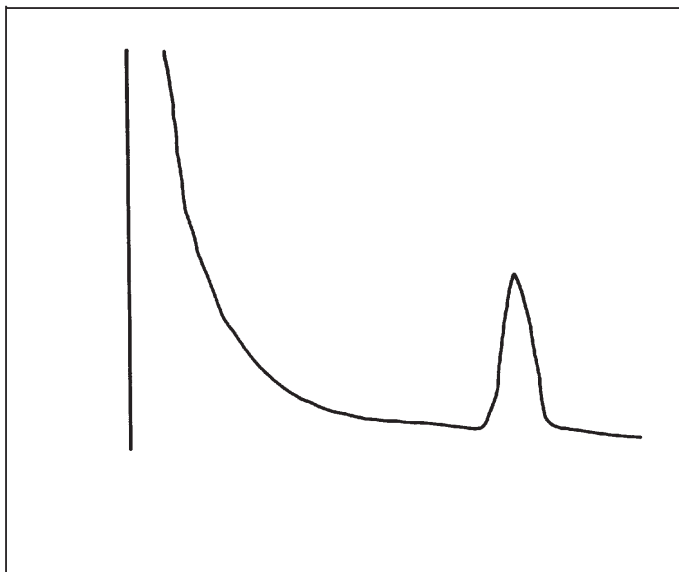
Figure 4.1 Gas chromatogram of polymer extract solution of 2,6-di-*tert*-butyl-*p*-cresol in carbon tetrachloride at 150 ºC
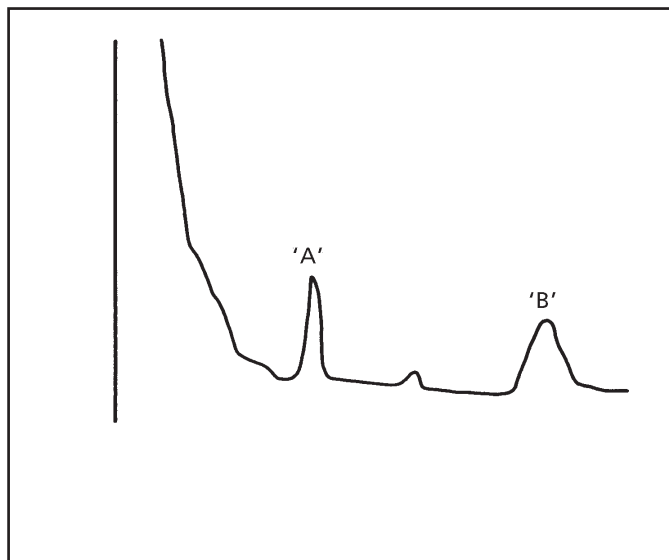*Reproduced from Gaeta and co-workers, Rubber Age [4]*

Figure 4.2 Gas chromatogram of polymer extract solution of Agerite Superlite in carbon disulfide at 165 ºC
Reproduced from Gaeta and co-workers, Rubber Age [4]

temperature of 330 °C. Helium was used as the carrier gas. Samples of the solution injected ranged in size from 0.05 to 0.20 ml. The chromatograph was programmed from 100 to 340 °C at a rate of 15 °C/min and was held at the upper limit for 1 hour. A 3.0 g sample of polypropylene was added to 150 ml of *p*-xylene in a round-bottom flask equipped with a reflux condenser and a magnetic stirrer. The mixture was heated under reflux and stirred until solution was complete, and then 1.0 ml of a 0.3% solution of biphenyl (or benzophenone) in *p*-xylene (internal standard for GC) was added. The solution was diluted with 150 ml of *p*-dioxane, cooled in an ice bath, and filtered. The filtrate was concentrated to about 1.0 ml on a rotary evaporator at 45-50 °C. *p*-Dioxane was added to bring the volume to approximately 6.0 ml. The solution was filtered once more and then chromatographed.

Lappin and Zannucci [5] showed that a number of ultraviolet light absorbers as well as antioxidants could be quantitatively determined on an SE-30 column. SE-30 has a maximum operating temperature of about 350 °C. This high temperature permits elution of some high molecular weight additives.

They examined two methods of separating the additives from the polymer. GC of a hexane extract of the polymer produced numerous extraneous peaks, probably owing to a decomposition of dissolved amorphous polymer in the injection port, rendering the chromatogram useless. When the polymer was dissolved in *p*-xylene and re-precipitated with an equal volume of *p*-dioxane, a relatively clean chromatogram was obtained from the filtrate. The position of decomposition peaks from unstable compounds, such as dilauryl 3,3´-thiodipropionate and distearyl pentaerythritol diphosphite, are predictable and do not interfere with the determination of those additives studied by Lappin and Zannucci [5].

They found that the optimum polymer sample size was 3 g, although runs were possible on samples as small as 200 mg. **Figure 4.3** is a chromatogram obtained for the extract of a polypropylene sample in which biphenyl is used as an internal standard. Benzophenone is another possible internal standard. Lappin and Zannucci [5] determined 4-(dodecyloxy)-2-hydroxybenzophenone (DOBP) and 2,6-di-*tert*-butyl-*p*-cresol (BHT) in polypropylene by this technique.

The precision of the BHT determination is good but the quantity found (0.02%) was less than the amount added (0.05%), possibly due to some losses of volatile BHT during polymer compounding. DOBP determinations ranged from 0.20 to 0.35% for a sample originally containing 0.30% of the additive. These data reflect the poor resolution between DOBP and some other compounds that appear as shoulders on the DOBP peak (**Figure 4.3**).

To demonstrate the scope of the method Lappin and Zannucci [5] determined a number of common polypropylene additives. Most of these were eluted without decomposition
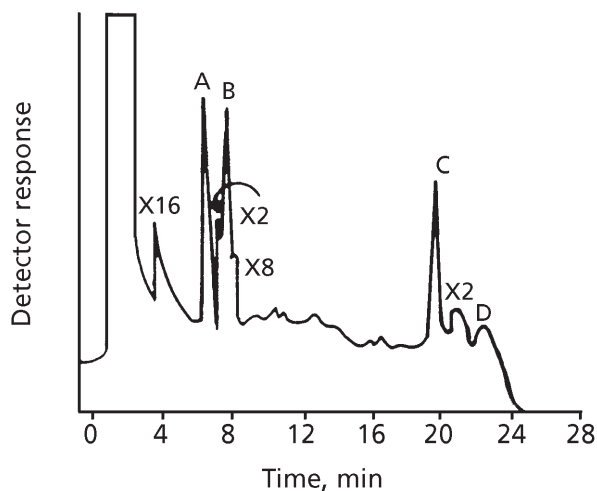
Figure 4.3 Chromatogram of a polypropylene extract. Peaks are (a) biphenyl, (b) butylated hydroxytoluene, (c) 4-(dodecyloxy)-2-hydroxy-benzophenone and (d) unknown impurity
Reproduced from Lappin and Zanucci, American Chemical Society [5]

in less than 1 hour. These additives include 1,3,5-trimethyl-2,4,6-tris (3,5-di-*tert*-butyl-6 hydroxybenzyl) benzene. However, pentaerythritol tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate) although stable, was not eluted from the column within 1 hour. A few compounds decomposed, as shown by peaks of low molecular weight fragments. For some compounds, such as dilauryl 3,3′-thio-dipropionate, thermal instability could be predicted from the structure of the additive, however, such a prediction is not always possible. The marked difference between the unstable 2,2′-thiobis (6-*tert*-butyl-*p*-cresol) and its stable isomer, 4, 4′-thiobis(6-*tert*-butyl-*m*-cresol), was unexpected. For additives other than those listed, the thermal stability must be determined by experiment.

Denning and Marshall [6] devised a method in which polymer extracts are examined for antioxidants and ultraviolet absorbers at two column temperatures in order to overcome the problem that whereas some compounds have a relatively low retention time, others of higher molecular weight have very long retention times at 250 °C.

Denning and Marshall [6] used a dual-column chromatograph, equipped with a heated flame-ionisation detector and an isothermal column oven. The oven was operated isothermally at 250 or 300 °C.

To extract the additives the polymer was refluxed with toluene for 20 minutes then the polymer was reprecipitated with ethanol. Relative retention data is given in **Table 4.1.**

Table 4.1 Separation of antioxidants			
Antioxidant	**Class of compound**	**Relative retention time (relative to Santonex R)**	**Column temperature, °C**
Topanol OC	Phenol	0.05	250
Polygard	Phosphite	0.09 Major peak	250
		0.31 Minor peak	
Irganox 1010	Phenolic ester	0.13	250
Nonex DCP	Phenol	0.21 Minor peak	250
		0.30 Major peak	
Santonox R	Phenol	1.0	250 and 300
Anullex PBA 15	Phenol	0.85	250 and 300
Nonox WSP	Phenol	2.63	250 and 300
Ionox 330	Phenol	4.79 Minor peak	300
		47.7 Major peak	
Irganox 1076	Phenolic ester	5.32	300
Topanol CA	Phenol	6.35	300
Tinuvin P	Benzotriazole	0.20	250
Tinuvin 326	Benzotriazole	0.64	250
Tinuvin 327	Benzotriazole	0.85	250
Cyasorb U 531	Aromatic ketone	1.0	250
Source: Author's own files			

Figures 4.4 and **4.5** are gas chromatograms representing the separation of groups of antioxidants and ultraviolet absorbers identified at 250 °C and at 300 °C.

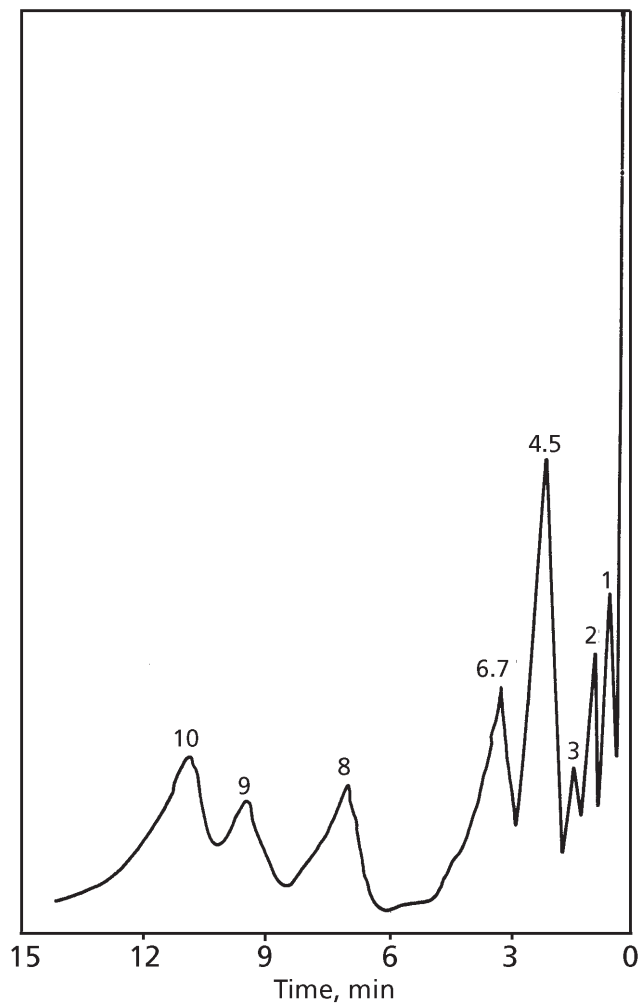Other methods for the determination of antioxidants are reviewed in **Table 4.2.**

Figure 4.4 Separation of antioxidants and UV absorbers at 250 °C. Peaks: 1 – Topanol OC, 2 – Polygard, 3 – Irganox 1010, 4 – Tinuvin P, 5 – Nonox DCP, 6 – Nonox DCP, 7 – Polygard, 8 – Tinuvin 326, 9 – Tinuvin 327, and 10 – Santonox R
Reproduced from Denning and Marshall, RSC [6]
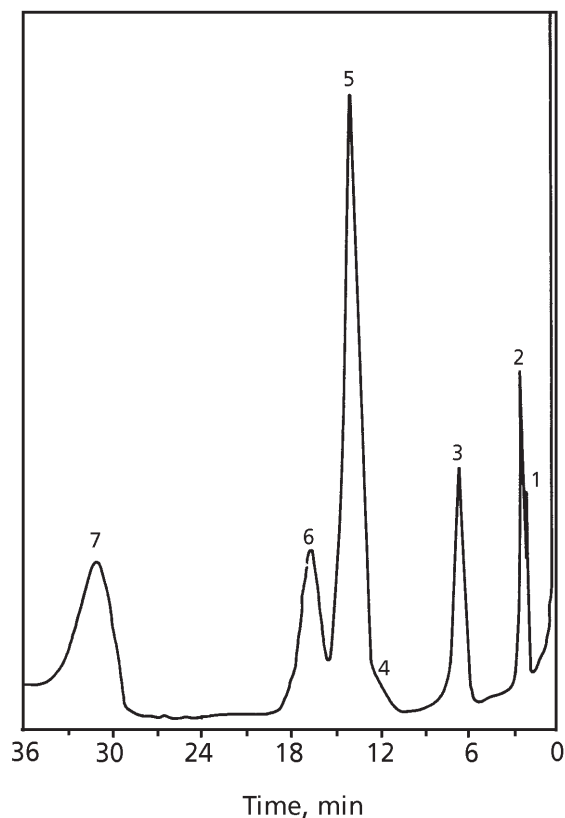
Figure 4.5 Separation of antioxidants at 300 ºC. Peaks: 1 – Anullex PBA, 2 – Santonox R, 3 – Nonox WSP, 4 – Ionox 330, 5 – Irganox 1076, 6 – Topanol CA, and 7 – unidentified
Reproduced from Denning and Marshall, RSC [6]

4.1.1 Secondary Antioxidants

Sedlar and co-workers [27] has described a gas chromatographic procedure, outlined below, for the determination of dilauryl β, β′ thiodipropionate antioxidant and its primary oxidation products in polyolefins, ethylene-vinyl acetate co-polymers, acrylonitrile-butadiene-styrene resins and high impact polystyrene. These workers examined the conditions under which di-lauryl-thiodipropionate and its oxidation products are hydrolysed, by 5 N methanolic potassium hydroxide at 80 °C, quantitatively to lauryl alcohol, thus making gas chromatographic determination possible. The method described next has the advantages of being rapid, accurate and simple. It has been applied successfully to the

Table 4.2 Separation of antioxidants – GLC techniques				
Substances separated	Stationary phase	Column temperature, °C	Other details	Ref.
2,6-Di-*t*-butyl-*p*-cresol, 2-(2- hydroxy-5-methyl-phenyl) benzo-triazole	25% LAC-2R/446 (adipate ester) + 2% H_3PO_4 on Chromosorb	135	H_2 carrier gas, FID Error: ± 1%	[8]
2,6-Di-*t*-butyl-*p*-cresol, 2,6-di-*t*-butyl-phenol	10% Apiezon N on Celite 545	164	H_2 carrier gas, FID, 10^{-3} M in the presence of others can be detected	[9]
2,4,6-Tri-*t*-butyl phenol				
Diphenylamine				
2,6-Di-*t*-butyl-*p*-cresol	Apiezon		FID	[10]
Phenyl-2-naphthylamine				
Halogenated bis-phenols	10% DC-710 silicone oil on Chromoport 80-100 mesh	225-250	30 cm glass column, 6.5 mm od, Carrier gas: 130 ml He/min	[11]
Low bp phenols	Capillary column coated with 10% xylenol phosphate	125	FID	[12]
Phenol and *5-t*-butyl derivatives	Silicone oil 550-carbowax 400 (3:2)	200	Mean deviation: 0.4%	[13]
Phenols and cresols	5% *w/w* of various phosphate esters of phenols	110	120 cm x 4.5 mm column, Pye-Argon chromatograph	[14]
Ionox 330	(a) 20% DC-710 Silicone oil on Chromosorb (b) 2% SE-30 Silicone gum on Chromosorb mesh	200-300 in 10 min	(a) 30 cm x 4.8 mm column (b) 30 cm x 1.6 mm stainless steel column	[15]
Low molecular weight phenols	Silicone-coated capillary column		Converted to trimethyl silyl esters before chromatography	[16]

Table 4.2 Continued...				
Substances separated	Stationary phase	Column temperature, °C	Other details	Ref.
2,6-Di-4-methylphenol	20% SE-30 on HMDS-treated 60 mesh Chromosorb W	200	Electron capture detector	[17]
Ionol 2,6-di-*tert*-butyl-*p*-cresol	Propylene glycol	200	-	[18, 19, 20]
Phenolic antioxidants	-	-	-	[21, 22, 23]
Antioxidants in rubbers	-	-	-	[24-27]
BHT, butylated hydroxy anisole	-	-	-	[28]
Topanol A Topanol O	-	-	Analysis of 11-bromoundecyl methacrylate and methylmethacrylate	[29]
Source: Author's own files *bp: boiling point* *HMDS: Hexamethyl disilazane*				

analysis of polypropylene samples containing 0.02 to 0.3% of dilauryl thiodipropionate and its oxidation products, the sample size being about 1.0 gram of polymer. The additives, including dilauryl thiodipropionate were extracted quantitatively from the sample under an atmosphere of nitrogen with a chloroform-ethanol-*n*-hexane (1:1:4) mixture by using a semimicro-extractor of the Soxhlet type. Dilauryl-thiodipropionate was separated from its oxidation products as well as from other additives by thin-layer chromatography on silica gel coated plates. The spots containing dilauryl thiodipropionate are extracted quantitatively with chloroform benzene (1:1) mixture and the extracts analysed by the method described next.

The peaks due to the solvent, lauryl alcohol and internal standard (*n*-octadecane) are well resolved. The retention data are chloroform (0.10), lauryl alcohol (0.68) and *n*-octadecane (1.00).

A series of hydrolyses at 80 °C in 5 N methanolic potassium hydroxide solution for 30 minutes carried out within the concentration range of 0.15 to 3.00 mg of dilauryl-β β´–thiodipropionate per 10 ml, gave slightly low recoveries (3%).

The conditions of hydrolysis described previously were found to be the most suitable. At higher temperatures, the oxidation of lauryl alcohol occurs so that a lower apparent amount of lauryl alcohol is found. At lower temperatures, on the other hand, the hydrolysis becomes incomplete. Similar conditions hold for the hydrolysis of dilauryl sulfonyl-β β´-dipropionate and dilauryl sulfonyl-β β´-dipropionate. The actual amount of the particular compound being determined in the sample can therefore be calculated by multiplying the observed value by a factor of 1.03, which accounts for the systematic error of the analysis.

4.2 Volatile Compounds

GC has been used extensively for the determination of more volatile components of polymers, e.g., monomers, residual solvents and antioxidants, and coupled with complementary techniques such as pyrolysis, photolysis and mass spectrometry for the elucidation of the structure of additives.

Roper [30] has discussed the problem of determining very low concentrations of volatiles in polymers. Methods for the determination of such volatiles frequently include application of heat to the sample and the sweeping action of an inert gas to separate the volatile components from the polymer. The volatiles are then analysed by GC. When there is a low concentration of volatile material, it is advantageous to concentrate it in order to improve the shapes of the chromatographic peaks.

To achieve this Roper [30] employed a trap-tube, the capillary portion of the tube is packed with a gas chromatographic column packing consisting of 20-30% of a suitable liquid phase on a granular diatomaceous type support. The tube is fitted with a suitable hypodermic needle so that it can be connected to the gas chromatograph through the injection port. The apparatus is arranged as in **Figure 4.6**. The gas chromatograph is equipped with a temperature programme and any suitable column which will separate the various volatile components.

The polymer sample to be analysed is weighed into the trap-tube, the sample size being chosen to give suitably sized peaks for measurement. The tube is connected to an inert-gas stream by means of butyl rubber tubing and heated to the proper temperature while the gas stream sweeps the volatile material into the packed section of the tube, which is usually cooled with dry ice. The temperature, sweeping rate, and sweeping time should be determined experimentally and will vary with the type of polymer being investigated. Melting the polymer is often necessary to rid it of volatiles. A micro combustion furnace is a suitable heater for the trap tube.

After the volatiles have been adsorbed in its packed section, the trap-tube is disconnected from the butyl rubber tube and moved to the chromatograph. With valve A open and
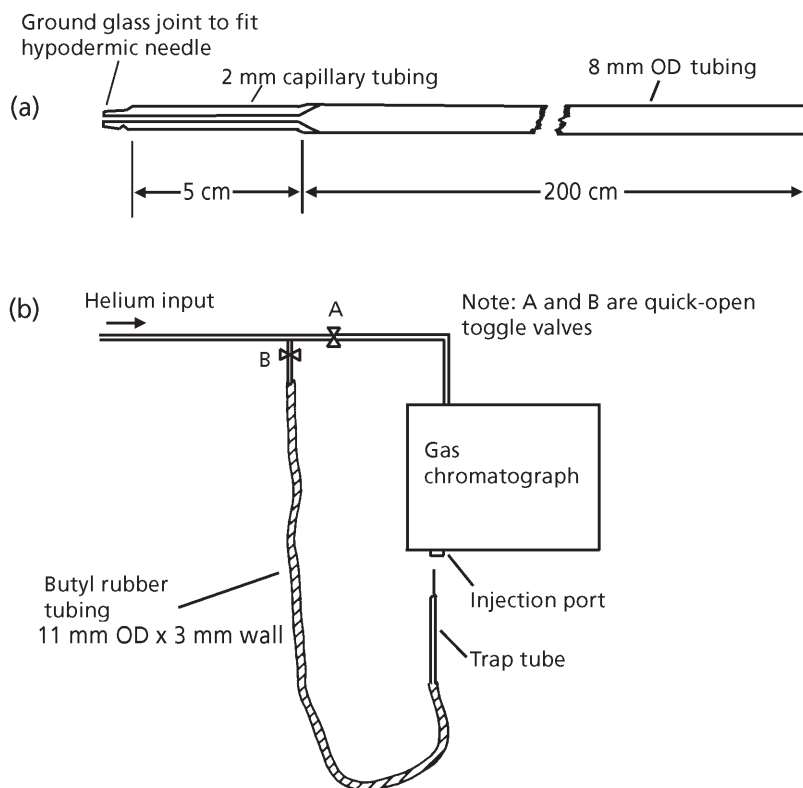
Figure 4.6 Head space method for volatiles in polymers: (a) borosilicate glass trap tube, (b) arrangement of apparatus
Reproduced from Roper, ACS [30]

valve B closed, the tube is connected to the butyl rubber tube with the heater positioned away from the capillary end. Then, with valve A closed too, the hypodermic needle is inserted in the injection port and valve B is opened. The heater, already at the proper temperature, is then moved to the capillary portion of the tube where the heat and carrier gas flow sweeps the volatiles from the packing through the hypodermic needle and into the gas chromatograph. In some cases it is necessary to programme the oven temperature of the chromatograph to get a suitable chromatogram.

It is advantageous to use an electronic integrator to determine the response in counts per microgram for the various components to be measured. With this information, the percentage of each volatile component of the sample can be calculated from the number of integrator counts in each peak.

In an alternative procedure the polymer is heated and the head-space atmosphere analysed by GC. The film or sheet, together with internal standard, is placed in a 250 ml sealed container and heated at 100 °C for 90 minutes.

GC has been used to study the kinetics of evolution of volatiles from polypropylene at 70 °C. Correlation chromatography and trapping volatiles on Tenax sorbents or activated charcoal were used to improve the detector signal. A series of direct injections of the polymer headspace followed by GC was used as a reference study of the kinetics of gas evolution. Data from the trapping studies differed from results obtained by direct injections and the correlation chromatographic studies both of which were in good agreement with each other [31].

Crompton and co-workers [32, 33] have extended the gas chromatographic technique to the determination in polystyrene of styrene and a wide range of other aromatic volatiles in amounts down to the 10 ppm level. In this method a weighed portion of the sample is dissolved in propylene oxide containing a known concentration of pure *n*-undecane as an internal standard. After allowing any insolubles to settle an approximately measured volume of the solution is injected into the chromatographic column which contains 10% Chromosorb 15-20M supported on 60-70 BS Celite. Helium is used as carrier gas and a hydrogen flame ionisation detector is employed.

Figure 4.7 shows a device [33] which is connected to the injection port of the gas chromatograph in order to prevent the deposition of polymeric material in the injection port of the chromatograph with consequent blockages. When a solution of polystyrene is injected into the liner, polymer is retained by the glass fibre and volatile components are swept on to the chromatographic column by the carrier gas.
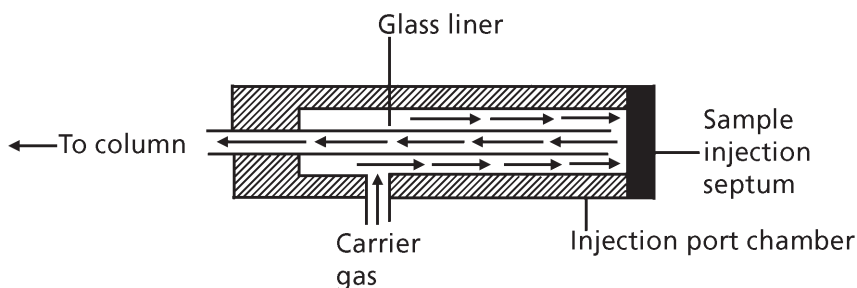

Figure 4.7 Injection port glass liner fitted to a gas chromatograph. The glass liner measures 60 mm x 40 mm od x 2 mm id and is very loosely packed with glass fibre
Reproduced from Crompton and co-workers British Plastics [33]

Figure 4.8 illustrates, by means of a synthetic mixture, the various aromatics that can be resolved, including benzene, toluene, ethyl benzene, xylene, cumene, propyl benzenes, ethyl toluenes, butyl benzenes, styrene and α-methyl styrene [33]. This method is described in detail next.

The apparatus consists of a gas chromatograph with a hydrogen flame ionisation detector and an injection port fitted with a glass liner, very loosely filled with glass wool (**Figure 4.7**).
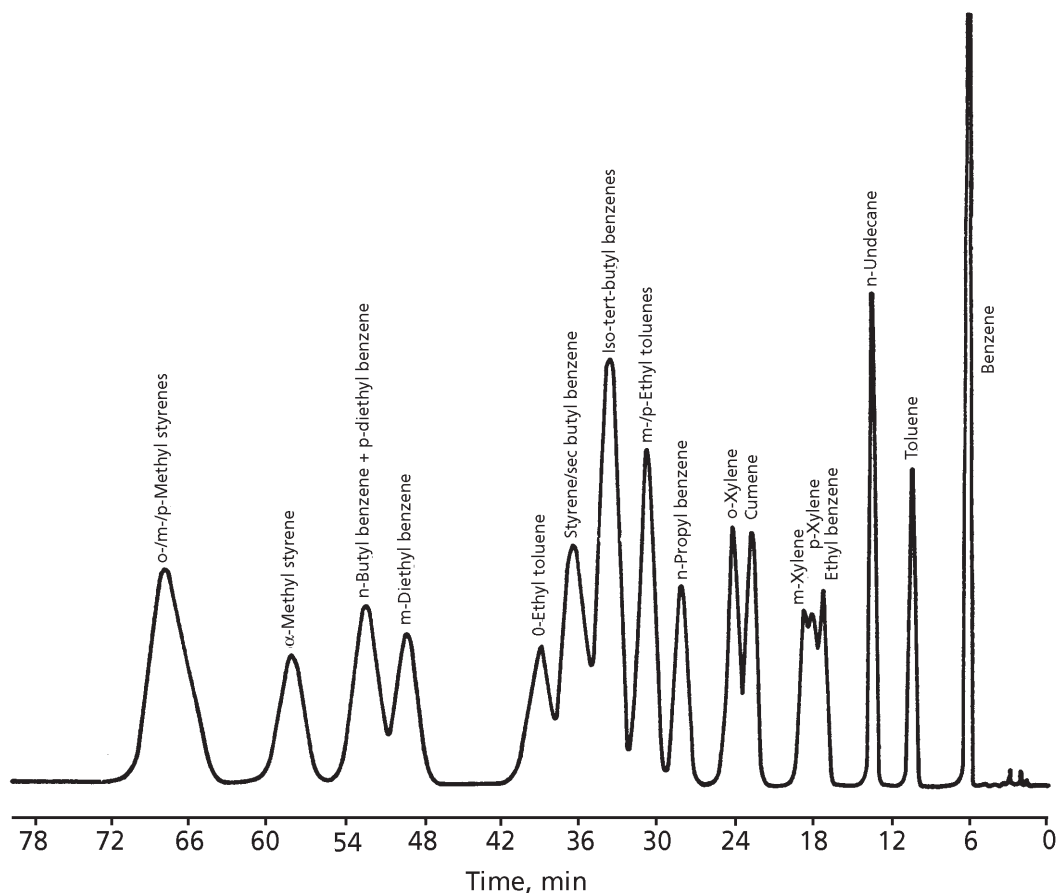

Figure 4.8 Gas chromatogram of a synthetic blend of hydrocarbons likely to occur in PS on a Carbowax 15-20M column at 80 ºC
Reproduced from Crompton and co-workers, British Plastics [33]

Retention distances (injection point to peak centres) are corrected for the gas hold-up of the column and are expressed reactive to styrene:

Benzene	0.17	*sec*-Butyl benzene	1.00
Toluene	0.29	*tert*-Butyl benzene	0.92
n-Undecane	0.40	Styrene	1.00
Ethyl benzene	0.47	*ortho*-Ethyl toluene	1.05
meta-Xylene	0.50	*meta*-Diethyl benzene	1.35
para-Xylene	0.50	*para*-Diethyl benzene	1.44
Cumene	0.62	*n*-Butyl benzene	1.44
ortho-Xylene	0.66	α-Methyl styrene	1.60
n-Propyl benzene	0.77	*ortho*-Methyl styrene	1.86
meta-Ethyl toluene	0.84	*meta*-Methyl styrene	1.86
para-Ethyl toluene	0.84	*para*-Methyl styrene	1.86
iso-Butyl benzene	0.92		

This method was eminently suitable for the determination of volatile expanding agents present in expanded cellular grades of polystyrene. Normal and isopentane are commonly used for this purpose. The method quoted next enables these and wide range of other volatiles to be determined in polystyrene with a reasonable degree of accuracy.

The solvent used to dissolve the polymer and internal standard was one dependent on the volatile compounds that occur in the polymer as shown in **Table 4.3**.

Other applications for the determination of aliphatics and aromatic hydrocarbons are reviewed in **Table 4.4**.

4.3 Monomers

Edkins and co-workers [34] have described a direct capillary GC method to monitor residual methylmethacrylate in polymethylmethacrylate. A short (5 m) crosslinked methyl silicone fused-silica capillary column with flame ionisation detection gave good separation efficiency and parts per million detection limits. Capillary gas-liquid chromatography was superior to packed column analysis (SP 1000) in terms of both analytical utility and ease of use.

Table 4.3 Choice of standards – determination of volatiles in polystyrene

The following are uncorrected retention distances (injection point to peak apex) and the corresponding relative values (2,4-dimethyl pentane = 1.00)

Component	Retention distances, mm	Relative value
Iso-pentane	21.5	0.30
n-Pentane	25.5	0.36
2,2-dimethyl butane	33.5	0.46
2-Methyl pentane + 2,3-dimethyl butane	44	0.61
3-Methyl pentane + cyclopentane	50.5	0.70
n-Hexane	57.5	0.80
2,4-Dimethyl pentane	72	1.00
Methyl cyclopentane	84.5	1.17

Note 1: The following solvents are recommended:

Present in sample	Solvent
n-Pentane	Propylene oxide
Iso-pentane	Propylene oxide
2,2-Dimethyl butane	Propylene oxide
Iso-butane	Propylene oxide
Cyclopentane	Methylene dichloride
Iso-pentane	Methylene dichloride
n-Pentane	Methylene dichloride
2,2-Dimethyl butane	Methylene dichloride
2-Methyl pentane	Methylene dichloride
2,3-Dimethyl butane	Methylene dichloride
3-Methyl pentane	Methylene dichloride
Cyclopentane	Methylene dichloride
n-Hexane	Methylene dichloride
2,4-Dimethyl pentane	Methylene dichloride
Methyl cyclopentane	Methylene dichloride
Iso-octane	Benzene

Note 2: The following internal standards are recommended when paraffins up to C_5 only, are present in the polymer

Present in sample	Internal standard
Isobutane and/or 2,2-dimethyl butane	*n*-Pentane
N- and/or iso-pentane	2,2-Dimethyl butane
Iso-octane	Methyl cyclopentane

Source: Author's own files

Table 4.4 Determination of volatiles in polymers			
Component	Polymer	Method	Ref.
Benzene, toluene, ethylbenzene, xylene, cumene, propyl benzenes, ethyl toluenes, butyl benzenes, styrene	PS	Solution in THF, GLC	[35]
Alkanes	PS	Heating sample, GLC	[36, 37]
Volatiles	Styrene-butadiene	GLC	[38, 39]
Volatiles	PVC, styrene acrylonitrile	GLC	[40, 41]
Volatiles	Poly-α-methyl styrene	GLC	[39, 42]
Volatiles	Polycarbonates (PC)	GLC	[43]
Volatiles	Polyethylene	GLC	[44]
Volatiles	PP	GLC	[45]
Volatiles	Rubber, polymers	GLC	[46-50]
Volatiles	Polyether coated film	GLC	[51]
Source: Author's own files *PVC: Polyvinylchloride* *THF: Tetrahydrofuran*			

Samples of polymethylmethacrylate were accurately weighed (~0.5 g) and dissolved in a weighed volume (~4.5 ml) of chlorobenzene in a 5 ml reaction vial. The vial was placed in a heating block and maintained at 80 °C for 6 hours, to ensure complete dissolution of the polymer. A 10 μl sample was removed from the vial and injected for analysis.

Table 4.5 shows spike recovery and duplicate data, which were each performed on about 10% of all samples. Good results for spike recoveries were obtained (83-115%), as well as precision of duplicates [0.3-7.1% relative standard deviation (RSD)]. The spike data is significant because it suggests both complete dissolution of the polymer and no or little adsorption of MMA to the polymer during dissolution. The RSD of the method, measured over a three day period, was calculated according to:

$$s = [\Sigma (X_i - X)^2/N - n]^{\frac{1}{2}}$$

where X_i represents the recovery (ppm) of a given concentration of MMA injected over the three day period, X is the mean recovery of that standard in ppm, *N* is the number of replications and *n* is the number of degrees of freedom subtracted for each

concentration. The reported result was calculated from injections of both digested and undigested standards, so it is a measure of variation from both instrument and sample preparation.

Multidimensional techniques of heart-cutting, cryotrapping, and back-flushing have been used to develop a capillary-based alternative to the packed-column techniques to determine residual vinylchloride monomer in PVC. This capillary-based method resolved some of the problems associated with the accuracy and reproducibility required for ultra-trace determination of this suspected carcinogen [52].

Horna and Churacek [1] studied the effect of precipitated co-polymers on the determination of residual ethylacrylate and methylacrylate in acrylic emulsions. Butyl acetate was used as an internal standard to compensate for the sorption of materials by the precipitated polymer.

Table 4.5 Analytical statistical results			
A. Spike Recovery Data			
Initially present	**MMA, µg/g added**	**Recovered**	**Recovery, %**
144.5	114.4	119.0	104
197.2	115.7	97.08	83.9
226.0	113.3	104.1	91.7
175.9	125.2	144.9	115.7
117.8	2412	2413	100.0
123.4	2413	2501	103.6
B. Duplicate Data[1]			
Replicate 1	**Replicate 2**	**% RSD**	
6510	6910	3.9	
7230	7260	0.3	
2700	2640	1.6	
1120	1180	3.7	
1790	1980	7.1	
[1]: *Reported results are corrected for dilution factor of polymer in dissolution solvent (~ 0.5 g PMMA/4.5 g solvent). RSD Method – 5.2% for a three day period Reproduced with permission from T.J. Edkins and co-workers,* Polymer Engineering and Science, *1990,* **30**, *23, 500 [34]*			

Pfab and Noffz [53] have described two methods, both based on GC, for the determination of styrene monomer and other volatiles in polystyrene. In one method an *ortho*-dichlorobenzene solution of the polymer is distilled to isolate volatiles as a concentrate in the distillate. The *ortho*-dichlorobenzene used to dissolve the polymer contains a known amount of toluene which is used as an internal standard. The distillate is chromatographed on a polyethylene glycol column using helium as a carrier gas and a katharometer detector.

This method is used to determine styrene and ethyl benzene in polystyrene. In their second method, Pfab and Noffz dissolve the polymer in methylene dichloride containing a known amount of 1-phenyl butane as internal standard. The polymer is then reprecipitated by the addition of excess methyl alcohol. The filtrate is chromatographed as described previously, except that a flame ionisation detector is used instead of a katharometer in order to increase the overall sensitivity of the procedure. This method is capable of determining styrene monomer, ethyl benzene, cumene and xylenes.

Shapras and Claver [38] have described a gas chromatographic method for the determination of various volatiles in polystyrene, styrene-acrylonitrile copolymers, styrene-butadiene, styrene-acrylonitrile-butadiene terpolymers and other co-polymers. In this procedure, the polymer is dissolved in dimethyl formamide containing a known amount of toluene as internal standard. A portion of this solution is injected into two columns in series comprising 20% Tween 81 on Chromosorb W, followed by 10% Resoflex-446 on Chromosorb W. Using a hydrogen flame ionisation detector, less than 10 ppm of various monomers and other volatile impurities can be determined in the polymer by this procedure. Shapras and Claver state that the polymer present in the solution injected into the gas chromatographic column deposits on the injection block and is removed by reaming after every 50 sample injections.

Other gas chromatographic methods available for the determination of monomers are reviewed in **Table 4.6**.

4.4 Oligomers

Utterback and co-workers [54] determined oligomers of polyoxymethylene glycols and ethers by derivatisation with ammonia then determination by capillary column GC. Okada [55] used temperature programmed GC to determine polymethylene oligomers. High temperature capillary GC has also been used to determine separate Novoloc phenolic and epoxy novolac oligomers [56].

Table 4.6 Gas chromatographic methods - determination of monomers			
Monomer	Polymer	Method	Ref.
MMA	PMMA	Effect of ageing on monomer content	[57]
Hydroxy ethoxylated methacrylate, methacrylic acid, dimethylacrylethane	In hydroxy-ethylmethacrylate monomer	-	[58]
Monomers	Poly-2-hydroxyethyl, acrylate, polybutylacrylate, polyethylacrylate, polyvinylpropionate	-	[36]
Vinyl acetate, 2-ethyl hexyl-acrylate	Copolymers	LD: 0.01%	[59]
Vinyl chloride	PVC	Effect of ageing on monomer content	[60]
Styrene	Rubber latices	Direct inspection of latex into GLC column	[61, 62]
Styrene, aromatic volatiles	Styrene copolymers	Emulsions and latices	[38, 63-66]
Styrene	PS	-	[67]
Monomers	Ethylacrylate – styrene copolymers	Emulsions	[68]
Diethylene glycol	Poly/ethanediol terephthalate	-	[69]
Ethylene oxide	Plastic surgical materials	-	[70]
Source: Author's own files *LD: Limit of detection*			

4.5 Hindered Amine Light Stabilisers (HALS)

Hindered amine light stabilisers in polymer materials have been generally analysed by means of GC or liquid chromatography after their extraction from the substrate materials [71-76]. However, the extraction process is sometimes troublesome especially for the oligomeric or polymeric HALS, which are often employed in practical use because of their lower migration out from the substrate materials. Moreover, the quantitative recovery of the higher molecular weight components in the HALS is not thoroughly attained by ordinary solvent extraction because of their lower solubility and possible decomposition during the extraction process.

Recently Kimura and co-workers [77] have developed a novel method to determine an oligomeric HALS in polypropylene materials using reactive thermal desorption-GC (RTD-GC) in the presence of an organic alkali, tetramethylammonium hydroxide [$(CH_3)_4NOH$]. This technique allowed the rapid and highly sensitive determination of the oligomeric HALS in polypropylene.

4.6 Plasticisers

Krishen [78] pointed out that one of the major drawbacks of previously published gas chromatographic techniques for the identification and/or determination of ester plasticisers of the type used in PVC is that, commonly, isothermal column conditions had previously been used, since relative retention data were available for these conditions. Only limited use had been made of temperature programming by earlier workers.

One of the major drawbacks of isothermal column operation is the necessity for using either two different columns or two different temperatures for the identification of both the original plasticiser and the products obtained from it by hydrolysis and esterification. The procedure, described next, overcomes this drawback.

Krishen [78] used a dual flame ionisation chromatograph equipped with a 1 mV recorder. Two stainless steel columns each 1.8 m x 13 mm od packed with 10% UCW-98 on 60-80 mesh Diatoport S were employed in the dual operation mode. The initial column oven temperature was 100 °C and after 4 minutes of isothermal operation, the temperature was programmed at a rate of 8 °C per minute to a maximum of 330 °C. The final temperature was held constant for 8 minutes. The injection block and the detector were maintained at 270 °C. The helium, hydrogen, and air pressures were 0.4 (Flowrator 0.8), 0.09, and 0.2 MPa, respectively.

Samples of the plasticisers were dissolved in tetrahydrofuran and then injected into the gas chromatograph. When the plasticisers were present in PVC, the polymer sample was dissolved in tetrahydrofuran, insoluble components were allowed to settle out, and a sample of the clear solution was injected into the gas chromatograph. A 1% solution of the polymer was suitable for this purpose when the plasticiser content of the polymer was between 10 and 40%.

A gas chromatogram obtained by Krishen [78] with a mixture of ester plasticisers is shown in **Figure 4.9**. Many commonly used plasticisers are well separated and can be identified by their retention times. The retentions calculated relative to di(2-ethylhexyl)phthalate (DOP), are shown in **Table 4.7**
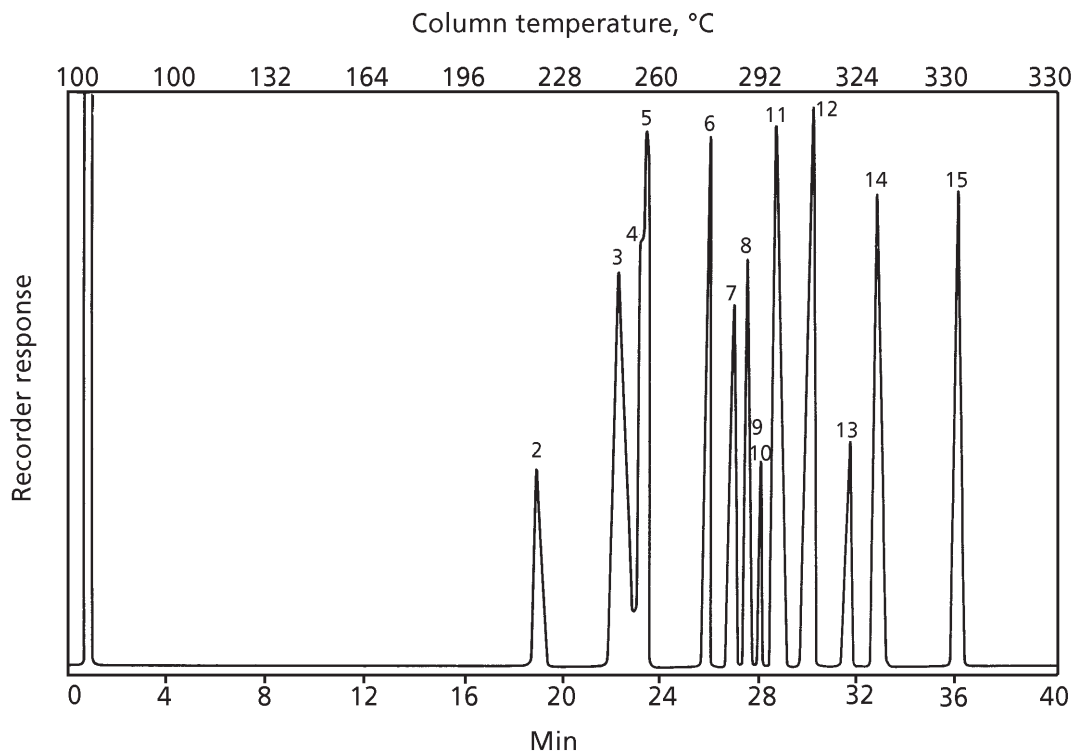
Figure 4.9 GC of ester plasticisers. 1: Tetrahydrofuran, 2: Triethyl citrate, 3: Methylphthalylethyl glycolate, 4: Ethylphthalylethyl glycolate, 5: Dibutyl phthalate, 6: Dibutyl sebacate, 7: Acetyltributyl citrate, 8: Butylphthalybutyl glycolate, 9: Butylbenzyl phthalate, 10: Trioctyl phosphate, 11: Di(2-ethylhexyl)adipate, 12: Di(2-ethylhexyl)phthalate, 13: Di(2-ethylhexyl), 14: Di(2-ethylhexyl)sebacate, 15: Di-*n*-decyl phthalate. *From Krishen, ACS* [78]

For these data, the column dead space was measured by injecting methane. Under programmed temperature conditions, relative retentions plotted against the carbon number produce a straight line. These relationships which are helpful for the identification of unknown components, are shown in **Figure 4.10** for a series of phthalate esters. The relative retentions for the phthalate esters of straight chain alcohols from butanol to decanol follow the straight line relationship. The relative retentions of the phthalate esters of branched chain alcohols homologous to 2-ethylhexanol are expected to fall on the lower line, phthalate esters of other series of alcohols with different branching will similarly form a family of parallel straight lines. These plots are extremely helpful in identifying components of complex mixtures of phthalate esters. Similar relationships for

Table 4.7 Relative retention data for plasticisers	
Plasticiser	Retention relative to DOP (100.00)
A Phthalates Dibutyl	76.9
Butyl benzyl	92.8
Di-(2-ethylhexyl)	100.0
Di-*n*-octyl	120.0
B Adipates Di-(2-ethylhexyl)	95.0
C Azelates Di-(2-ethylhexyl)	105.4
D Citrates Triethyl	62.5
Acetyltributyl	89.1
E Sebacates Dibutyl	85.9
Di-(2-ethylhexyl)	108.7
F Glycolates Methylphthalylethyl	73.6
Ethylphthalylethyl	76.4
Butylphthalylbutyl	91.3
G Phosphates Trioctyl	92.8
Reproduced with permission from A. Krishen, Analytical Chemistry, *1971,* **43**, *1130 [78]*	

the relative retentions of di-(2-ethylhexyl) esters of various acids are shown in **Figure 4.11**. Since 2-ethylhexanol is extensively used in ester plasticisers, the relative retention of an unknown plasticiser may be utilised to make a tentative identification of the dibasic acid by using the plot in **Figure 4.11**.

Although the relative retentions of the plasticisers are helpful for the identification, the complexity of mixtures, normally encountered, necessitates hydrolysis and esterification to obtain information about the components of plasticisers. A definite identification of the original plasticiser can be obtained only after the identification of the constituent alcohols and acids has been made. The simple hydrolysis and esterification scheme, described previously, followed by GC is helpful in identifying these products as shown in **Figure 4.12**.
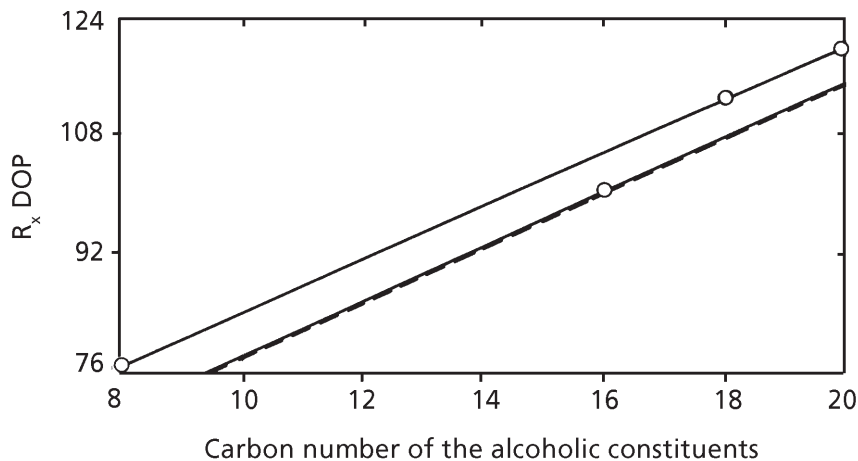
Figure 4.10 Carbon number-relative retention relationship for phthalate esters. Upper line: phthalates of *n*-alcohols, Lower line: Phthalates of 2-ethyl alkyl alcohols. *From Krishen, ACS* [78]
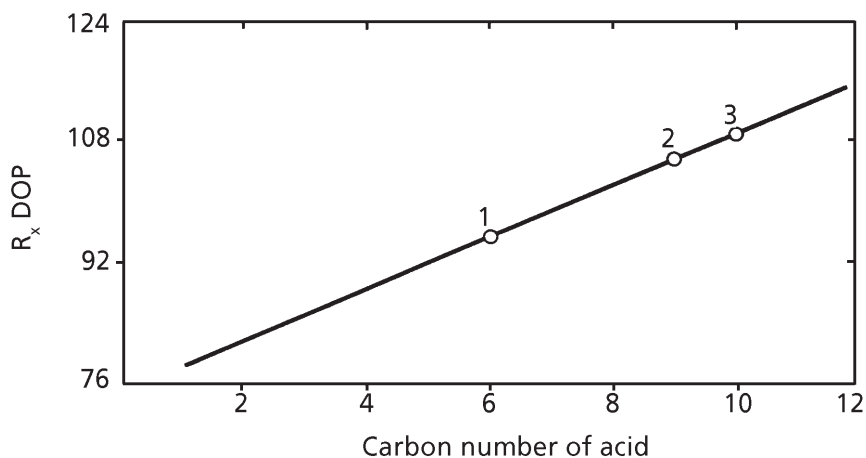

Figure 4.11 Carbon number-relative retention relationship of di-(2-ethylhexyl) esters of acids. 1: Adipic, 2: Azelaic and 3: Sebacic. *From Krishen, ACS* [78]
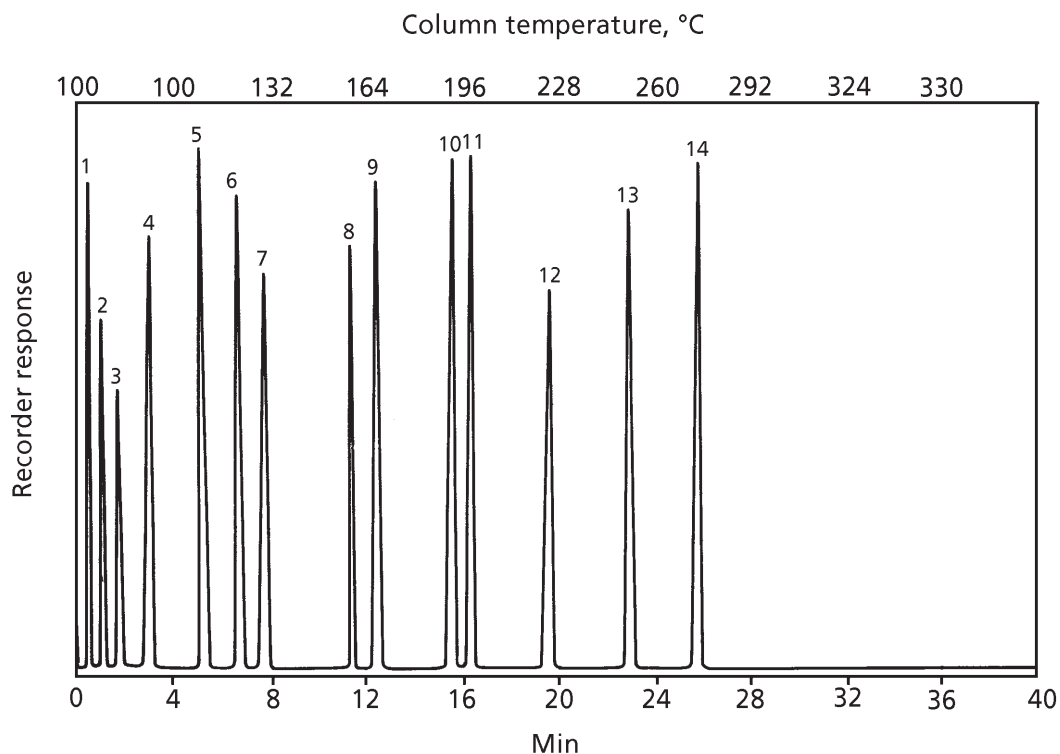
Figure 4.12 GC of alcohols and methyl esters of acids. 1: Methanol, 2: Butanol, 3:Pentanol, 4: Hexanol, 5: Heptanol, 6: 2-Ethylhexanol, 7: Octanol, 8: Dimethyl adipate, 9: Decanol, 10: Dimethyl-*o*-phthalate, 11: Dodecanol, 12: Tetradecanol, 13: Methyl palmitate, 14: Methyl stearate
Reproduced from Krishen, ACS [78]

Since the gas chromatographic conditions used for the alcohols, and the methyl esters of the acids are identical to those used for the original plasticisers, it is very easy to establish whether the plasticisers have been completely reacted. Presence of non-hydrolysable components in a mixture can also be detected by examining the gas chromatograms of plasticisers before and after hydrolysis as the original gas chromatographic peak will still be observed. The identification of unknown alcohols and methyl esters of acids is facilitated by their relative retentions given in **Table 4.8**. The relative retention and carbon number relationship for straight chain primary alcohols shown in **Figure 4.13** can be used for identification of members of this homologous series of alcohols. Slight deviations from linearity at the lower end of the plot may be caused by polarity of the alcohols and their lower boiling points.

| Table 4.8 Relative retention data for hydrolysis products	
Component	Retention relative to DOP (100.00)
Methanol	0.034
Butanol	1.82
Pentanol	3.98
Hexanol	8.04
Heptanol	15.5
2-Ethylhexanol	21.0
Octanol	24.5
Dimethyl adipate	37.0
Decanol	40.0
Dimethyl-*o*-phthalate	51.1
Dodecanol	53.0
Tetradecanol	64.3
Methyl palmitate	76.1
Methyl stearate	84.8
Reprinted with permission from A. Krishen, Analytical Chemistry, *1971,* **43***, 1130 [78]*	
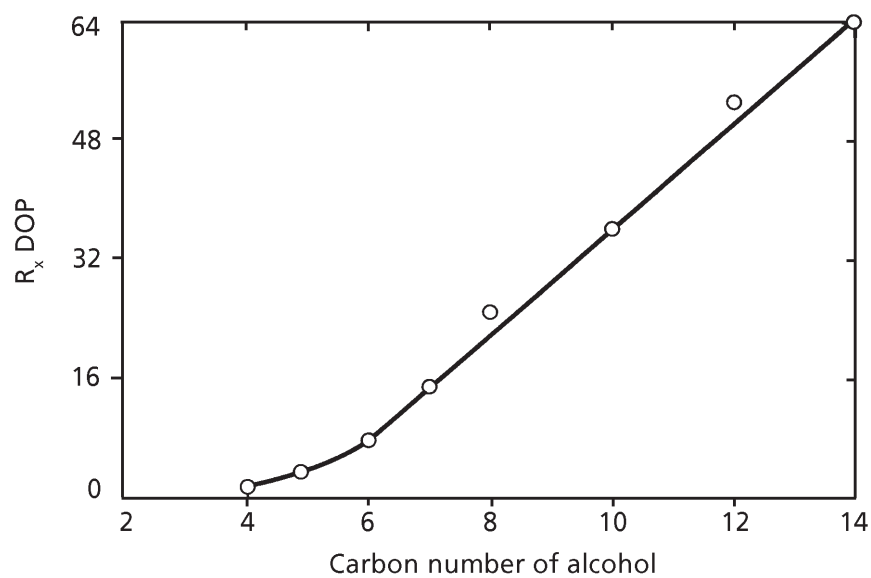
Figure 4.13 Carbon number-relative retention relationship for *n*-alcohols
Reproduced from Krishen, ACS [78]

Most polymers contain quite complex additive systems which are incorporated during manufacture to impart beneficial properties during manufacturing operations, e.g., protective antioxidants, slip agents etc, and during end-use, e.g., antioxidants, UV stabilisers, plasticisers and anti-static agents, flame retardants, antioxidants and thermal stabilisers. The first stage in the examination of a polymer, either from the point of view of identifying the polymer or identifying and determining additives present must be to separate gross polymer from gross additives. It may then be necessary to separate the gross additive fraction into individual additives by a chromatographic procedure in order to facilitate the identification of individual additives.

Separation of gross polymer from gross additives is necessary so that examination of the polymer is not interfered with by additives and conversely that the additives are not interfered with by the polymer. Many different procedures have been studied for the removal of gross additives from the polymer and some of these are discussed next.

The acid component of the plasticisers, derived from inorganic acids like phosphoric acid, cannot be identified directly by this technique but their presence may be inferred from the relative retention of the original plasticiser and that of the alcohol obtained by hydrolysis. Similarly, although the epoxidised vegetable oil plasticisers cannot be chromatographed directly under the gas chromatographic conditions used, identification of a group of methyl esters derived from these plasticisers on hydrolysis esterification, can be used to establish their presence. The temperature programmed gas chromatographic conditions used to chromatograph the plasticisers and their alcoholic and acidic components along with relative retention-carbon number relationships established for various compounds represent a scheme of significant help in identification of ester plasticisers.

Bloom [79] discussed the gas chromatographic determination of phthalic acid ester plasticisers in PVC. He found that although the lower molecular weight plasticisers could be satisfactorily resolved by thin-layer chromatography, GC was needed for the higher molecular weight esters and, indeed, he used this technique to identify and determine such compounds. Bloom [80] used spinal glass columns (2.4 m x 1.8 mm) which were packed with 1% of QF-1 on Chromosorb Q (100 to 120 mesh) and temperature programmed from 160 °C to 234 °C at 3 °C per minute, with nitrogen (20 ml per min) as carrier gas and flame ionisation detection. Methyl arachidate was used as internal standard. Twenty-four of the esters were sufficiently well separated by this technique to be analysed. Further plasticisers were separated by increasing the column temperature by only 1.5 °C/min above 200 °C. Rectilinear calibration graphs were obtained with 2 to 16 μg of an ester per ml, and limits of detection ranged from 5 to 100 ng.

Zulaica and Guiochon [80] described a technique whereby adipate and phthalate plasticisers are mildly pyrolysed at the gas chromatograph injection port thereby eliminating the need for a solvent extraction procedure on the polymer sample.

Turnstall [81] has described a gas chromatographic method for the determination of plasticisers in propellent compositions. This procedure which might also be applicable to polymer extracts involves extracting the sample with dichloromethane and concentration of the extract for analysis on a column (2 m x 3.175 mm) of 5% of Antarox CO-990 on AW-DMCS Chromosorb G (80 to 100 mesh); the column was operated at 185 °C, with nitrogen as carrier gas (25 ml per minute) and flame ionisation detection. The method permitted the measurement of dimethyl phthalate, dimethyl sebacate, triacetin, diacetin, and diethyl phthalate.

Two general methods of plasticiser determination were distinguished between by Guiochon and Henniker [82]: with and without preliminary extraction. Either may precede infrared spectrometry or GC. The most common method is to use ether to extract the plasticisers to be determined. If a quantitative analysis is required, the sample should be thin (0.1 mm or less) and should be extracted for several hours (usually 10 hours) to ensure that extraction is complete. If extraction is to be followed by spectrometry, care must be taken to eliminate all solvent by drying for 2-3 hours at 80 °C. If the analysis is to be done by chromatography, drying is unnecessary since the solvent is much more volatile than the plasticiser and will be well separated.

The infrared spectrum immediately reveals the chemical type of a single plasticiser or of the principal one if there are several. Comparison with authentic spectra often leads to the unequivocal identification of the principal plasticiser if its spectrum is available in a collection, and under good conditions homologous or isomeric plasticisers may be distinguished, for example, di-*n*-octyl and bis-2-ethylhexyl phthalates. The chemical type of secondary plasticisers (phthalates, phosphates, esters of di-acids, etc.) may be established with a degree of certainty depending on the analyst's experience and the presence of absorption peaks that do not interfere with other substances extracted from the original polymer. The spectra of di-*n*-octyl and bis-2-ethyl-hexyl phthalates are compared in **Figure 4.14**. It is evident that the difference in the region from 1000 cm^{-1} to 900 cm^{-1} which is used to distinguish these substances would be easily masked by the presence of an impurity absorbing at these frequencies. The spectrum of dioctyl phthalate containing 10% of tri-cresyl phosphate is added for comparison (**Figure 4.15**). The impossibility of distinguishing phthalates in the presence of this phosphate is evident. Nevertheless, knowing the nature of the principal plasticiser, a determination of the phosphate by means of its peak at 990 cm^{-1} could be undertaken.

The same extraction technique may be followed by GC on a special, sufficiently rapid, column. A single plasticiser is identified by its retention data with, however, an uncertainty which may be practically eliminated by the use of a chromatogram obtained on a column of different polarity **Figure 4.16** shows on the one hand the poor resolution of three plasticisers: (a) di-ethyl phthalate, (b) di-methyl sebacate and (c) tributyl phosphate on a non-polar column; and on the other hand, the good separation of these substances on a
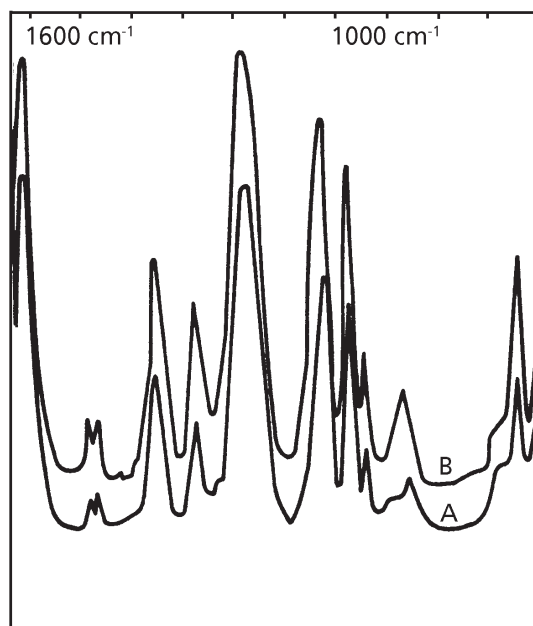
Figure 4.14 Infrared spectra for (a) di-*n*-octyl phthalate and (b) bis-2-ethyl-hexyl phthalate
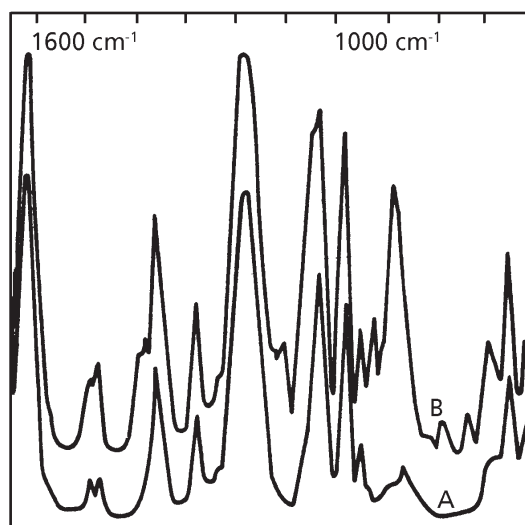*Reproduced from Guiochon and Henniker, British Plastics [82]*

Figure 4.15 Infrared spectra of (a) dioctyl phthalate, and (b) dioctyl phthalate with an
added 10% tricresyl phosphate
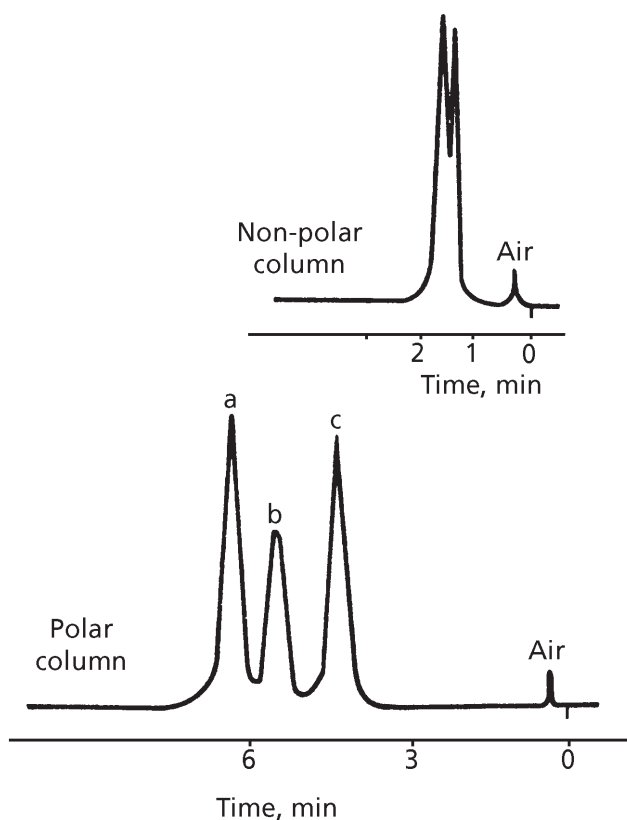*Reproduced from Guiochon and Henniker, British Plastics [82]*

Figure 4.16 GC showing the poor resolution of the plasticisers (a) diethyl phthalate, (b) dimethyl sebacate, and (c) tributyl phosphate – on a non-polar column, and the good separation of these substances on a polar column
Reproduced from Guiochon and Henniker, British Plastics [82]

polar column. The two chromatograms are recorded in a period of 0.5 - 1 hour, depending on the nature of the plasticiser, the spectogram being obtained in 10 minutes. These times are negligible compared to the time of extraction.

GC chromatography has the advantage of providing the identification, with practically equal ease, of secondary plasticisers with a concentration of possibly only 1% of that of the principal plasticiser. At the same time traces of acid esters or heavy alcohols may easily be detected in commercial plasticisers, as well as symmetrical esters that are usually found in unsymmetric plasticisers.

The direct analysis of plasticisers in a polymer is of considerable interest as it would eliminate the preliminary extraction. Effectively this is possible by infrared spectrometry

in certain favourable cases in which one can establish the chemical type of the main plasticiser, but to draw the maximum of information from spectrometry, it would be necessary to apply differential spectrometry techniques. **Figure 4.17** compares the spectra of pure polyvinyl chloride and PVC plasticised with 5% dibutyl phthalate. The presence of a phthalate can be detected or, if its identity is known, its concentration determined by means of the peak at 1725 cm^{-1}.

On the other hand, GC, because of the physical separation it effects, furnishes both a qualitative and a quantitative analysis of polymer-plasticiser mixtures with almost the same ease as the analysis of plasticisers alone, and this is discussed further in Chapter 5.1. It suffices to submit the sample, prepared as for the pyrolysis of plastics, to a controlled pyrolysis in order to disengage the vaporised plasticisers. The polymer is partially degraded, but its pyrolysis products were in all the cases studied by Guiochon and Hennicker [82] much lighter than the plasticisers and in no way prevented their separation and identification. **Figure 4.18** shows the separation obtained of four plasticisers: (a) dibutyl succinate, (b) tributyl phosphate, (c) dimethyl sebacate and (d) diethyl phthalate and the pyrolysis products of polyvinyl chloride. The latter are eluted during the first minute of operation.

The quantitative analysis of most of these plasticisers is possible with a relative standard deviation of 5%. The technique can be extended to many cases, though this needs care because of the possible thermal degradation of plasticisers not yet studied and requires an
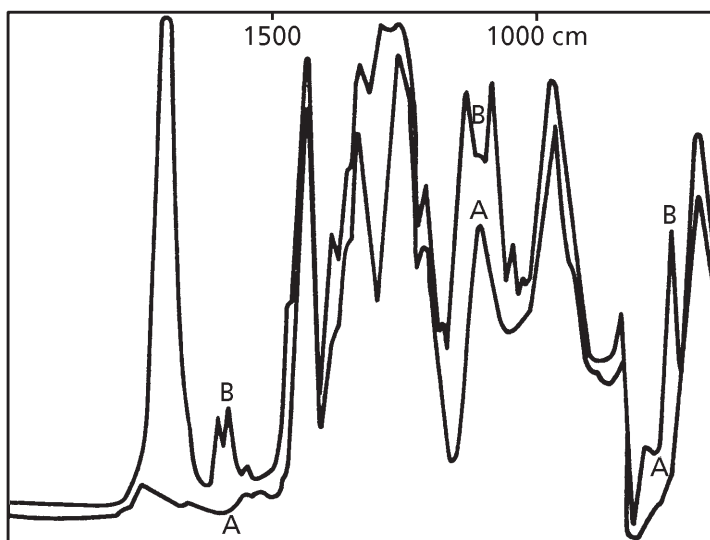

Figure 4.17 Comparison on IR spectra of (a) pure PVC and (b) PVC plasticised with 5% dibutyl phthalate
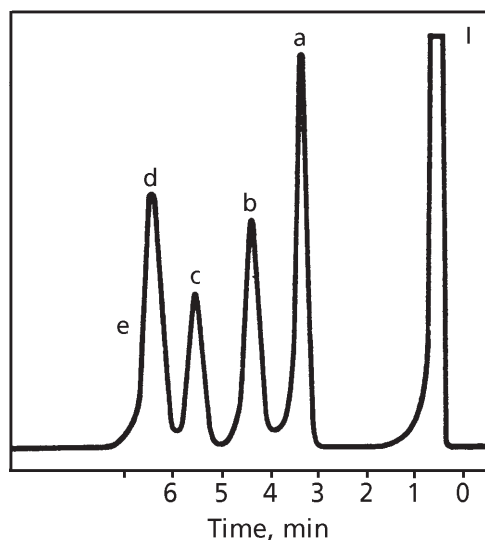*Reproduced from Guiochon and Henniker, British Plastics [82]*

Figure 4.18 Gas chromatogram showing separation of (a) dibutyl succinate, (b) tributyl phosphate, (c) dimethyl sebacate, and (d) diethyl phthalate. I pyrolysis products of PVC
Reproduced from Guiochon and Henniker, British Plastics [82]

examination of each particular case. It is also always possible for plasticisers to remain unextracted in the analysis sample or fail to be eluted from the column and escape detection. For example tricresyl phosphates and heavier products, mainly the so-called non-migrating plasticisers (polyesters, polyacrylontrile), are quite unsuitable for determination by GC. Non-migrating plasticisers, also present a problem in infrared spectrometry. They cannot be extracted by solvent and thus, must be regarded as polymer mixtures with the difficulties that implies. Other applications of GC to the determination of plasticisers in polymers are reviewed in **Table 4.9**.

Table 4.9 Determination of plasticisers in polymers by gas chromatography			
Plasticiser	**Polymer**	**Method**	**Ref.**
Phthalate and acetyl fatty acid esters	Plasticised PVC	10% SE-30 column packing, temperature programming	[83, 84]
Adipate and phthalate esters	PVC	Silicone oil or neopentyl-polysebacate on glass bead column	[85, 86]
Plasticisers	Miscellaneous polymers	-	[82, 87-90]
Reproduced with permission from G. Guichon and J. Henniker, British Plastics, *1964, 37, 74, [82]*			

4.7 Organic Peroxides

GC has also been used to determine certain types of organic peroxides. Bukata and co-workers [91] for example, described procedures involving chromatography of heptane solutions of peroxide (**Table 4.10**) on phthalate/diatomaceous earth or silicone/diatomaceous earth columns and using helium as the carrier gas. No doubt, this type of procedure could be easily adapted to the examination of solvent extracts of polymers.

Hyden [92] describes a gas chromatographic procedure for the determination of di-*tert*-butyl peroxide. This is based on the thermal decomposition of the peroxide in benzene

| Table 4.10 Gas chromatography, retention times for organic peroxides					
Compound	Column length, m	Column type	Temperature, °C	Helium pressure at inlet, MPa	Retention time, min
Tert-butyl hydroperoxide	2	A	80	0.14	22.7
Tert-pentyl hydroperoxide	1	A	80	0.10	19.89
Tert-butyl peracetate	1	A	100	0.14	6.5
Tert-butyl peroxyisobutyrate	1	A	100	0.14	15.3
Di-*tert*-butyl peroxide	2	A	80	0.14	8.1
Di-*tert*-pentyl peroxide	1	A	80	0.10	15.4
2,5-Dimethyl-2,5-di (*tert*-butyl peroxy)-3-hexane	1	O	138	0.10	4.9
2,5-Dimethyl-2,5-di (*tert*-butyl peroxy) hexane	1	O	138	0.10	6.9
n-Heptane	2	A	80	0.14	6.1
n-Dodecane	1	O	138	0.10	3.1
m-Pentane	1	A	100	0.14	0.4
n-Nonane	1	A	100	0.14	4.9
A: Dodecyl phthalate on diatomaceous earth *O: Silicon grease on diatomaceous earth* *Reproduced with permission from S.W. Bukata, L.L. Zabrocki and M.F. McLaughlin,* Analytical Chemistry, *1963,* **35**, *7, 885 [91]*					

solution into acetone and ethane when the solution is injected into the gas chromatographic column at 310 °C. The technique is calibrated against standard solutions of pure di-*tert*-butyl peroxide of known concentration.

Certain types of peroxides used in polymer formulations are extremely stable and un-reactive. This applies to substances such as dicumyl peroxide used as an ingredient of some self-extinguishing grades of polymers:
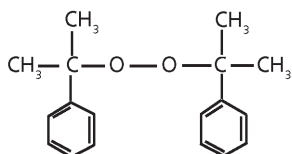
This substance cannot be determined by polarography and will not react with many of the reagents normally used for determining organic peroxides.

Brammer and co-workers [93] have described a method for determining dicumyl peroxide in polystyrene, which is not subject to interference by other organic peroxides or additives that may be present in the polymer. The dicumyl peroxide is extracted from the polymer with acetone and then separated from any other additives present by thin-layer chromatography on silica gel. The gel in the area of the plate containing dicumyl peroxide is then isolated and digested with potassium iodide in glacial acetic acid followed by titration of the liberated iodine by titration with very dilute sodium thiosulfate solution. This procedure has a precision of ± 12% of the determined value with polymers containing 0.25 to 0.5% dicumyl peroxide. It is a rather time-consuming procedure but has the advantage of avoiding all risk of interference from other types of peroxides present in the sample.

As well as occurring as an unbound solvent extractable component in polymers, peroxides can also exist in a form in which they are chemically bound to the polymer. Bradley and Heagney [94] have described a method for the analysis of surface peroxides on polyester film. In this method sodium iodide is dissolve in boiling isopropyl alcohol, and the solution is introduced while hot into the loading flask of a reactor vessel and is purged with nitrogen. Samples of the polyester film, wound on stainless-steel spiral reels are inserted in the reactor flask, and are heated under reflux in a mixture of isopropyl alcohol and acetic acid in an atmosphere of nitrogen. The sodium iodide solution is then forced into the reactor flask by nitrogen pressure, and the entire mixture is refluxed for 30 minutes. Use of the spiral reels keeps the surface of the film free to make contact with the sodium iodide reagent. Oxidising agent on the film releases free iodine from the reagent, and the iodine is subsequently determined by potentiometric titration with 0.001 N sodium thiosulfate. As little as 10^{14} to 10^{15} molecules of peroxide per cm^2 of film can be determined by this procedure.

4.8 Rubber Antidegradants

Gotti [95] described a procedure for the identification of antidegradants in vulcanised rubber mixes in which part of an extract of the sample is acetylated and then analysed by GC and the remainder is subjected to thin-layer chromatography. The results of the two analyses are interpreted separately, then, compared with each other. He discusses the characteristics displayed by a range of commercial antidegradants. The technique is suitable for compounds containing amino- or phenolic-hydroxy groups.

Wize and Sullivan [24, 96] have used high temperature GC for the analysis of mixtures of amine type antidegradants in rubber. They used a separation column constructed of aluminium packed with 20% Apiezon L on 30-60 mesh Chromasorb W. Analysis was carried out on an acetone extract of the rubber sample, employing diphenyl amine as an internal standard. Using column temperatures up to 310 °C they were able to separate a range of antidegradants including 1,2-dihydroxy-2,2,4-tri-methyl-6-ethoxy-quinaline, *N*-isopropyl-*N*´-phenyl-*p*-phenylenediamine, *N*-phenyl-2-naphthylamine, *N,N*´-di-2-octyl-*p*-phenylenediamine and *N,N*´-diphenyl-*p*-phenylenediamine. Near quantitative determinations were obtained for all these substances. Apiezon L was found to be distinctly superior as a mobile phase to other substances tried. Thus Dow-Corning 710 Silicone fluid and butanediol succinate were too volatile at operating temperatures up to 310 °C, whilst silicone rubber, although sufficiently non-volatile, did not give the high degree of resolution obtained with Apiezon L.

4.9 Miscellaneous Polymer Additives

Kunaver and co-workers [97] in their papers on application of inverse GC in paint formulations mentioned that this technique could be used to characterise polymers/oligomers, pigments, solvents and additives in both cured and uncured coating materials.

The basic principle of inverse GC is that the polymeric material investigated is used as a stationary phase in a conventional gas chromatographic column in ordinary gas chromatographic equipment as shown in **Figure 4.19,** where 1 is the carrier gas cylinder, 2 is the injector, 3 is the column, 4 is the micro syringe, 5 is the thermostatted oven 6 are pressure gauges, 7 is the soap bubble flow meter, 8 is the integrator/plotter, 9 is the detector and 10 is the pressure regulator. The interactions between this stationary phase and well defined volatile probes (solvents), which are injected into the column, are presented as the differences in the retention time of these probes. The specific retention volume can then be calculated for each probe and these are the data for the determination of several thermodynamic properties of the material investigated.
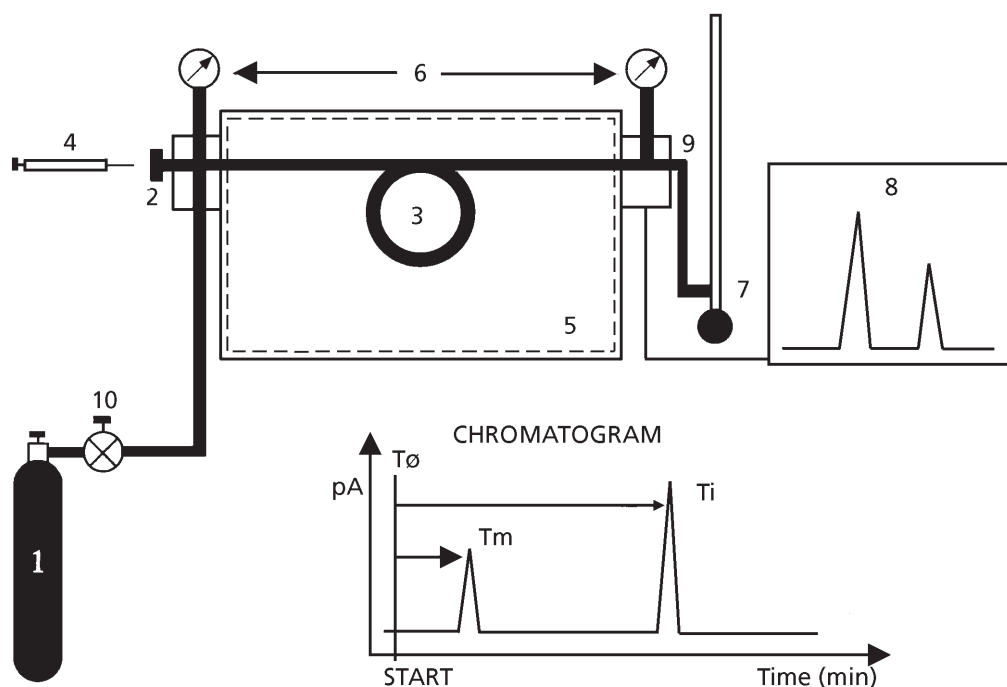
Figure 4.19 IGC instrument
Reproduced from Kunaver and co-workers, Journal of Colour Chemistry [97]

Polymers containing polar groupings are often one of many components of a coating composition. Other components can be plasticisers, additives, solvents, fillers and pigments. Non-dispersive interactions among these components may affect numerous properties of the system, including the rheology, the mechanical properties and the adhesion characteristics. Almost all materials mentioned previously, have some electron donor or electron acceptor character and the non-dispersive enthalpy of such interactions can be estimated as the enthalpy of the acid/base interactions.

Reverse GC has also been used to characterise acid-based interactions in the components of polymer additives [98].

Epoxidised soybean oil is a common additive in polymers such as PVC. To determine epoxidised soybean oil it was converted into fatty acid ethers with tetramethylammonium hydroxide, and these derivatives were analysed by capillary GC using flame ionisation detection. For PVC the epoxidised soybean oil was extracted with toluene, derivatised

and analysed. A short capillary column was used to separate the methyl esters of mono-, di- and triepoxyoctadecanoic acid [99].

Dioxolane derivatives of epoxidised soybean oil prepared *in situ* in extracts from polymer samples have been separated [100] using GC. Derivative peaks were used to measure the levels in PVC and vinyl chloride-vinylidine chloride films.

Ethyl acetate extraction followed by GC with electron capture was used for routine, simultaneous determination of epichlorohydrin, 3-chloro-1,2-propanediol, and 1,3-dichloro-2-propanol in aqueous solutions of poly(amido amine)-epichlorohydrin resin. These impurities were detected at detection limits in the microgram per gram range [101].

Because of their relatively low viscosity and good curing properties, Mannich base products are frequently selected as curing agents for epoxy resins. A direct gas chromatographic method with flame ionisation detection has been described for the determination of residual levels of phenol, formaldehyde, and benzyl alcohol in Mannich formulations used as curing agents. This sensitive method [102] linear over a broad range of concentrations.

Sensory evaluation panels and GC has been used to characterise odours from commercial polyethylene (PE). Tenax GC collection tubes were used to trap the odour-active volatiles at ambient temperature [103].

Esposito [104] identified polyhydric alcohols in resins by programmed temperature GC. Mono and dicarboxylic acids are identified in alkyd and polyester resins by Esposito and Swann [105] who transesterify the resins to form methyl esters and then examine these on silicone grease or Carbowax columns using programmed temperature GC. Similarly, Percival [106] first removes solvent and monomer from resin and then subjects it to methanolysis prior to GC on a silicone SF 96 column. Esposito and Swann [107] identified esters produced from polyols present in synthetic resins, by programmed temperature GC on a Carbowax 20-M column over the temperature range 50 °C to 225 °C. They prepared the esters by reacting the polyol with butyl amine then acetic anhydride and then extracting the reaction product with chloroform.

Kumar [108] described a GC method for the determination of polyethylene glycol in high-density polyethylene.

4.10 Identification of Additives by a Combination of GC and Infrared Spectroscopy

Some of the limitations encountered in applying GC to the unequivocal identification of polymer additives have already been discussed at the beginning of this chapter. In addition

to these limitations there are others. Retention times are purely relative and not always exactly reproducible; even when the chemical class of the sample constituents is known, identification by comparison of the retention time of the unknown with those of standards requires exact reproduction of column operating conditions.

Difficulty can also arise when non-symmetrical peaks are produced; the peak-maximum retention time of a component then depends on concentration. Peaks can also overlap, and certain combinations of substances are often difficult to separate. Chromatographically, a single peak is no criterion of purity, since more than one substance may be present, the components present could often be resolved if their presence was suspected and alternative column operating conditions were selected.

Confirmation of homogeneity of fractions is therefore required together with unequivocal identification and accurate quantitative determination of the product. The analytical method used should involve some property of the molecule other than boiling-point. Often, only fractional milligram amounts of material can be recovered from a column. Of the few techniques that are applicable to these small quantities of material, mass and infrared spectroscopy are particularly suited.

The use of fraction collecting techniques in conjunction with GC is now well established [109-115] and is an attractive proposition in additive identification problems, despite the fact that little published work has yet appeared on the application of this technique to polymer additives.

In this technique, the separated compound is swept by the carrier gas as it emerges from the gas chromatographic column through a cold trap, where it condenses. The material in the trap is then either transferred to an infrared gas cell for examination in the vapour phase, or is transferred as a liquid to a suitable micro cell or may be condensed on a cold surface as a solid for examination by conventional spectroscopic techniques.

Beam condensers to focus the energy beam of infrared spectrometers in an area of 1 mm x 5 mm [116] or smaller [117] enable the use of smaller infrared cells and potassium bromide pressed plates [118, 119] than before. Infrared cells have been developed which require only a milligram or less of liquid to fill them [116, 119-121]. Techniques and apparatus for trapping and transfer of milligram and smaller quantities of separated fractions to infrared cells have been developed [116, 120, 121, 66]. Of these the ultra-micro cavity cell is particularly noteworthy. These are made by ultrasonically drilling cavities in rectangular blocks of sodium chloride. The Type 'D' 'ultra-micro' cavity cell has a sample area of 1 mm x 4.5 mm and cell thicknesses between 0.05 mm and 1 mm. Beckman Instruments Incorporated cell 'ultra-micro' cavity cells in several thicknesses between 0.1 mm and 0.025 mm. In general these cells have disadvantages compared to those made by other companies. There is a micro cell available in which the collection of

the gas chromatographic fraction and the spectrum run are carried out in the same cell without the sample actually being handled. These cells have path lengths between 0.01 and 0.10 mm and a minimum capacity of 0.2 μl. The cells are extruded in one piece from silver chloride and are unaffected by water or most organic or inorganic solvents. The system may be applied to the collection of low and high boiling liquids as well as solid GC fractions, which may be examined in the neat or solvent diluted condition.

Cells have also been described for infrared spectroscopy of fractions while still vaporised in the gas stream emerging from the gas chromatographic column [122, 123] and also, for obtaining the vapour spectra of fractions after trapping and revaporising them [121, 124, 125].

Trapping of gas chromatographic fractions in dry-ice cooled glass or metal [121] capillary tubes is fairly efficient for high boiling compounds, decreasing in efficiency with lower boiling substances. Presumably, with the lower boiling substances, losses are due to some of the gas chromatographic fraction being swept through the trap as a fog or as frozen particles [126]. When helium is used as the carrier gas it is possible that small amounts of helium impurities, notably water [120] can be trapped out together with the gas chromatographic fraction. In these circumstances it is necessary to carefully dry the carrier gas entering the gas chromatograph in order to eliminate any interference effects in the subsequent infrared spectroscopy of trapped fractions.

Various other workers have described techniques for collecting individual gas chromatographic fractions and transferring these as liquids to micro infrared cells. These include Grasselli and Snavely [127] who were able to examine 0.4 μl of a liquid sample in the infrared without the use of beam condensers. Their fraction trapping technique is efficient enough to permit quantitative collection of fractions. Blake and co-workers [128] describe a similar technique for collecting and obtaining the infrared spectra of gas chromatographic fractions in the 10-100 μg range. The equipment is simple, inexpensive, and spectra may be scanned with a simple table top infrared spectrometer without beam condensers using a cell made by drilling a 1 mm diameter hole in a cube of sodium chloride.

Sloane and co-workers [129] described a specular reflectance system for the infrared analysis of micro-sized samples. They compare the advantages and limitations of this technique with other micro infrared techniques. Samples are mounted on small metal mirrors (**Figure 4.20**), which reflect the light beam back through the sample. A transmission spectrum is obtained but the effective path length is twice that of the actual sample thickness and a given absorption band consequently has twice the absorbance obtained by conventional transmission measurements. This system was applied successfully to gas chromatographic fractions, and is particularly useful for the examination of non-volatile liquids such as, for example, dioctyl phthalate. Crystalline solids are easily deposited and
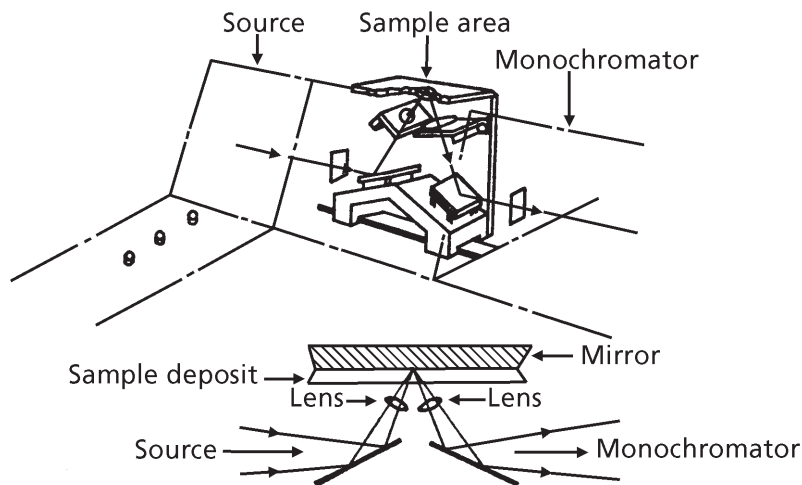
Figure 4.20 Infra red spectroscopy of micro-sized samples. Top: optical path through micro specular reflectance (MSR) accessory. Bottom: optical path through transparent sample mounted on MSR accessory
Reproduced from Sloan and co-workers, Journal of Applied Spectroscopy [129]

handled on the metal mirrors, but crystallinity effects on the spectrum must be carefully watched out for. Its limitations include a 'stray-light' artefact, polymorphism effects and difficulties in obtaining sample uniformity.

Anderson [124] has described in detail a technique for collecting individual products separated from mixtures by GC and subsequently used the technique for their identification by vapour phase infrared spectroscopy using a Hilger H800 double beam spectrometer. The trap and infrared cell used by Anderson are shown in **Figure 4.21**. He claimed that the technique would identify and determine, to within ± 2%, amounts as low as 5 μmol of all substances having a boiling point up to about 175 °C. Heated gas cells enable liquids of higher boiling point to be examined. Naturally as the infrared spectrum of a compound in the liquid and vapour form are different it is necessary to compare spectra obtained by the above technique with spectra of standard vapours. Generally speaking, the additive constituents of polymers have a boiling point which is appreciably higher than 200 °C and hence cannot handled in infrared gas cells. For such substances, infrared examination as a liquid or a solid, as is discussed next, is more relevant. Obviously, in order to avoid volatilisation during polymer processing and their subsequent lifetime most types of additives used in polymer formulations are fairly high melting point solids. Volatile
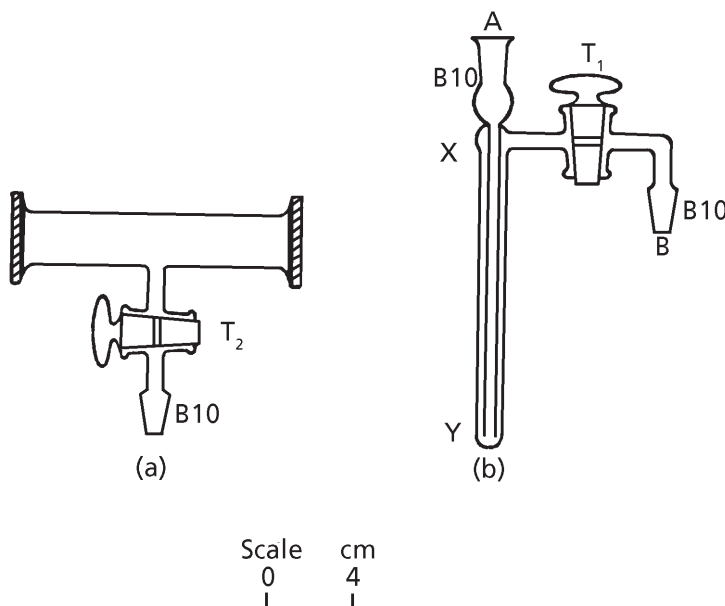
Figure 4.21 Trap for collecting products separated by GC
Reproduced from Anderson, RSC [124]

constituents are, however, sometimes encountered, namely, expanding agents, plasticisers, lubricants, adhesives, solvents, monomers and degradation products of additives or of the polymer itself, and infrared gas cell techniques can be of value in the examination of gas chromatographic fractions containing these types of substances.

Haslam and co-workers [121] have studied in detail the collection of volatile and liquid fractions emerging from a gas chromatographic column and their subsequent identification by infrared spectroscopy. They applied these techniques to various polymeric materials encountered in the plastics industry. They incorporated several of the techniques developed by Bellamy and Williams [113] into their procedures, but, unlike them, found that this technique could not be applied effectively to substances with a boiling point much in excess of 120 °C. Moreover, they found that many of the standard infrared spectra of substances encountered in the plastics industry were recorded only for liquid compounds and not for the corresponding vapours.

All the fraction-collecting apparatus described by Haslam [121] is used in conjunction with gas chromatographic columns operated under reduced pressure and with katharometer detection. This gas chromatographic equipment is of two types:

Type 1. Apparatus involving a column thermostatically controlled within the range 0 °C to 130 °C and a katharometer at room temperature. This apparatus is used for separating mixtures when the highest-boiling constituent boils below 160 °C at atmospheric pressure.

Type 2. Apparatus involving a column and katharometer contained within the same thermostatically controlled chamber and maintained at some temperature in the range 100 °C to 200 °C. This apparatus is used for the separation of mixtures with constituents boiling up to 250 °C, which give trouble in apparatus of type 1 owing to condensation in the katharometer.

The traps shown in **Figures 4.22** and **4.23** have been successfully used with apparatus of type 1 for the condensation of substances boiling in the range - 100 °C to +160 °C. The packing used is small Dixon rings held in place by a small loose-fitting piece of glass rod. The efficiency of this type of trap varies between 85 and 95%, depending on the chemical class of substance. **Figure 4.24** shows a four-way tap to which four such traps may be attached. The tap is connected to the exit of the katharometer by means of the minimum length of stainless-steel tubing (internal diameter 1 mm) brazed into a metal cup. This in turn is cemented to a glass socket with Araldite cement. The exit ends of the four traps are connected via rubber tubing and separate stopcocks to a vacuum manifold. The traps are partly immersed in liquid nitrogen contained in 0.5 litre Thermos flasks.

A preliminary chromatogram indicates the complexity of the mixture. On a second run, the traps are switched in by following the recorder trace and any overlap between peaks is allowed to go to waste. The delay time between the recorder signal and the component reaching the trap is negligible.

Having condensed the desired component in a trap it has to be decided whether to record the spectrum in the vapour state (method 1 below) or the liquid phase (method 2 next). Bellamy's method [113] is retained for identifying all components that, from the gas-chromatographic evidence, would appear to boil below 60 °C. Small amounts of such substances in liquid form are readily lost by vaporisation in attempting the transfer to a small liquid infrared cell.

Haslam and co-workers [121] developed four techniques for infrared examination of gas chromatographic effluents.

Method 1 - Liquids of boiling point up to 60 °C

Figure 4.22 shows how the low-boiling component is transferred to the infrared gas cell. The design of the apparatus is different, but the procedure for transference is identical
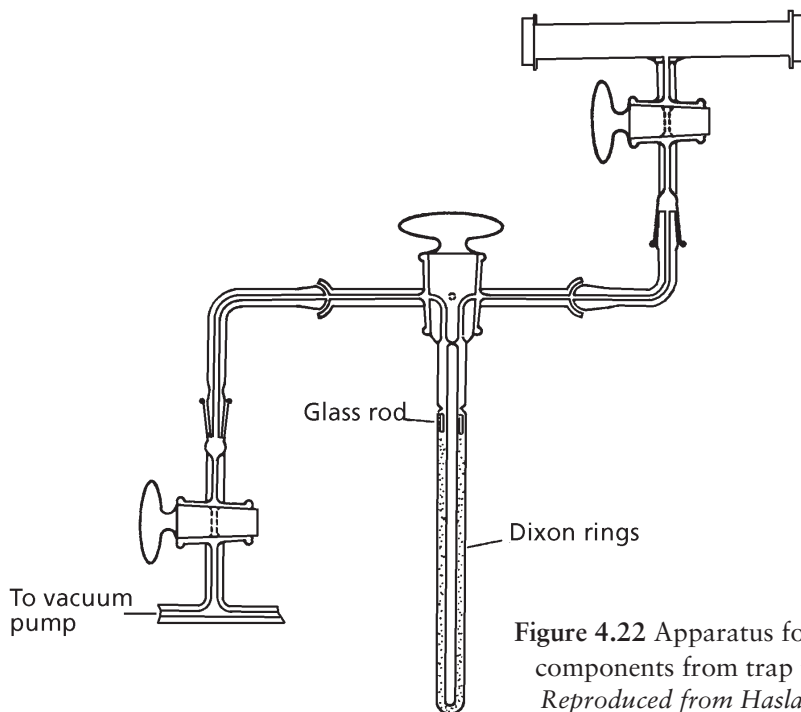
Glass rod

Dixon rings

To vacuum
pump

Figure 4.22 Apparatus for transfer of volatile
components from trap to infrared gas cell
*Reproduced from Haslam and co-workers,
RSC [121]*

Dessicant

Glass rod
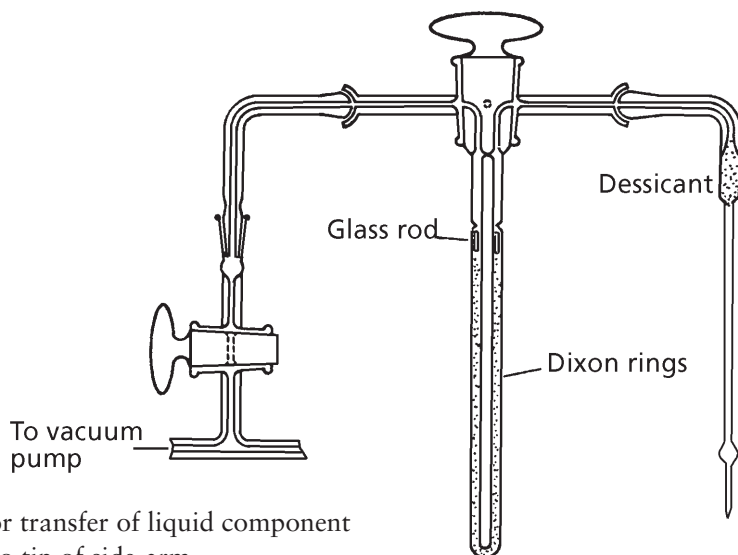
Dixon rings

To vacuum
pump

Figure 4.23 Apparatus for transfer of liquid component
from trap to tip of side-arm
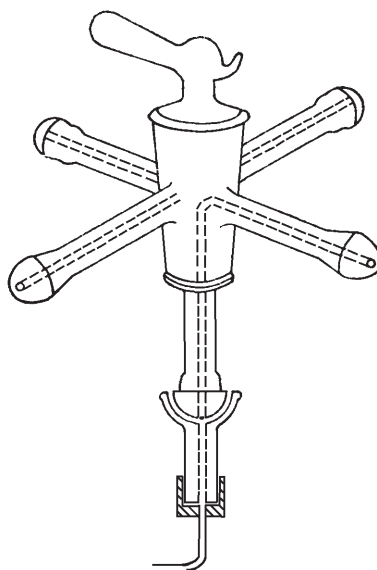*Reproduced from Haslam and co-workers, RSC [121]*

Figure 4.24 Tap to which four collection traps may be attached. Used for trapping of gas chromatographic fractions
Reproduced from Haslam and co-workers, RSC [121]

to that described by Bellamy and Williams [113] except that no heat is applied to the trap.

The infrared gas cell is designed to obtain the strongest possible absorption from a small amount of sample. The intensity of absorption depends only on the number of molecules in the path of the radiation beam; this is increased by reducing the cross-sectional area of the cell, which must not be reduced to an extent such that the energy transmitted is insufficient to record the spectrum. The intensity may also be increased by passing the beam several times through the same volume of gas, as in reflecting cells of the type described by White and co-workers [123]. Unfortunately, these cells are difficult to construct and must be specially designed for a particular instrument. Consequently Haslam [121] used an efficient straight single-pass cell.

In order to attain optimum light transmission, such a cell is inserted at a point where the area of the spectrometer beam is least; this will be where a focus of the beam is formed in the centre of the cell. At a few centimetres on either side of the focal position the beam is rectangular, this, therefore, is the most economical shape for the cell. To decide the dimensions of the cell it was assumed that 1 ml of gas at NTP would be available. Condensation of liquids boiling up to 100 °C may occur on the walls of the cell at pressures above 11 MPa - the cell must therefore be of capacity about 9 ml.

The image to be found in the centre of the cell should normally have the length and width of the entrance slit of the spectrometer. Knowing the f number of the instrument it is possible to calculate the size of the rectangular aperture required to admit the radiation cone in terms of the length of the cell. For the instrument used (Hilger H800, aperture f 11) the dimensions for a 9 ml cell are: length, 10 cm; height, 1.5 cm; width, 0.6 cm (**Figure 4.22**). The body consists of rectangular brass tube (1 mm thick) cut from wave-guide tubing and has the internal dimensions stated above. A flat brass flange is brazed on each end of the tube, and a short side-arm (stainless steel capillary tubing) is brazed in one side of the body. A glass capillary tap that will just slide over the side-arm is cemented in place by filling the space between the two tubes with Araldite resin; by this means, the volume of the side-arm is rendered negligible. Two rock-salt windows are attached to the flanges with Picene wax. Although the cell is designed for an f 11 system, it will give acceptable performance, although with some loss of energy, on an f 7 spectrometer.

Method 2 - Liquids boiling above 60 °C

If the gas-chromatographic evidence indicates that the substance boils above 60 °C, the fraction condensed in the trap is treated as shown in **Figure 4.23**. The trap and contents are held in liquid nitrogen while the apparatus is completely evacuated. After testing the system for leaks, the source of vacuum is cut off. The flask containing the liquid nitrogen is removed from the trap and placed over the side-arm so that the bulb is just immersed in the refrigerant. As the trap attains room temperature, the small amount of liquid in it distils through the desiccant and is condensed round the sides of the bulb of the side-arm. The liquid is encouraged into the capillary tip by lowering the vacuum flask containing the liquid nitrogen until only the last 6.5 mm of the tip is immersed. The bulb is then warmed with the fingers. During this distillation the trap is not warmed, as this may cause some of the liquid to distil in the wrong direction. The apparatus may be left for 1 or 2 hours in order to achieve complete distillation of higher-boiling liquids. Having obtained the liquid in the capillary tip, this tip is broken off at the constriction just below the bulb. **Figure 4.25** shows a piece of apparatus which may used to transfer the liquid to the micro infrared cell. It has a rubber teat and a very fine internal capillary. The device has a detachable tip, which is discarded after use and permits close control over the transfer operation. In the design of a small liquid cell, first consideration must be given to reducing the cross sectional area, the precise area required for a particular spectrometer being found by trial and error. The radiation beam of the instrument is obstructed at the cell-mounting position, to find the least dimensions at which workable energy transmission is retained. A cross-section of 5 mm x 1.5 mm is suitable for the Hilger H800 spectrometer, although the resulting cell could be used satisfactorily on other instruments, namely, the Perkin-Elmer 21, the Perkin-Elmer 137 (Infracord) and the Grubb-Parsons GS2A.
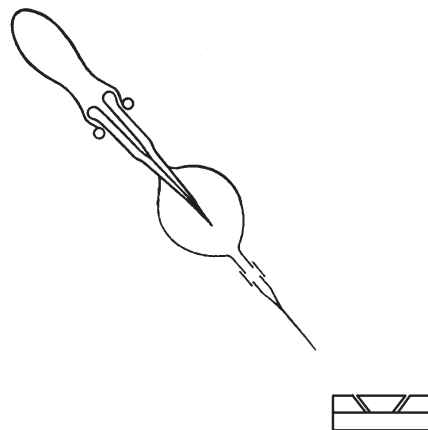
Figure 4.25 Pipette for transferring liquid to micro infrared cell
Reproduced from Haslam and co-workers, RSC [121]

Most of the sample placed in a normal infrared liquid cell is used in the filling tubes rather than in the area exposed to the beam. Consideration was therefore given to a cell in which the filling tubes need not be occupied with liquid, and a suitable design is shown in **Figure 4.26**. The two rock-salt plates are about 20 mm x 10 mm x 3 mm in size. Two holes are drilled in one plate with a No. 86 drill; these holes taper inwards, as shown, being 7 mm apart on the inside and 12 mm apart on the outside of the plate. A gold-foil washer (25 µm thick) is cut, the inner space being 1.5 mm wide and approximately 7 mm in length (just sufficient to clear the edges of the filling holes); the width of this washer is about 2 mm. The cell is first stuck together with gold amalgam. The washer is immersed in mercury for a short period and withdrawn after a layer of amalgam has formed on its surface. The cell is then carefully assembled in a small clamp and left under pressure for 24 hours for the amalgam to set. The space between the plates outside the washer is then filled with Araldite 700 resin and a reasonable surplus of resin is allowed to bridge the edges of the plates on all four sides. The resin was found to be necessary, as the gold amalgam is a poor adhesive and the cell tends to open up and channel; the amalgam joint acts as a barrier to prevent the resin from contaminating the cell window.

The cell is filled by inserting a capillary needle containing the liquid into one filling hole. Provided that the thickness of the cell is less than the diameter of the needle, the liquid will run in to fill the cell area. It is essential that no free space be left in the cell behind the filling holes; such space will not immediately fill by capillary action and air bubbles trapped here may subsequently run into the useful part of the cell and are most difficult to
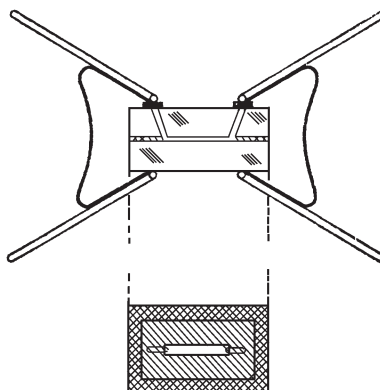
Figure 4.26 Micro infrared cell for liquid samples
Reproduced from Haslam and co-workers, RSC [121]

remove. When the cell is filled, the outer ends of the filling tubes are covered by two small squares of nitrile-rubber sheet, held in position by 'butterfly' spring clips. This method forms an excellent seal without displacing the contents of the cell by air pressure, as may occur with stoppers that are pushed or screwed into the filling tubes.

The amount of liquid required to fill the cell by the method described previously (as opposed to the theoretical capacity of the cell calculated from the dimensions) is determined experimentally by weighing the cell on a microbalance before and after filling. For six fillings with *n*-dodecane (density 0.766) the weights recorded were 0.53, 0.36, 0.27, 0.29, 0.67 and 0.31 mg. This compares with the calculated capacity of 0.20 mg of *n*-dodecane (7 x 1.5 x 0.025 x 0.766). With this cell, infrared spectra have been obtained from 0.5 to 1.0 µl portions of liquid samples, but practice is required in the transfer of these small volumes. On the other hand, 2 to 3 µl of liquid presents no difficulty.

Method 3

This is an extremely simple, but effective method. The back plate of the oven is removed and the copper pipe (3.2 mm internal diameter) from the katharometer is cut, leaving approximately 12.7 mm protruding beyond the oven wall. An Agla syringe barrel containing a tiny piece of cotton-wool (2 to 3 mg) is connected into the exit-gas stream by sleeving one end of the barrel over the copper pipe with silicone-rubber tubing. This entails running a preliminary chromatogram and 'breaking into' the gas stream at the appropriate point in the chromatogram on a second run. The piece of cotton-wool, although not particularly efficient, has the effect of stopping 'vapour fog' from

passing straight through the barrel. The syringe barrel is cooled during this operation by packing solid carbon dioxide round the outside. Having wetted the cotton-wool with the unidentified component, the syringe barrel is removed from the gas stream and a specially adapted nozzle is inserted. This nozzle consists of a fine piece of hypodermic tubing sleeved and cemented into the normal Agla glass nozzle and filed flush with the glass at one end. This had the effect of cutting down the 'dead' volume of the syringe to the minimum. The syringe is held nozzle uppermost, the piston is inserted and the air expelled. The sample is then expressed from the cotton-wool by pressure of the piston directly into the micro infrared liquid cell.

Unfortunately, it has been found that 10 to 12 µl of sample are needed in order to express sufficient liquid to fill the cell. However, if insufficient liquid is available, a drop of carbon disulfide is placed on the cotton-wool from a second syringe and the carbon disulfide solution of the sample is expressed into the cell.

This method proved valuable in the examination of a sample of acrylic sheet known from elemental analysis to contain phosphorus. Dry vacuum distillation of the polymer and solvent extraction both yielded a liquid, which, on direct infrared examination, proved to be an impure material containing phosphate or phosphite. The vacuum distillate at 200 °C was submitted to gas-liquid chromatographic examination on a 1.8 m (6.35 mm diameter) column packed with 30% *w/w* of silicone E301 on Celite maintained at 130 °C. A sample of the main component was taken by method 3 and the infrared spectrum obtained was readily identified as that of triethyl phosphate.

In a modification of method 3, Haslam and co-workers [121] fitted a heated outlet pipe to the back of the katharometer and condensed the vapour in the trap shown in **Figure 4.27**. The outlet pipe consists of a stainless-steel tube (1 mm internal diameter) approximately 23 cm long and terminates in a brass plug tapered to fit a B7 cone. The opposite end is joined to the copper exit pipe of the katharometer with silicone-rubber tubing. The pipe is heated directly by passing approximately 0.5 V at 10 A through it from a variable transformer. The lagging is of asbestos string and fire clay cement covered by a second layer of asbestos string.

The trap is connected into the gas stream at the appropriate point in the chromatogram. The lower part of the trap is immersed in liquid nitrogen and the fraction condensed. The subsequent procedure is similar to that described for method 2, the small amount of substance being vacuum-distilled into the tip, which is then broken off, and the liquid is transferred to the micro infrared cell.

In a recent review of development in polyolefin characterisation the use of high temperature GC coupled with Fourier transform infrared spectroscopy for the determination of antioxidants in polyolefins is discussed.
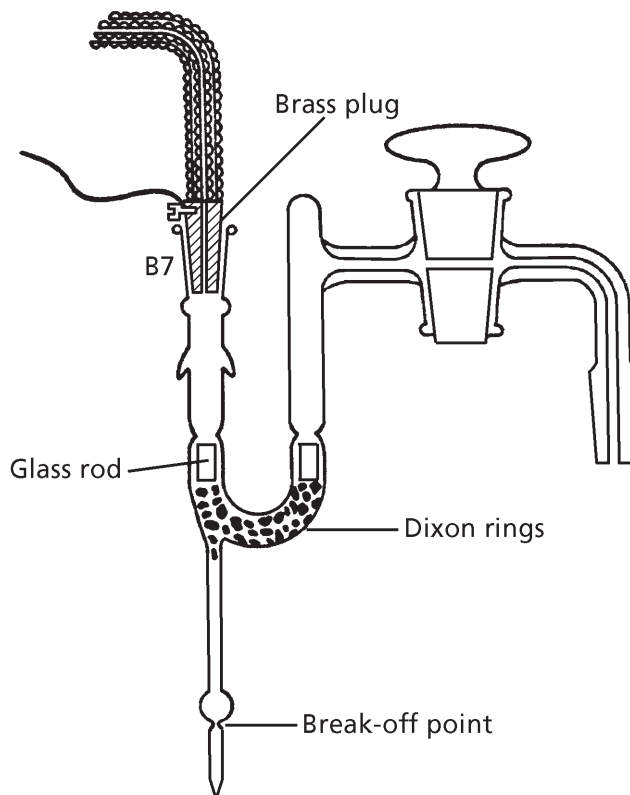
Figure 4.27 Trap used for collection of fractions emerging from gas chromatographic column
Reproduced from Haslam and co-workers, RSC [121]

Jansen and Haas [130] have studied the out-gassing phenomena of polymers by utilisation of thermal desorption GC-Fourier transform infrared spectroscopy. The detection limit of volatile compounds was in the order of 1 μg/g for 100 mg samples.

4.11 Identification of Additives by a Combination of GC and Mass Spectrometry

Element-specific chromatograms using an atomic emission detector (AED) have provided information on the types of additives in a variety of polymer extracts. The high resolution of capillary GC and the selectivity and sensitivity of the AED complemented mass

spectrometry and infrared spectroscopy for the characterisation of additive mixtures in supercritical fluid extracts from a rubber sample [131].

Mass spectrometry techniques have been described for the analysis of rubber compounds. A GC/mass spectrometric procedure has been described [132] for the single injection separation and identification of allergenic vulcanisation agents and antioxidants from isoprene rubber. Mass spectral fragmentation mechanisms were proposed for each of the additives studied.

A GC/mass spectrometry technique has been use to determine traces of phenol in PVC [133].

The samples were pre-concentrated using a solid phase extraction cartridge, recoveries exceeded 90% and down to 10 ppm of phenol could be determined.

Semi-volatile and non-volatile additives in polycarbonate (PC) and PC/polybutylene terephthalate blends have been determined without chromatographic separation using a particle beam interface for direct introduction of the samples into the mass spectrometer. Antioxidants, UV stabilisers, flame retardants, and slip agents were among the additives determined. The key to this approach was the speed and simplicity of identifying multiple additives in a single matrix [134].

Mineral water samples, stored in PE-lined aluminium/cardboard packages were incubated at 40 °C, and then volatiles in the mineral water were analysed by sniffing the effluent from a gas chromatographic column. The effluent was sensorially evaluated for the intensity of descriptors such as synthetic, sickly, musty, metallic or dry. Components detected by sniffing were subsequently identified by GC/mass spectrometry as aromatic hydrocarbons and carbonyls [135].

Ogawa and co-workers [136] analysed the compounds resulting from the deterioration of antioxidants in nitrile rubber sheet by ozone.

Lindstrom and co-workers [137] carried out a quantitative determination of low molecular weight compounds migrating from polybutylene adipate and polyethylene succinate during ageing by hydrolytic degradation in water and phosphate buffer. This was achieved by solid-phase extraction in combination with GC/mass spectrometry. Monomers detected include adipic acid, 1,4-butanediol, for the polyethylene adipate and succinic acid and 1,4-butanediol from polybutylene succinate.

Several dimers and trimers i.e., hydroxybutyl-adipate, hydrobutyl-succinate, di(hydroxybutyl) adipate, di(hydroxybutyl) succinate and hydrobutyl-disuccinate were also detected.

The extracted degradation products were identified and quantified by a ThermoFinnigan GCQ (San Jose, CA, USA). The column used a wall-coated open tubular (WCOT) fused silica CP-WAX 58 (FFAP)-CB column from Varian (25 m x 0.32 mm id, od 0.2 µm). Helium of scientific grade purity from AGA (Stockholm, Sweden) was used as carrier gas at the constant velocity of 40 cm/s. The initial oven temperature was 40 °C, which was held for 1 minute. The oven was heated to 250 °C for 15 minutes. Electron impact mode (EI) detection was used with an electron energy of 70 eV. The mass-range scanned was 35-400 *m/z* and the ion source and transfer line temperatures were 180 and 250 °C, respectively. The injector temperature was set to 250 °C. A sample (1 µl) was injected in splitless injection mode and two blanks were run between each sample by injecting clean methanol (0.15 M HCl).

GC/mass spectrometry has also been used to determine diols, adipic acid and cyclomonodiol adipates in aliphatic polymers [138], isobutyronitrile, benzoyl peroxide, lauryl peroxide and tetramethyl succinonitrile in polystyrene [139] additives in polypropylene [140] crosslinked rubbers [141] and other polymers [142, 143].

Styrene and styrene dimers at concentrations of 13 and 43 mg/kg, respectively, were the major components among the 20 compounds identified by GS-MS in polystyrene monomer by this equilibrated headspace method.

4.12 Pyrolysis GC

Wang [144] has described a pyrolysis GC method for the determination of polymeric additives in polymers. Generally, these higher molecular weight substances could be directly analysed by GC or liquid chromatography. Wang applied the technique to the determination of low levels of polyacrylamide in polyvinyl/alcohol. Because of the large number of pyrolysates produced from the polyvinyl/alcohol matrix, an atomic emission detector was used to selectively detect the nitrogen containing fragments by pyrolysis of polyacrylamide.

Oguri and co-workers [145] used Curie Point pyrolysis-GC to determine the composition of an uncured polyester resin comprising an acrylate co-polymer, a crosslinked accelerator and various additives.

Wang and co-workers [146] have pointed out that low levels of monomers can only be approached by pyrolysis/trapping techniques but can also achieved by derivatisation. An example is quoted of the determination of fumaric acid and itaconic acid in emulsions by pyrolysis-GC in which these acids are reacted with methylamine to form cyclic iodine type functional groups. The derivatisation products produce a stable pyrolysate which can be detected at low concentrations.

Cope [147] has described a pyrolysis/gas chromatographic procedure for the determination of tetrakis(hydroxymethyl)phosphonium hydroxide and tris(2,3-dibromo-propyl)phosphate flame retardants on polyesters and surface tris(2,3-dibromopropyl)phosphate have been determined on the surface of retardant polyester fabrics [148]. The technique used to determine these, involved extraction of the fabric with an organic solvent followed by analysis of the solvent by X-ray fluorescence for surface bromine and by high pressure liquid chromatography for molecular tris(2,3-dibromopropyl)phosphate.

Haslam and co-workers [149] employed a procedure based on pyrolysis for the determination of polyethyl esters in methacrylate co-polymers. The alkoxy groups in the polymers were pyrolysed to their corresponding alkyl iodides which were then determined by chromatography on a dinonyl sebacate column at 75 °C. Similarly, Miller [150] determined acrylate ester impurities in polymers by converting the alkoxy groups to alkyl iodides which were gas chromatographed on a di-2-ethyl hexyl sebacate column at 70 °C. Perry [151] has reviewed the application of pyrolysis/GC to the identification of volatile and non-volatile components of polymers.

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5 Thin-Layer Chromatography

Thin-layer chromatography (TLC), like gas chromatography (GC), comes into its own when dealing with mixtures of substances. TLC using plates coated with 250 µm absorbent is an excellent technique for separating quantities of up to 20 mg of additive mixtures into their individual components and provides enough of each to prepare a recognisable infrared (IR) or ultraviolet (UV) spectrum which can be compared with spectra of authentic known compounds. However, this technique does not conveniently handle larger quantities and in these cases separation on the 50 to 500 mg scale can be carried out with only a small loss of resolution by chromatography on a silica gel or alumina packed column. The separated bands are marked under UV light, removed from the plate and extracted with diethyl ether. Separations on this scale provide sufficient of each fraction for full characterisation by nuclear magnetic resonance spectroscopy (NMR) and mass spectroscopy (MS), as well as IR spectroscopic techniques.

Polymer additives - mould release agents, plasticisers, antioxidants and UV absorbers, with molecular weights extending beyond 1000 - are generally unsuitable for GC or liquid chromatographic (LC) analysis because of their low volatility, lack of chromophore or thermal instability.

The identification of mixtures of unknown additives in solvent extracts of polymers presents some difficult problems. The solvent extract is usually available in only fairly small quantities, often consists of a complex mixture requiring preliminary separation into pure components before identifications can be attempted, and is frequently a mixture of compounds of completely unknown type.

TLC using plates coated with 250 µm adsorbent is an excellent technique for efficiently separating up to 20 mg of total additive mixtures into their individual components. This technique provides a few milligrams of each component, sufficient to prepare a recognisable IR or UV and mass spectra, which can be compared with the spectra of authentic known compounds. However, the technique does not conveniently handle larger quantities, although preparative TLC using thicker coatings will achieve larger scale separations with some loss of resolution.

Numerous works have been published on the experimental technique of TLC which will not be discussed further except in so far as is relevant to its application to additive identification. Dohmann [1] provides an excellent short review of techniques available. He discusses TLC in the normal sense of the word, i.e., with plate layers up to 250 µm thick and 20 cm x 20 cm or 20 cm x 8 cm in area and also discusses preparative layer chromatography which, with some loss in resolution, can separate considerably larger quantities of compounds on plate layers up to 2 mm thick and 100 cm x 20 cm in area.

Table 5.1 illustrates the differences in scale of operations between normal analytical TLC, preparative layer chromatography and preparative column chromatography. Separations which have been successfully achieved by analytical TLC may be transferred directly to the preparative layer, because the same sorption media with the same grain size are used in each technique. However, it is not always possible to transfer directly, separations which have been successfully achieved by analytical TLC to preparative column chromatography with equal success because appreciably different adsorbent grain sizes are used in the two techniques.

Halpaap [2] discusses in some detail the experimental technique of preparative layer chromatography with sample quantities between 0.1 and 100 mg, using plates up to 100 cm x 20 cm in area and adsorbent layers up to 2 mm thick.

Table 5.1 Comparison of thin-layer and column chromatography			
	Analytical TLC	**Preparative layer chromatography (laboratory scale)**	**Preparative column chromatography (laboratory scale)**
Quantity of substance mixture applied	Several micrograms	0.1-50 g	1-250 g
Average grain size of adsorbent (silica gel), µm	5-25	5-25	50-500
Quantity of solvent required	10-100 ml	2-5 litres	5-100 litres
Purity of substances	High purity	High purity only small inter-mixed zones	Less purity larger intermixed zones
Duration of development	Less than 1 h	Less than 1 day	1 to several days
Source: Author's own files			

Stahl [3] has also discussed the general experimental technique of preparative layer chromatography using plates 40 cm x 20 cm in area with up to 1 mm thick coatings. He confirmed that when layer thicknesses are increased appreciably above 250-500 µm a loss in resolution of separated compounds occurs, although this is not so important when the substances to be separated have a sufficiently large difference in retention factor (R_f) value in the range 0.3-0.8. In these particular circumstances the advantages of achieving good separation with larger sample sizes are combined. However, for the separation of substances which differ in R_f value by 0.2 or less, layer thickness should be limited to a maximum of 250 µm with consequent limitations on maximum sample size. In fact, in problems concerned with the identification of additives in polymers, the total quantity of polymer extract sample available for analysis will be rather small, typically 10-100 mg, and in the author's experience, in most instances, true TLC using 250 µm thick layers is admirably suited for the separation of small quantities in the order of 0.1 to 2 mg with excellent resolution. Consequently in this section attention is mainly focused on the technique involving thin-layers of adsorbent up to 250 µm.

Polymer extraction procedures using organic solvents do not extract all types of organic additives from polymers, also many inorganic compounds and metallo-organic compounds, (e.g., calcium stearate) are insoluble. The presence of metals will have been indicated in the preliminary examination of the polymer. Most types of organic polymer additives, however, can be readily extracted from polymers with organic solvents of various types.

The first step is to solvent-extract the total additives from the polymer in high yield and with minimum contamination by low molecular polymer. Extracts should be used for analysis without delay as they may contain light or oxygen sensitive compounds. When delay is unavoidable, storage in actinic glassware under nitrogen in a refrigerator minimises the risk of decomposition.

Additives coated on to the surface of a polymer (e.g., antistatic additives) can be removed easily by washing with a low-boiling solvent, which does not attack the polymer. These extracts can be concentrated under vacuum at 35-40 °C prior to further analysis. Total internal plus external additives can be extracted from low and high-density polyethylene (HDPE) and polystyrene (PS) by procedures involving solution or dispersion of the polymer powder or granules (3 g) in cold redistilled sulfur-free toluene (50-100 ml), followed in the case of polyethylene (PE) by refluxing for several hours. Rubber-modified PS does not completely dissolve in toluene if it contains gel. Methyl ethyl ketone or propylene oxide are alternative suitable solvents for PS. Dissolved polymer is then reprecipitated by the addition of methyl alcohol or absolute ethanol (up to 300 ml), and the polymer removed by filtration or centrifuging. The additive-containing extract can then be concentrated to dryness as described previously. Alternative procedures for the extraction of PE and polypropylene (PP) involve refluxing with chloroform for 6 hours or contacting with cold diethyl ether for 24 hours or Soxhlet extraction with diethyl ether, methylene dichloride,

chloroform or carbon tetrachloride for 6-24 hours followed by concentration of the extract. Methylene dichloride is a particularly good solvent for PP extractions because of its high volatility and also its small extraction of atatic material from the polymer, compared with other solvents. In addition to additives, most solvents also extract some low molecular weight polymer with subsequent contamination of the extract. To overcome this, Slonacker and Sievers [4] have described a procedure for obtaining polymer-free additive extracts from PE based on low temperature extraction with *n*-hexane at 0 °C. This procedure is also applicable to PP and PS.

The possible complications in additive identification that can arise in TLC due to additive degradation by light, heat or oxygen during solvent extraction operations have been well illustrated in the case of the phenolic antioxidant Ionox 330 (1,3,5-trimethyl-2,4,6-tri(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene). When 10 µl of a 1% methanol solution of this compound was applied immediately after the solution had been prepared, at the base of a silica gel coated plate and the chromatogram then developed by elution with cyclohexane:benzene (4:1) and then a suitable spray reagent applied, it was found that only one spot, due to undegraded Ionox 330, appeared part way up the plate. However, when a 1% methanolic solution of Ionox 330, which had been allowed to stand in air for 10 days was chromatographed under the same conditions it was found that two compounds were present, Ionox 330 and, also a degradation product of Ionox 330 which remained unmigrated at the baseline on the chromatogram. Approximately 50% of the Ionox 330 had degraded during the 10 days standing period, presumably due to oxidation by air possibly assisted by the UV component of daylight.

5.1 Experimental

5.1.1 Preparation of Thin-layer Plates for Analysis

Plates (20 cm x 20 cm) coated with a 250 µm thickness of Merck silica gel G254 or GF 254 (UV fluorescent) are suitable for the separation of polymer additives. These plates can either be prepared in the laboratory using an adjustable spreader or prepared plates can be obtained commercially.

The glass used to prepare plates should be cleaned with chromic acid, then with deionised water, avoiding detergents, and dried in an air oven prior to coating with silica gel in a clean laboratory atmosphere. Conditioning in an air oven for 30 minutes at 120 °C in a vertical position should be followed by storage in a desiccant box until the plates are required for use (**Figure 5.1**). The plates should preferably be used within 1-2 hours of preparation so that their activity does not change appreciably and to reduce the possibility
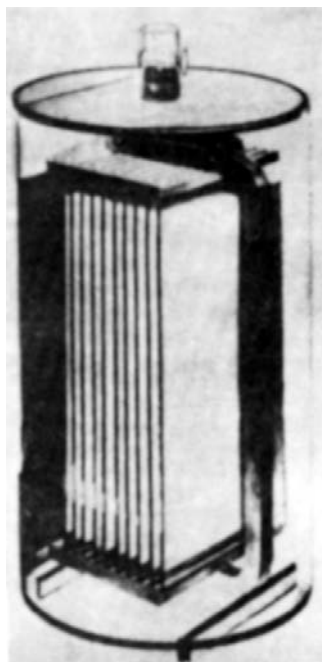
Figure 5.1 Perspex vacuum-desiccator with dry rack for 10 plates, 40 x 20 cm
Reproduced from Stahl, Laboratory Practice [3]

of contamination of the silica gel layer by volatile impurities in the laboratory atmosphere which might interfere in the subsequent evaluation of the plates.

5.1.2 Application of Polymer Extract to Plate

Regular application of the sample is particularly important for successful separations. For this purpose, 'spotting' as a band is not recommended, and manual application using a pipette requires considerable skill. The procedure suggested by Ritter and Meyer [5] obviates these disadvantages. In this procedure the sample is sprayed on to the layer as a band by means of an automated applicator. With this instrument a band up to 35 cm long can be applied in a short time. The reversing points of the applicator are practically free from hysteresis so that undesired thickening of the band at the ends does not occur.

In order to minimise washing-out of the sprayed solution at high sample volumes the most volatile solvent possible is chosen, e.g., diethyl ether or ethylene dichloride. Where

appropriate the plate may be warmed beforehand so as to achieve rapid evaporation of the solvent.

A convenient trial sample size of solvent solution of a polymer extract for application as a band on a 250 µm thick, 20 cm x 20 cm plate is 1 ml of a 1% solution, i.e., 10 mg. Depending on the type of separation obtained, larger or smaller sample volumes can then be applied as necessary. A further approximate guide for polymer extract sample size for a 250 µm thick, 20 cm x 20 cm plate is 0.1-1 mg of polymer extract dissolved in 1 ml solvent per gram of gel loading on the plate. These sample sizes can be increased by a factor of approximately 100 (i.e., 10-100 mg) dissolved in a few millilitres of solvent when carrying out preparative layer chromatography on 20 cm x 40 cm plates with gel thicknesses in the range 750-1500 µm.

5.1.3 Selection of Chromatographic Solvent

Finding a chromatographic development solvent (or mixture of solvents) for the separation of an unknown mixture of additives is not always easy. In some cases a separation is not obtained with a single solvent or solvent combination but necessitates the preparation of several chromatograms using different solvents.

An unknown mixture should be first chromatographed on 20 cm x 5 cm plates with solvents of different polarities to obtain an idea of the types of compounds present in the sample and to reduce the possibility of missing any of the sample components. Solvents of low polarity, such as *n*-hexane, tetrachloroethylene and carbon tetrachloride, cause polar sample constituents to migrate more readily. Solvents of intermediate polarity such as toluene, benzene, chloroform and methyl cellosolve have a greater elutive effect on polar sample components, whereas highly polar solvents such as dioxan, methylene dichloride, ethyl acetate, nitromethane, acetone, lower alcohols and water elute polar sample constituents towards the solvent front, i.e., R_f values near unity. Mixtures of 40/60 petroleum spirit and up to 10% (*v/v*) ethyl acetate are very useful general solvents for the separation of unknown mixtures.

Seher [6] has discussed the application of two-dimensional TLC on silica gel to the separation of antioxidants, using development with chloroform in one direction and benzene in the other, and claims separations superior to those obtained in single dimensional chromatography with either of these solvents. Van der Heide and co-workers [7] have described a range of neutral, acidic and basic solvents for the separation of the types of compounds used as additives in polymers. Van der Neut and Maagdenberg [8] describe a scheme for the separation of antioxidants in which they first chromatograph the mixture with a particular solvent and thereby separate the antioxidants into groups according to R_f ranges. Based on this preliminary classification, a second solvent system is

selected and then, if necessary, a third and fourth until complete identification is achieved. In all, nine solvent systems are specified together with four detection reagents. The scheme has been applied, with success, to over 30 antioxidants. New antioxidants can be easily inserted into the scheme. However, the success of this system depends to a large extent on the reproducibility of the R_f values obtained, and the authors do not, unfortunately, give any account of their experimental procedure. Various solvent systems which have been referred to in the literature [9] for the separation of polymer additives on thin-layer plates are referred to in **Table 5.2**.

Table 5.2 Separation of antioxidants - thin-layer chromatographic methods				
Substances separated	**Stationary phase**	**Mobile phase**	**Detection**	**Ref.**
Phenolic antioxidants	Silica Gel G	Methanol - cyclohexane (1:24)	30%Molybdophosphoric acid + ammonia vapour	[4]
Organotin stabilisers	Not stated	Acetic acid - isopropyl ether (1-5:98-5)	20% Molybdophosphoric acid + ammonia vapour	[10]
Antioxidants	Not stated	Light petroleum - ethyl acetate (9:1)	(a) Ethanolic 2,6-dichloro-*p*-benzoquinone-4-chloramine + 2% aq. $Na_2B_4O_7$ (b) Diazotised *p*-nitroaniline	[11]
Organic stabilisers	Kieselgel G	Ethanol-free chloroform		[12]
Phenolic antioxidants	Polyamide powder	Methanol - water (3:2) or methanol - carbon tetrachloride (1:9)	Diazotised sulfanilic acid	[13]
Phenyl salicylate Resorcinol benzoate	Kieselgel G	Dichloromethane or isopropyl ether - light petroleum (40-60°) (7:3)	UV	[14]
BHA, 2,6-di-*t*-butyl-*p*-cresol	Silica gel	Chloroform	20% Molybdophosphoric acid + ammonia vapour	[15]
Antioxidants	Polyamide powder	Methanol - acetone - water (6:1:3)	Diazotised sulfanilic acid or molybdophosphoric acid	[16]
Antioxidants	Kieselgel G		α,α'-Diphenyl-β-picryl hydrazyl (free radical)	[17]

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Table 5.2 Continued...				
Substances separated	**Stationary phase**	**Mobile phase**	**Detection**	**Ref.**
Antioxidants	Alumina + 5% Plaster of Paris on a microscope slide	Petroleum ether - dioxane (10:1)	5% Ethanol, phosphomolybdic acid	[18]
Antioxidants	Silica gel	Acetone, chloroform, benzene, carbon tetrachloride or binary mixtures		[19]
Antioxidants	(a) 10% starch in polyamide powder (b) 10% PVC in polyamide	Methanol – acetone - water (3:1:1), light petroleum – benzene - acetic acid - DMF (40:40:20:1)		[7]
Antioxidants	Silica Gel G	Benzene	0-5% $Fe_2(SO_4)$, in sulfuric acid + 0.2% $K_4Fe(CN)_6$ (1:1)	[20]
BHA: tert-butyl-4-hydroxyanisole *DMF: dimethyl formamide*				

5.1.4 Detection of Separated Compounds on the Plate

Detection techniques should be carried out immediately after the chromatogram has been developed, in order to reduce to an absolute minimum any opportunity for volatile sample constituents to be lost by evaporation from the plate. Detection of the separated compounds on the plate is achieved by examination under UV light which locates some, but not all, types of compounds, and by spraying with a range of general or specific spray reagents. Merck GF 254 silica gel contains an inorganic fluorescing additive, which is not extracted in the methanol pretreatment discussed previously. Silica gel is suitable for most types of separations. Alumina (alumina Fluka type D5F) and cellulose powders (MN cellulose powder 300 F254; Macherey Nagel & Co.) are both available in fluorescent forms. Exposure of plates to 254 nm radiation permits visualisation of substances on the plate which absorb above 230 nm as a dark area on a blue fluorescent background. Fluorescent indicators which are activated by long wavelength UV light may also be incorporated in the adsorbent. The sodium salts of hydroxypyrene-sulfonic acids are particularly suited for this purpose. The separated polymer constituents show

on the chromatogram, partly as dark zones, partly as zones which fluoresce brightly. The Merck silica gel HF 254+366 contains two fluorescence indicators, long and short UV light sensitive. To incite fluorescence, apparatus is needed which will allow a choice of short or long wave UV radiation. The non-fluorescent silica gel, Merck G254, reveals the presence of polymer constituents which have an intrinsic fluorescence under short wave (254 nm) or long wave (366 nm) UV light.

To locate separate compounds on the plate with a minimum risk of missing any sample constituents, 1 ml of a 1% solution of the polymer extract in a low-boiling solvent such as diethyl ether or methylene dichloride is applied as a continuous band along the baseline of each of two 20 cm x 20 cm plates coated with GF254 and G254 silica gel, the solvent is allowed to evaporate, the chromatograms are developed and then the resulting plate is examined under 254 and 366 nm UV light sources. After marking off the position of any compounds seen, with a stylus, the plates are sprayed with the general spray reagents shown in **Table 5.3** to reveal the presence of any compounds which were not visible under UV light.

Table 5.3 General spray reagents for location of compounds on 20 cm x 20 cm silica gel coated thin-layer chromatography plates	
A. Reagents applied to GF254 plate without subsequent heating*	
(i) Potassium permanganate	0.1 N in aqueous sodium carbonate (5% *w/v*)
(ii) Potassium permanganate	2% *w/v* in aqueous sulfuric acid (6% *v/v*)
(iii) Potassium permanganate	0.1% *w/v* in sulfuric acid (96%)
(iv) Antimony pentachloride	2% *w/v* in carbon tetrachloride
(v) Phosphomolybdic acid	3% *w/v* in ethanol, then expose plate to ammonia vapour
B. Reagents applied to GF254 plate with subsequent heating*	
	Heat treatment of plate
(i) Sulfuric acid aqueous (20% *w/v*)	5-15 min at 120 °C, then 5 min at 150 °C
(ii) As (ii) under A	5-15 min at 120 °C, then 5 min at 150 °C
(iii) Phosphoric acid (10%) methanolic	5-15 min at 120 °C, then 5 min at 150 °C
(iv) Perchloric acid (2%) methanolic	5-15 min at 120 °C, then 5 min at 150 °C
(v) As (iv) under A	5-15 min at 120 °C, then 5 min at 150 °C
(vi) Phosphomolybdic acid (20% *w/v*) in methanol or methyl cellosolve, then expose plate to ammonia vapour	5-15 min at 120 °C, then 5 min at 150 °C
*Spray 20 cm x 2 cm wide sections of plate with each reagent using an aluminium or glass mask with suitable aperture. *Source: Author's own files*	

A further general test for organic compounds on the plate involves holding an electrically heated 25 cm long copper wire, set at red heat, a few millimetres above the plate along the length in which the chromatogram has been developed. After a few seconds exposure, many types of organic compounds reveal themselves by charring or otherwise discolouring.

Further information on the nature of some particular classes of additives can then be obtained by spraying fresh plates with more specific chromogenic reagents (**Table 5.4**).

Figure 5.2 shows a typical thin-layer chromatogram obtained for three phenolic antioxidants following spraying with a 1% ethanolic solution of 2,6-dichlorobenzoquinone chlorimine.
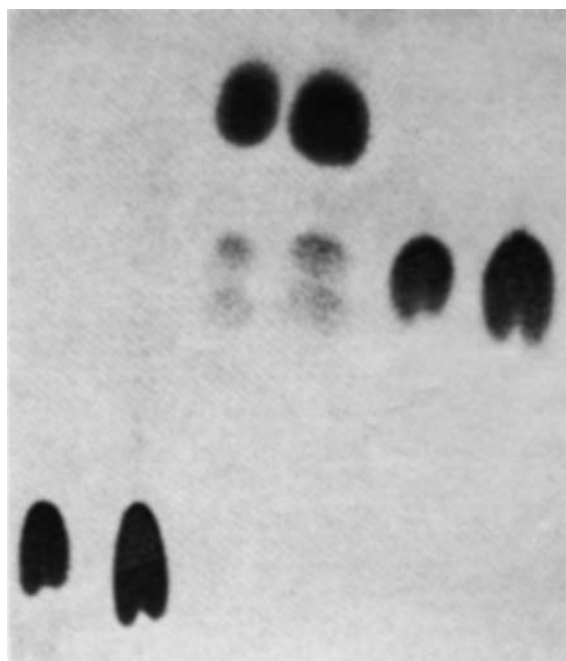
Figure 5.2 Thin-layer chromatography of antioxidants. Three phenolic antioxidants developed with dichlorobenzoquinone chlorimine spray reagent (2:6)
Source: Author's own files

Additive type	Spray reagent*	Ref.
Table 5.4 Chemical analysis of additives in plastics: specific spray reagents for location of compounds by thin-layer chromatography		
Phenolic antioxidants	(i) 2,6-Dichlorobenzoquinone chlorimine (1-2% in ethanol followed 15 min later by 2% borax in 40% aqueous ethanol).	[6, 8]
	(ii) α,α′-Diphenyl picryl hydrazyl (0-1% in 95% aqueous ethanol).	
	(iii) Palladium chloride. Mix 150 ml palladium chloride with 100 ml of 2 N hydrochloric acid.	[11, 17]
	(iv) Diazotised *p*-nitroaniline. Mix 5 ml 0.5% *p*-nitroaniline in 2 N hydrochloric acid with 0.5 ml 5% sodium nitrite until colourless and 15 min later add 15 ml 20% sodium acetate.	[17] [11]
Amine antioxidants	Diazotized *p*-nitroaniline. Mix 5 ml 0.5% *p*-nitroaniline in 2 N hydrochloric acid with 0.5 ml 5% sodium nitrite, until colourless and 15 min later add 15 ml 20% sodium acetate.	
Dialkyl thiodipropionates	Potassium platinoiodide. Mix 5 ml 5% platinum tetrachloride in 1 N hydrochloric acid with 45 ml 10% potassium iodide and 100 ml water.	[17]
Phthalate ester plasticisers	Resorcinol. Spray with 20% aqueous resorcinol in 2% aqueous zinc chloride and heat to 150 °C. Then spray with 4 N sulfuric acid and heat for 20 min at 120 °C. Spray with 40% potassium hydroxide to produce orange spots. Phthalic acid and phthalates also react.	[22, 23]
Acids and bases	Bromocresol green, bromocresol purple, bromophenol blue, methyl red. All 0-5% in 50% aqueous ethanol.	[3, 24] [2, 25]
Carboxylic acids	Sodium dichlorophenolindophenol (1% ethanolic).	[2, 26]
Aliphatic (primary, secondary and tertiary) amines, long chain quaternary salts and amine oxides	Cobalt thiocyanate. 10 g $Co(NO_3)_2 6H_2O$ and 10 g ammonium thiocyanate made up to 100 ml. Produces a blue colour.	[2, 27]
Alkanolamines	Ninhydrin. Heat plate for 5 min at 110 °C, spray with 0-2% ninhydrin in acetone and heat for 5 min at 110 °C to produce colours. Further colours then produced upon spraying plate with 0-2% alizarin in acetone.	

Table 5.4 Continued...		
Additive type	**Spray reagent***	**Ref.**
Alkyl phenols	Phenols coupled as *p*-nitrophenol azo dyes applied to plate of silica gel impregnated with alkali. Separated azo dyes located as yellow/red colours upon exposure of plate to ammonia vapour.	
Carbonyl compounds	Carbonyl compounds in sample converted to 2,4 dinitrophenylhydrazones, applied to thin-layer plate and plate developed. Separated 2,4-DNPH compounds located as yellow or brown colours upon spraying plate with 2% sodium hydroxide in 90% ethanol.	[20]
Organic peroxides	Hydriodic acid. Spray plate with a reagent comprising 40 ml glacial acetic acid and 0.2 g zinc dust added to 10 ml of 4% aqueous potassium iodide, then spray with fresh 1% starch solution. Peroxides (and certain other types of oxidising agents) revealed by liberation of free iodine. Alternatively use 2,6-dibromobenzoquinone chlorimine.	[28]
*Spray 20 cm x 2 cm wide sections of the plate with the various reagents using an aluminium or glass mask with suitable aperture. DNPH: 2,4-dinitrodiphenylhydrazine Source: Author's own files		

5.1.5 Evaluation of Developed Plates

It is well known that the quantity of sample that can be processed by TLC is subject to an upper limit. The reason for the limit is that, as the weight of the sample is increased, so the area occupied by each fraction on the chromatogram increases. Ultimately, the resolution becomes unacceptable because contiguous fractions overlap. Purdy and Truter [21] have described several methods of quantifying TLC and these are discussed next under separate headings. Further experimental details are given in this chapter on TLC are discussed in Chapter 4, Section 3.

5.1.6 Spectroscopic Methods

In this method a known weight of sample mixture is chromatographed on a thin-layer plate, usually coated with silica gel, by normal procedures. The test compound (or compounds) is extracted from the plate with a suitable solvent and the extract diluted to a standard volume with solvent prior to spectrophotometric examination. If the compound contains a

chromophore it may be determined directly; if not, before application to the plate, it must first be submitted to a chromogenic reaction if it is intended to use visible spectroscopy or alternatively, UV spectroscopy can be used if the compound absorbs in this region of the spectrum. For spectrophotometric analysis the fractions from a single chromatoplate will provide sufficient material.

Several difficulties which are specific to the spectrophotometric method might be encountered. One of them arises from the fact that substances which absorb electromagnetic energy are invariably extracted from the absorbent material as well as the sample. The absorption spectrum of the impurity is non-specific; the intensity falls steadily as the wavelength increases, and at 400 nm it becomes small enough to be ignored. If the extent of interference by adsorbent impurities is small then its effect may be cancelled out by suitable calibration procedures. By chromatographing known weights of pure reference compounds and determining the optical densities of the final solutions obtained from the plate, specific extinction coefficients may be calculated in terms of the weight of the sample applied to the chromatogram. To minimise the errors introduced by extractable impurities, three refinements can be considered.

A portion of the adsorbent, equal in area to that of the sample, is removed from an unoccupied part of the chromatogram. It is processed in the standard manner and the extract is used as the blank solution in the spectrophotometer. The contribution of the blank in the UV region of the spectrum is by no means a negligible proportion of the actual measurement and it is also rather variable.

To diminish further both the magnitude and the variability of the blank, the film may be pre-washed by allowing suitable solvents to ascend the film as in the development of a chromatogram (see Section 5.9).

Ganshirt and Morianz [29] tested an alternative method for eliminating the optical contribution from the adsorbent. Pure solvent was used as the spectroscopic blank instead of an extract from the adsorbent, and the absorption spectrum was recorded over a wide waveband. Subsequently a line was drawn across the base of the absorption peak (**Figure 5.3**) and it was assumed that the gap between this line and the corresponding line for the unchromatographed compound represents the optical density curve of the impurity from the adsorbent. The contribution of the sample is measured from the maximum to this baseline.

The coefficient of variation for the methyl and propyl esters of *p*-hydroxy benzoic acid were ±3.2% (13 determinations) and ±4.8% (14 determinations).
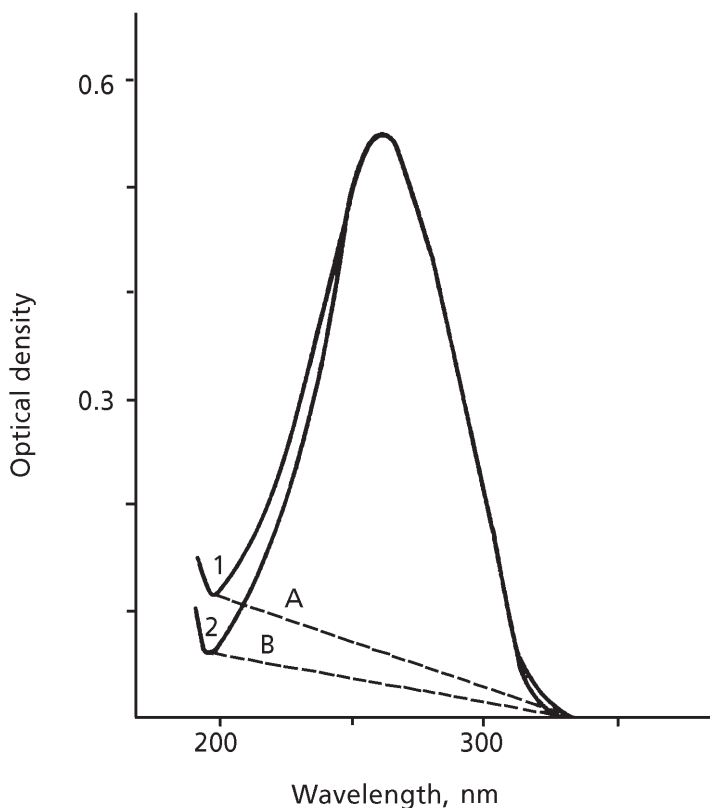
Figure 5.3 Elimination of adsorbent impurity contribution in spectroscopy of thin-layer chromatography isolates. Optical density of propyl-*p*-hydroxybenzoate: 1 – sample recovered from chromatogram; 2 – original sample. The gap between the base-lines A and B represents the contribution of the impurities originating in the adsorbent
Reproduced from Ganshirt and Morianz, Archiv der Pharmazie [29]

5.1.7 Optical Densiometric Analysis

Hefendahl [30] discovered that there is a linear relationship between the 'extinction area' of a spot on the densiometric trace of a chromatogram and the weight of material in the spot. To make the chromoplate translucent he sprayed the adsorbent with an ethereal solution of paraffin and then measured the optical density of the chromatogram as a function of the distance from the origin (**Figure 5.4**). The area under the peak, measured
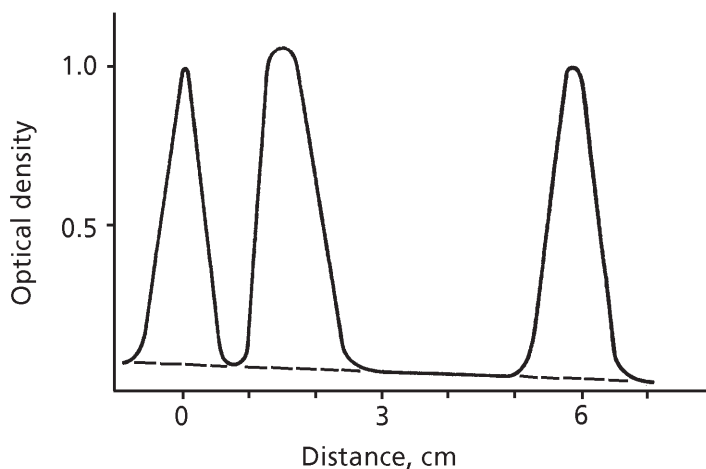
Figure 5.4 Optical densiometric analysis of thin-layer chromatograms. Optical density of a chromatogram as a function of distance from the origin
Reproduced from F.W. Hefendahl, Planta Medica [30]

to the dashed baseline is a linear function of the weight of material in the spot. Scanning photodensitometers for TLC plates are commercially available. The extinction area varies from one chromatogram to another so a standard is required for each chromatogram prepared.

5.1.8 Methods Based on Spot Size

As with densiometric analysis, methods based on spot size avoid all the difficulties connected with the recovery of the sample and with the extraction of impurities from the adsorbent [31]. An additional advantage is that they may be applied with equal facility to adsorption or partition chromatograms. To illustrate the method, the determination of the cholesterol content of wool wax alcohols by adsorption chromatography will be described.

A series of standard solutions of cholesterol were prepared by serial dilution. Equal volumes (2 μl) of a solution of known concentration of the sample and of each of the standard solutions were spotted on to the adsorbent alternatively. For high accuracy a micrometer syringe should be used, but also, a capillary pipette (Drummond Microcap), could be used.

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After the chromatogram had been developed in cyclohexane containing 10% acetone, the solvent-free adsorbent was sprayed with sulfuric acid and the chromoplate was warmed. The result is shown in **Figure 5.5**.
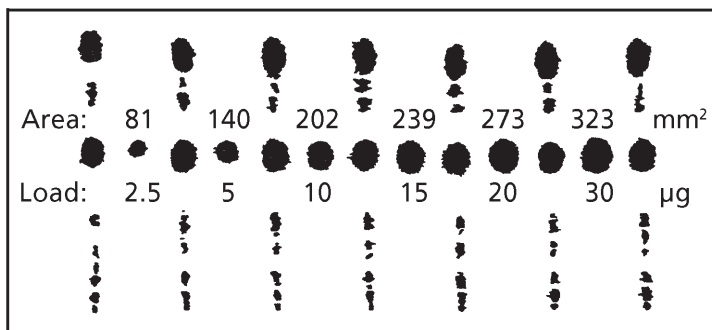
Figure 5.5 Quantitative evaluation of thin-layer chromatoplates based on spot size. Set of cholesterol standard interspersed with the same sample of wool wax alcohols. Adsorbent: silica gel G; solvent: cyclohexane:acetone (9:1); chromogenic reagent: sulfuric acid
Reproduced from A. Seher, Nahrung [31]

In Seher's method [31] the results for the standards are plotted in the form of area *versus* weight (**Figure 5.6**), and the weight corresponding to the mean area of the unknown samples is read from the graph. The weight of cholesterol is 9.2 µg per spot, corresponding to 30.7% of the sample.

Purdy and Truter [33] discovered that the square root of the area is a linear function of the logarithm of the weight of material in the spot. Statistical tests by these workers showed that the goodness of fit with their relationship is more satisfactory than for any of the earlier proposals.

The advantages of using the linear relationship between √A and log W are that the experimental work can be substantially reduced, and statistical evaluation of the accuracy is possible. Only two standard solutions, one of which is prepared from the other by dilution, are required to determine the equation of a straight line. Equal volumes of the two standard solutions and the test solution are chromatographed simultaneously, and the weight of the compound in the sample is calculated from the equation:

$$\log W = \log W_s + \left(\frac{\sqrt{A} - \sqrt{A_s}}{\sqrt{A_s} - \sqrt{A_d}} \right) \log D$$
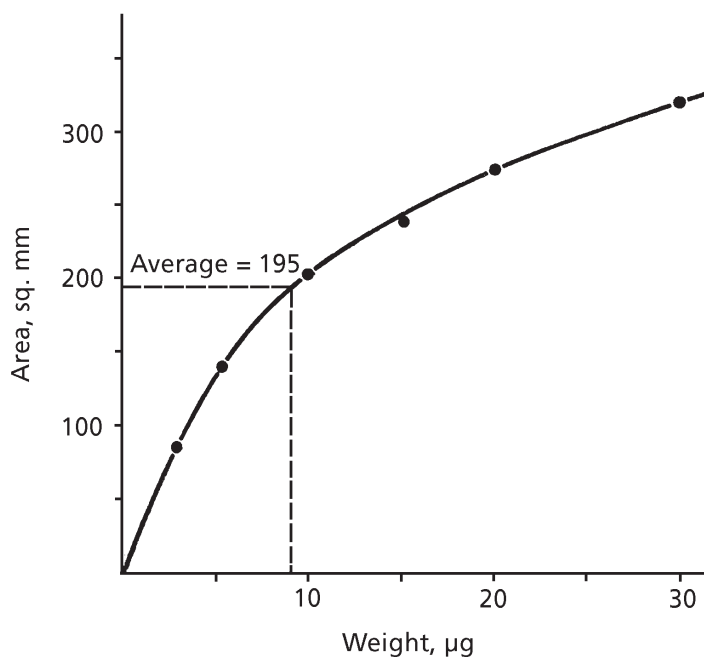
Figure 5.6 Plot of area *versus* weight for cholesterol standards shown in **Figure 5.5**
Reproduced from A. Seher, Nahrung [31]

Where the subscipts s and d refer to the standard and the diluted standard, respectively, and D is the dilution factor.

The six standards shown in **Figure 5.5** can be used to test the validity of the relationship √A and log W (**Figure 5.7**). For a statistical determination of the accuracy of the process, any standard may be taken as the 'unknown' and its value may be calculated from any combination of two from the remaining five standards. Altogether ten separate combinations are possible for each 'unknown'. As there are six possible 'unknowns' the entire data represent 60 separate values.

Attaway and co-workers [34] discuss in some detail the application of the optical density and spectrophotometric methods discussed previously to the determination of esters by TLC. They used glass plates coated with Silica Gel G. Chromatoplates were developed by the ascending technique, using benzene or trifluorotrichloroethane:methylene chloride (60:40) as developing solvents.
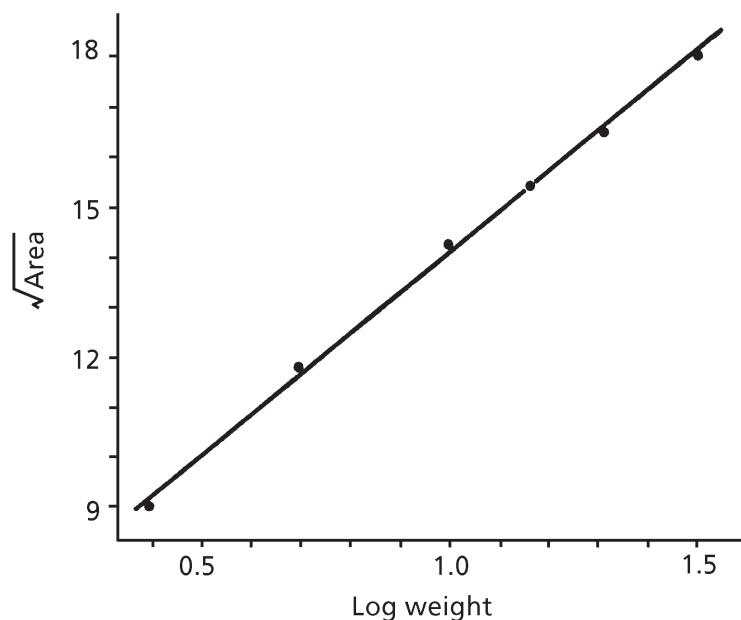
Figure 5.7 Plot of the data in **Figures 5.5** and **5.6** in the form √ area *versus* log weight
Reproduced from Purdy and Truter, Analyst, RSC [33]

Detection sprays were mixtures of potassium permanganate and sulfuric acid and, also, vanillin in 96% sulfuric acid. To minimise differences between individual chromatoplates, standard R_f values of the esters were computed using citronellal as an internal standard.

Quantitative estimations were based on optical density measurement using a densitometer for spots of lowest concentration (0.5-5 nl) per spot and on spectrophotometric measurements for spots of higher concentration. Only those compounds reacting with vanillin/H_2SO_4 could be studied accurately with the transmission densitometer as the spots formed with $KMnO_4$/H_2SO_4 could not be measured by the light transmission method. The spectrophotometric procedure was not only limited to materials sensitive to vanillin, but could only be used satisfactorily with a portion of the vanillin-sensitive substances. **Figure 5.8** shows a typical curve obtained by reading a set of varying concentration spots using the densitometer. The graph is seen to be linear to a concentration of about 5 nl/spot.

The application of TLC to various particular types of polymer additives is discussed in the next section.
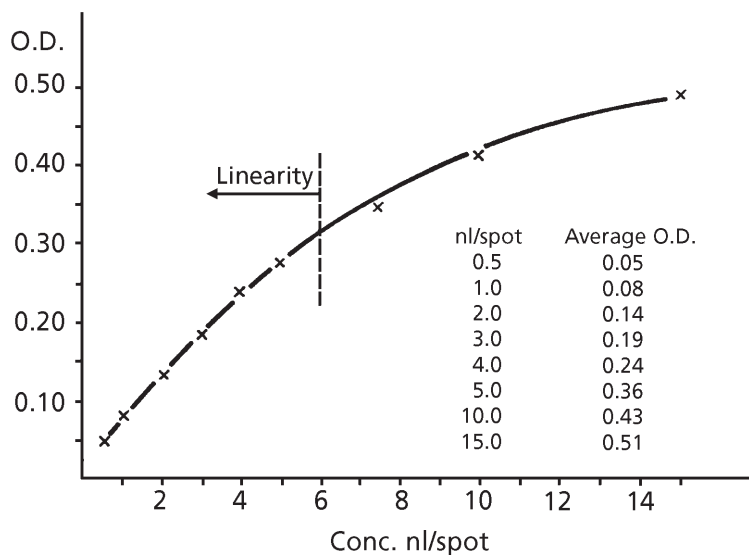
Figure 5.8 Quantitative densitometric estimation of caryvyl acetate spots on thin-layer plate. Spots visualised with concentrated sulfuric acid – vanillin spray
Reproduced from Attaway, Walford and Edwards, ACS [34]

5.2 Antioxidants

Quantitative procedures are described next for determining Santonox R (4,4′-thio-bis-6-*tert*-butyl-*m*-cresol), and the UV stabiliser Cyasorb UV 531 (2-hydroxy-4-*n*-octoxybenzophenone) in PE, in amounts down to 20 ppm in polymer with an accuracy of ±20% of the determined amount.

5.2.1 Determination of Santonox R

5.2.1.1 Polyethylene Extraction Procedure

Polymer (5 g) is weighed accurately into a 500 ml round-bottomed flask. Toluene (65 ml) is added and then heated on a boiling water bath for 90 minutes using a reflux condenser.

The flask is removed from the water bath and 85 ml of absolute ethanol is immediately poured down the condenser to precipitate the dissolved PE from the hot toluene solution.

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After cooling to room temperature, the condenser is removed, the flask is stoppered and shaken well. The solution is filtered through a No.42 Whatman filter paper into a 250 ml beaker. The flask and residue are washed with a further 100 ml of ethanol.

The toluene/ethanol solution is evaporated almost to dryness on a boiling water bath with the aid of a stream of nitrogen and finally to dryness using only the nitrogen stream. If more polymer is precipitated during the evaporation, the solution is refiltered into a smaller beaker. The residue is washed into a 2 ml volumetric flask with chloroform and diluted to the mark.

The extract is applied to a thin-layer plate and the chromatogram developed. The concentration of Santonox R in the PE is estimated by visually comparing the intensity of the spot obtained with corresponding spots from known quantities of Santonox R.

Place 20 µl of the chloroform extract of the polyethylene sample as a spot on a thin-layer plate. Also apply 20 µl aliquots of standard solutions of Santonox R in chloroform (0.05%, 0.04%, 0.03% *w/v*). Develop the chromatogram to a distance of 10 cm in a chromatography tank containing petroleum ether (40:60)/ethyl acetate (5:1 *v/v* mixture) as the eluent.

Inspect the plate under UV light (254 nm) and compare the intensity of the Santonox R spot from the PE extract with the intensities of the standard spots. If the spot is of lower intensity than that of the 0.03% *w/v* standard then a new chromatogram should be developed using standards of Santonox R in chloroform (0.025%, 0.015% and 0.005% *w/v*).

Visually compare the intensity of the spot obtained from the PE extract with the standard spots and thus estimate the percentage level of Santonox R in the chloroform solution. Spray the thin-layer plate with a 2% *w/v* ethanol solution of 2,6-dibromo-*p*-benzoquinone-4-chlorimine. Allow the thin-layer plate to dry and re-spray using a 2% *w/v* aqueous solution of borax. Re-estimate the amount of Santonox R present in the chloroform solution by visually comparing the purple spots produced.

Calculation

Santonox R from 5 g of PE was concentrated into a 2 ml chloroform solution.

Thus the wt.% of Santonox R in HDPE:

= 2/5 x the level of Santonox R present in the 2 ml chloroform solution (as determined by TLC in % *w/v*).

Simpson and Currell [32] use TLC in the determination of additives such as antioxidants (also UV absorbers and organotin stabilisers) in plastic formulations. Comparatively small samples of the plastics materials are required, and, by means of the techniques described, it is

possible to identify additives in extracts containing several different components. The method described next can be used to detect additives down to between 10 and 1 µg per sample and both qualitative and more accurate quantitative determinations are made possible.

Simpson and Currell [32] used commercially prepared thin-layer plates of which there are three main types: layers on glass, layers on a flexible backing of polyester or aluminium, and silica gel impregnated glass fibre. The Merck thin layers on glass were found to be most suitable because the layers were robust and were not rubbed off easily, they were not attacked by reagents and were of a suitable thickness (0.25 mm) to receive a reasonable sample loading. Another advantage is that the plates are fitted into an Eastman Kodak 'Chromatogram' sandwich chamber, thus obviating the need for a large developing tank and reducing considerably the time required for solvent saturation of the tank. The plates used for the separation of all three types of additives in question were Merck Kieselgel GF254 (silica gel containing a fluorescent additive).

The elution solvents used were benzene-ethylacetate-acetone (100:5:2) for antioxidants and chloroform-hexane (2:1) for UV absorbers and butanol-glacial acetic acid (97:3) for organotin compounds. An ethanolic solution of 2,6-dichloro-*p*-benzoquinone-4-chlorimine was used as spray reagent for antioxidants and UV stabilisers.

Figure 5.9 illustrates, on one plate, the complete series of separations of mixtures of antioxidants. When this diagrammatic representation is considered in conjunction with **Table 5.5** it will be seen that quite good identification of the various substances is obtained.

It was possible to detect down almost to 1 µg per spot applied in certain cases and at least 10 µg per spot applied. More quantitative estimation, by comparison with standards, was carried out by Simpson and Currell [32] in a number of instances and it is possible to differentiate between 5 and 10 µg per spot applied; one such sample is butylated hydroxytoluene.

Dobies [35] has described detailed procedures for determining various antioxidants in PE and PP films. A feature of this method is that it requires only a small polymer sample (5 g) for the determination of down to 0.02% antioxidant compared to sample sizes of up to 1 kg in previously reported procedures. They describe the extraction procedure used for isolating the antioxidants from the polyolefins, the TLC separation of various antioxidants used industrially, and a quantitative determination of the antioxidant to detect 0.02-0.20% of an antioxidant by the use of the double beam scanning densitometer. The six antioxidants he studied were: 4,4´-butylidene (2-*tert*-butyl-5-methyl)phenol; 4,4-thiobis(6-*tert*-butyl-*m*-cresol); pentaerythritol tetrakis(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate); 2,2´-methylenebis(4-methyl-6-*tert*-butylphenol); octadecyl (3,5-di-*tert*-butyl-4-hydroxyphenyl) acetate and 2,6-di-*tert*-butyl-*p*-cresol.
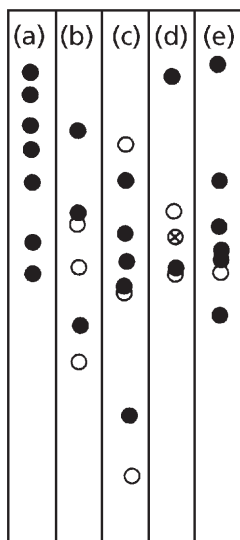
Figure 5.9 Thin-layer chromatograms of mixtures of antioxidants. Mobile phase: benzene – ethyl acetate – acetone (100:5:2). Columns are (a) phenols, (b) amines, (c) hydroquinones, (d) miscellaneous antioxidants, and (e) mixtures of unknown extract formulations
Reproduced from Simpson and Currell, RSC [32]

In this method PE or PP film (5.0 g (Wb); precut into strips approximately 2.5 x 2.5 cm) is weighed into the extraction thimble, 130 ml of the *n*-heptone - *n*-octane extraction solvent are added to the 250 ml flat bottom flask with a few glass beads - the extraction apparatus is connected and heated to boiling. After 3 hours, the system is allowed to cool to room temperature, and the solvent drained into the 250 ml flat bottom flask. The extraction thimble and extraction apparatus are rinsed down with 25-50 ml of the extraction solvent and drained into the 250 ml flask then concentrated to 10 ml by gentle evaporation.

Ethanol-water (3:1) is used as TLC solvent and an ethanolic solution of phosphomolybdic acid used as spray reagent. The excellent calibration curve obtained by this procedure for 2, 2′methylene bis (4-methyl-6-*tert*-butyl phenol) is illustrated in **Figure 5.10**.

TLC has been used extensively for the determination of phenolic and amine antioxidants and UV stabilisers in plastics and rubber [17, 32, 36-58].

Table 5.5 Results obtained in the separation of antioxidants				
Substance	Type of derivative	R_f value	Locatable by ultraviolet	Locatable by reagent
Nonox SP	Phenolic	0.61 0.93	- -	Blue Purple
Nonox TBC	Phenolic	0.98	-	Yellow with red ring
Nonox WSP	Phenolic	0.85	-	Yellow
Nonox EX	Phenolic	0.56	-	Yellow
Nonox WSL	Phenolic	0.82	-	Yellow with red ring
BHT	Phenolic	0.98	-	Yellow with red ring
2246	Phenolic	0.75	-	Yellow
Nonox CI	Amine	0.65 0.84	+ -	- Red
Nonox DPPD	Amine	0.66	+	Yellow
Nonox OD	Amine	0.56	+	-
Nonox ZA	Amine	0.43 0.38	- +	Yellow -
Santoflex 75	Hydroquinone	0.15 0.61 0.74	+ + -	- Yellow Blue
Santoflex AW	Hydroquinone	0.80 0.51 0.55	+ + +	- Blue -
Santoflex R	Hydroquinone	0.26 0.53	- +	Blue Blue
DLTDP	Miscellaneous	0.61	+ (very faint)	-
Nonox NS	Miscellaneous	0.52	-	Blue
Superlite	Miscellaneous	0.64 0.93	+ -	- Red
Polygard	Miscellaneous	0.52 0.61	+ + (faint)	- -
Nonox HO	Unknown formula	0.46 0.64 0.60 0.99	- - - -	Blue Blue Blue Red
Nonox WSO	Unknown formula	0.58	+	Yellow
Irganox 1076	Unknown formula	0.57 0.75	+ +	- Red
2246: 2,2´methylene bis(4-methyl-6-tert butyl phenol) From Simpson and Currell, RSC [32]				
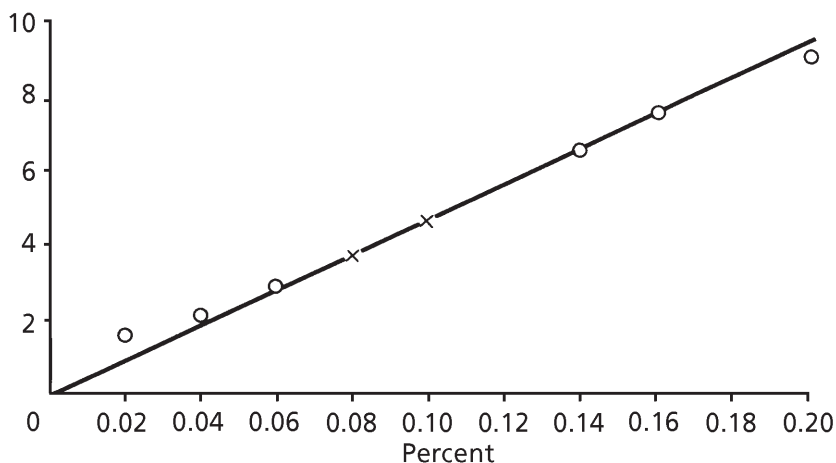
Figure 5.10 Thin-layer chromatography calibration curve for 2,2′-methylenebis(4-methyl-6-*tert*-butylphenol)
Reproduced from Dobies, Journal of Chromatography [35]

5.3 Ultraviolet Stabilisers

Crompton [59] has described a simple direct thin-layer method for the determination of UV 531 ultraviolet stabiliser in hot toluene extracts of HDPE. Interference was encountered from a number of additives, namely, dilauryl thiodipropionate, Ionox 330, Ionol CP, Topanol CA, Santonox R and Polygard.

UV 531 is extracted from the polymer by precipitation of the polymer with ethanol from a hot toluene solution as described previously. An aliquot of the extract is applied to a thin-layer plate and chromatographed. The zone corresponding to UV 531 is removed from the plate and extracted with ethanol. The concentration of UV 531 is determined by measuring the UV absorption peak near 295 nm in ethanol solution and referring to a calibration graph.

To estimate 7(-6 butoxy-5-methylbenzotriazol-2-yl) 3-phenylcoumarin in polymer granules, the sample was extracted from the ground or chopped sample by heating under reflux with chloroform [60]. The extract, together with a chloroform solution of an authentic sample of the brightener was applied to two Kieselgel G plates, and chromatograms developed with benzene-chloroform (2:3) or benzene. The spots were detected by their fluorescence under UV radiation.

Other methods for the determination of UV absorbers in polymers are reviewed in **Table 5.6**.

Table 5.6 Thin-layer chromatography of ultraviolet absorbers in polyethylene		
	Extraction method	**Ref.**
Benzophenone and salicylic acid types	Solvent extraction, TLC	[40]
Benzophenone type Salicylate type	Solvent extraction, TLC	[32]
Benzotriazole type	For quantitative estimation	[14, 36-38, 41-45, 53]
Salicylate type Substituted acrylonitriles Organonickel type UV absorbers and optical brighteners	Solvent extraction, TLC	
Optical whiteners	Solvent extraction, TLC	[61]
Source: Author's own files		

5.4 Plasticisers

Campbell and co-workers [62] carried out a systematic study of the thin-layer separation of the plasticiser mixtures used in polyvinylchloride (PVC) formulations.

Tetrahydrofuran extracts of the PVC were mixed with methyl alcohol to reprecipitate the polymer or diethyl ether Soxhlet extractions of PVC were applied to a Merck fluorescent silica Gel G plate which was developed with ethyl acetate-isooctane (15:85 *v/v*) or methylene chloride or diethyl ether – petroleum ether (40-60). After development the plate was sprayed with 2% ethanolic resorcinol, then 4 N sulfuric acid. The plates were then heated to 135 ºC and sprayed with 25% sodium hydroxide to locate the plasticisers.

Phthalates gave orange-brown spots, adipates gave purple spots, and sebacates, azelates and phosphates gave virtually colourless spots, all on a pale pink background. When the orange-brown spots of the phthalate esters were scraped from the chromoplate and the scrapings were dropped into approximately 5 ml of water, an intense yellow-green fluorescence was observed. Similarly spots containing sebacate and azelate esters displayed a rather weak fluorescence when so treated.

When the developed plate was sprayed with a 2% ethanolic 2,6-dichloroquinone chlorimide solution, then heated for 10 minutes at 100 °C, resprayed with a 5% aqueous borax solution, and heated again for 10 minutes at 100 °C, phosphates gave a bright blue colour and other esters gave no reaction.

The R_f values, recorded for the 15 plasticisers studied, when developed with the selected solvent systems are listed in **Table 5.7**. Values quoted are the means of three results, di

Table 5.7 R$_f$ values of some plasticisers in three solvent systems			
Plasticisers	Ethyl acetate/ iso-octane (15:85)	Methylene chloride	Ether/40-60 petroleum ether (20:80)
Dimethyl phthalate	0.20	0.32	0.20
Diethyl phthalate	0.30	0.35	0.30
Di-*n*-butyl phthalate	0.46	0.45	0.50
Di alphanol phthalate	0.57	0.60	0.65
Di-iso-octyl phthalate	0.60	0.67	0.70
Dicapryl phthalate	0.65	0.67	0.75
Di-2-ethyl hexyl phthalate	0.66	0.65	0.75
Di-isodecyl phthalate	0.65	0.67	0.70
Butyl benzyl phthalate	0.40	0.52	0.40
Tritolyl phosphate	0.32	0.50	0.35
Trixylyl phosphate	0.40	0.45	0.35
Trioctyl phosphate	0.37	0.22	0.15
Dibutyl adipate	0.54	0.33	0.50
Di-2-ethylhexyl adipate	0.67	0.40	0.70
Di-2-ethylhexyl azelate	0.75	0.45	0.75
Di-iso-octyl azelate	0.73	0.50	0.75
Di-2-ethylhexyl sebacate	0.68	0.55	0.85
Reproduced from Campbell and co-workers, Laboratory Practice *[62]*			

alphanol phthalate, tritolyl phosphate, and trixylyl phosphate afforded elongated rather than circular spots. With this type of spot the R$_f$ value was simply measured to the centre of the spot.

Sokolowska [63, 64] detected and determined tritolyl phosphate in PVC by extracting the additive with diethyl ether for 16 hours, the solvent was evaporated off, and a solution of the residue in chloroform was applied to layers of Silica gel G. Chromatograms were developed with benzene - ethyl acetate (20:1) and the spots of tritolyl phosphate were located with 0.5 N ethanolic - potassium hydroxide and diazotised 4-nitroaniline solution. The contents of total phenols and *o*- and *p*-cresols were determined by mixing the test solution (20 ml) containing 0.25 to 2 mg of phenols per litre, with diazotised 4-nitroaniline solution (5 ml). Borate buffer solution (28.42 g of Na$_2$B$_4$O$_7$ 10H$_2$O and 13 g of sodium hydroxide per litre (20 ml) was added and these solutions were then diluted to 50 ml with water and after 15 to 30 minutes, the extinction was measured at 485 nm against a

blank. The results were compared with a calibration graph prepared with standard phenol solution. The standard deviation of this method was ±0.045 mg/l (12 determinations). Formaldehyde in concentrations up to 10 mg/l does not interfere in the method.

Burns [65] has carried out an extensive study of the TLC of phthalate, sebacate and adipate ester systems and also chlorinated waxes such as Cleroxide, Cereclor S, Pliabrac and hexylene glycol, used in PVC formulations. He employed 1 mm thick layers of Silica Gel G activated for 3 hours at 110-115 °C for achieving separations. Burns [65] found that benzene - ethyl acetate (100:1) was much more efficient than the benzene - ethyl acetate (20:1) mixtures. He also used freshly redistilled dichloromethane (DCM), iso-octane - ethyl acetate acid (4:4:1), and benzene - DCM (4:1) as migration solvents.

He used several visualising reagents including Universal Indicator, Ultraphor (a water soluble fluorescent indicator), 4 N sulfuric acid, 20% alcoholic resorcinol (1:1) and a saturated solution of iodine in chloroform. The sample was applied to the plate as a benzene solution. Burns [65] found that 5 µl was an optimum sample size. Using DCM as the migration solvent it was found that diiso-octyl azealate and dioctyl adipate were not separated. However, migration in two dimensions first with DCM, then with benzene:dimethyl ether (100:1) successfully achieved this separation.

Bloom [66] reported R_f data for 27 esters in this and other solvent systems. This procedure separated most of the phthalate esters examined, but was not suitable for esters of higher molecular weight for which he had to resort to gas liquid chromatography. Walker and Ganshirt [67] also studied the separation of phthalate esters. The esters were recovered from aqueous solution obtained by autoclaving plastic sheet with steam at 120 °C then by extracting the aqueous layer with carbon tetrachloride. The extract was subjected to TLC on silica gel (0.2 mm thick) containing a fluorescent reagent with light petroleum - ethyl ether - acetic acid (80:20:1) as solvent. The spots were located under UV light irradiation, the esters being extracted with chloroform and the extinction of each solution measured at 280 nm. The method was applied to the determination of bis-(2-ethylhexyl) phthalate in PVC.

Kataeva and Kofanov [68] developed a procedure for the determination of butanol, hexanol, iso-octanol and nonanol esters of phthalic, adipic and sebacic acids.

These esters were determined by TLC on plates coated with Silica gel KSK-3.5. The extract was evaporated to dryness and the residue dissolved in methanol and applied to the plate, together with control samples and 5 to 10 µg of a mixture of materials contained in the film. The chromatogram was developed with nitromethane, DCM, chloroform, dichloroethane, benzene or toluene as solvent, dried for 5 to 10 minutes at 150 °C, sprayed with a 0.5% solution of 4-dimethylamino-benzaldehyde and sulfuric acid - ethyl ether (1:1), and heated for 15 to 20 minutes at 150 °C to hydrolyse the esters to yield the alcohols, which react

with 4-dimethyl aminobenzaldehyde to give reddish-brown spots on a grey background. The sensitivity of the reaction increases with increasing molecular weight of the alcohol, from 15 µg for butanol to 1 to 2 µg for esters of dodecyl alcohol. Other thin layer methods for the determination of plasticisers are reviewed in **Table 5.8**.

Table 5.8 Determination of plasticisers in polymers		
Plasticiser	Polymer	Refs.
Phthalic acid esters	PVC	[65-68, 70-76]
Adipate esters	PVC	[67, 68]
Sebacic acid esters	PVC	[62, 65, 77, 78]
Miscellaneous carboxylic acid esters	PVC	[62, 68, 70-76, 79-81]
Phosphoric acids esters	PVC	[47, 62, 63, 82]
Epoxy esters	PVC	[82]
3-Aminocrotonic esters	PVC	[83]
Diphenylthiourea esters	PVC	[84]
Octyl fatty acid esters	PVC	[75, 76]
Source: Author's own files		

5.5 Organotin Stabilisers

TLC as described by Belpaire [69] with hexane - glacial acetic acid (12:1) as eluting agent is satisfactory for the identification of thioacids and thiols. A small amount of the original tin stabiliser is dissolved in the elution solvent, applied to a TLC plate coated with a 0.25 mm thick layer of Kieselgel G as the stationary phase, and eluted with the hexane - glacial acetic acid mixture. After drying, the stationary phase is sprayed with 0.1% solution of catechol violet in 95% ethanol, blue spots appearing where tin compounds are present. The approximate R_f values are 0.17 for dibutyltin (wide band) and 0.27 for dioctyltin.

If mixed tin stabilisers are believed to be present, for example, a thio-compound and a dialkyltin dialkylcarboxylate, it is advantageous to acidify the acetone filtrate after removal of the dialkyltin oxides with hydrochloric acid, evaporate most of the acetone on a water-bath under an air-jet, cool and extract by shaking with diethyl ether. The ether extract then contains hemiesters, acids, and so on, liberated from the other types of tin stabilisers originally present and can be examined further. Although reaction products produced by

the action of sodium hydroxide or acetone are often present, esters of maleic and benzoic acids have been identified in this way.

Simpson and Currell [32] used butanol - glacial acetic acid (97:3) as the mobile phase and sprayed the developed plate with catechol violet solution followed by irradiation of the plate for 10 minutes with UV radiation and a respray with catechol violet solution to detect the separated compounds as blue spots. This procedure can be applied to the detection of organotin compounds in PVC using a preliminary extraction of the additives from 5 g polymer with diethyl ether for eight hours. Ether is removed by evaporation and ethanol added to precipitate polymer which is then filtered off. If more accurate quantitative results are required it is necessary to perform an extraction additional to the diethyl ether extraction by using an azeatrope of carbon tetrachloride - methanol (2:1) for a further four hours.

Detection limits are typically 1-10 µg. Diagrammatic representation of the separations are to be found in **Figure 5.11**, and details of the results obtained are given in **Table 5.9**.
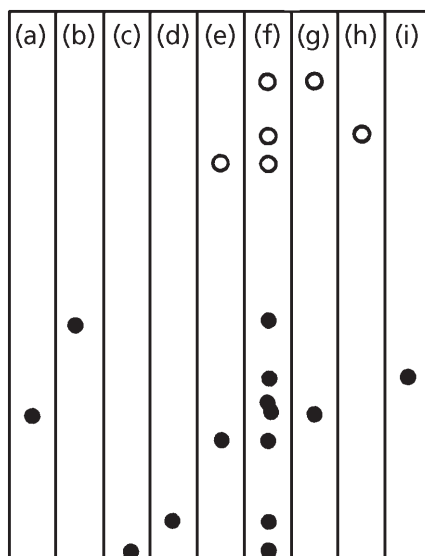
Figure 5.11 Thin-layer chromatogram of organotin compounds. Mobile phase: butanol – glacial acetic acid (97:3). Columns are (a) dibutyltin-dilaurate, (b) dioctyltindilaurate, (c) butyltintrichloride, (d) dimethyltindichloride, (e) diphenyltinchloride, (f) mixture, (g) hexabutyltin, (h) tributyltinlaurate, and (j) dibutyltin bis-(2-ethylhexylthioglycollate)
Reproduced from Simpson and Currell, RSC [32]

Table 5.9 Results obtained in the separation of organotin compounds			
Substance	R_f value	Spot located on spraying	Spot located only after UV irradiation and spraying
Dibutyltin dilaurate	0.29	+	-
Dioctyltin dilaurate	0.46	+	-
Butyltin trichloride	0.00	+	-
Dimethyltin dichloride	0.04	+	-
Diphenyltin dichloride	0.21 0.76	+ +	- -
Hexabutylditin	0.26 0.96	+ -	- +
Tributyltin laurate	0.82	-	+
Dibutyltin bis-(2-ethylhexylthioglycollate)	0.33	+	-
Reproduced from Simpson and Currell, RSC, *[32]*			

Udris [85] discusses the problem of the detection of organotin stabilisers and phthalate ester plasticisers when they are present together in solvent extracts of PVC. He points out that IR spectroscopy whilst it may show the presence of major components of such mixtures may miss the minor ones which may also be present, such as, phenol derivatives and metal carboxylates. These can be separated and identified by TLC followed by IR or UV spectroscopy.

Metal salts present in tin stabilisers can be identified by diluting the sample with diethyl ether, centrifuging (or filtering) and examining the precipitate by IR spectroscopy and by emission spectroscopy (for metals).

Various other thin-layer methods for the determination of organotin compounds are reviewed in **Table 5.10**.

5.6 Epoxy and Other Heat Stabilisers

Kreiner [82] used activated Silica Gel G and a solvent consisting of a mixture of DCM and 1,1,1-trichlorethane (TCE) as development solvent for the separation of epoxy stabilisers and other compounds in extracts of PVC.

Table 5.10 Organotin type stabilisers in PVC		
Thin-layer chromatography		**Ref.**
Dibutyltin-dilaurate	Solvent extraction, TLC for identification of organotin compounds	[32]
Dioctyltin-dilaurate		
Butyltintrichloride		
Dimethyltinchloride		
Diphenyltin dichloride		
Hexabutylditin		
Tributyltin laurate		
Dibutyltin bis-(2-ethyl-hexylthioglycollate)		
Dibutyltin bis(2-ethyl hexyl) thioglycollate	Solvent extraction, TLC	[32, 86-88]
Di-*n*-octyltin maleate	Solvent extraction, TLC	[89]
Stabilisers	Various methods	[10, 90-95]
Dibenzyltin bis (isooctyl-mercaptoacetate)	Solvent extraction, hydrolysis to glycol, TLC of 3,5-dinitrobenzoates	[96]
Dibenzyltin bis (butyl-mercaptoacetate)		
Dibenzyltin bis(cyclohexl-mercaptoacetate		
Di-*n*-octyl tin maleate	Study of degradation products of this compound produced on processing	[97]
Thermal degradation products		
Source: Author's own files		

The addition of increasing amounts of TCE was found to give greater movement to and fractionation of the epoxy additives. These separations were mainly due to the inhibitor, 1,4-dioxane, which is normally present at the 3% level in most commercial TCE. A 3:1 ratio of inhibited TCE to DCM produced the best epoxy movement with the least interference from other plasticisers that might be present. A minor failing of this system was a frequently observed, weak solvent front attributable to the dioxane. Although the front did not hinder the identification of any of the materials studied, the system was modified by addition of a small amount of methyl ethyl ketone to smooth the dioxane front. This yielded moderately increased R_f values without disturbing the quality of the fractionations. The increase in R_f values was, in fact, helpful since more fractions were now visible in several of the samples.

Kreiner [82] used a slurry containing a 2:1 weight ratio of water to Silica Gel G (E Merck AG, Darmstadt) to prepare layers 250 to 300 μm thick which were dried for 1 hour at 110 °C in a forced air oven and cooled in a desiccator and stored until used. All samples were applied to the layers as 1% solutions in acetone with 2 and 5 μl disposable capillary pipettes. A 20 μg (2 μl) sample size was used for all analyses except the triglycerides, in which case a 50 μg (5 μl) sample was used. R_f data is listed in **Table 5.11**.

Various other workers have studied the application of TLC to the determination of epoxy type stabilisers in PVC [79, 82, 83, 98-102].

Mazur [83] has described a procedure for the determination by TLC of the three amino crotonic ester of 2,2´-thiodiethanol and ethane diol stabilisers in rigid PVC. The sample is macerated with water, 3% acetic acid, ethanol or heptane at 40 °C for 10 days. The solvent is evaporated and the residue dissolved in chloroform. The solution is applied to a layer (0.25 mm thick) of Silica Gel G and the chromatogram developed with hexane - acetone (3:2) or chloroform and dried at 20 °C for 10 minutes. The spots of the two separated stabilisers are located with a 0.2% aqueous solution of tetrazotised *o*-dianisidine. Down to 0.5 μg of either substance can be determined by this procedure.

Urea and diphenylthiourea stabilisers can be detected in PVC by extracting a cut-up sample of foil (5 g) with ethyl ether under reflux for 4 hours followed by filtration and evaporation. The extract (0.02 ml) is applied to a Whatman No.3 paper and the chromatogram is developed with methanol - acetone - water (10:1:1). The chromatogram is dried, and the spots of urea and diphenylthiourea are located with 4-dimethylaminobenzaldehyde solution. The R_f values and were 0.50 and 0.84 mg for the two compounds - the limit of detection was 0.5 mg.

The determination of PVC heat stabilisers of the phenyl-amine, 2-phenylindol, dicyanodiamine and aminocrotonic ester types have been studied by Hagen [103], Schröder and co-workers [104], Korn and Waggon [105-108] and Waggon and co-workers [109].

5.7 Optical Whiteners

The determination of optical whiteners in polymers by TLC and paper chromatography has been discussed by various workers [61, 110-112]. These compounds include stilbene, cumarin, cyanine, imidazol, oxazol, thiozol, benzidine, pyrinidazol and carbostyryl derivitives.

Wandel and co-workers [113] carried out separations on thin-layers of alumina and Kieselgel G using acetone - petroleum ether (30:70) and methylene chloride as the migration solvents and an UV light source for locating the separated compounds.

No.	Sample	Trade name	Manufacturer	Rf x 100		Colour
				A	**B**	
1	Epoxidised soybean oil	Paraplex G-62	Rohm & Hass	0, 3, 5, 9, 11, 15, 19, 21, 25, 27, 31	0, 3, 5, 7, 9, 13, 19, 22, 27, 29, 32, 36	Rose, brown yellow
2	Epoxidised linseed oil	Drapex 10.4	Argus	0, 3, 5, 8, 10, 15, 18, 20, 25, 26, 30	0, 3, 4, 7, 9, 15, 18, 20, 25, 26, 30	Rose, brown, yellow
3	Isooctyl epoxy stearate	Estynox 408	Baker Castor Oil	25, 39	30, 34, 55	Rose, brown, yellow
4	2-Ethylhexyl epoxy tallate	Flexol EP8	Union Carbide	25, 40	30, 34, 56	Rose, brown, yellow
5	Butyl epoxy tallate	Truflex E-64	Teknor Apex	22, 32	28, 50	Rose, brown, yellow-green
6	Butyl ester of epoxidised linseed fatty acid	Epoxol 8-2B	Swift Chemical	0, 11, 23, 30	0, 16, 29, 50	Rose, brown, yellow
7	Di(iso-decyl)-4,5-epoxy tetrahydro-phthalate 3,4-epoxy-6-methylcyclohexyl-methyl	Flexol PEP	Union Carbide	25, 28	33, 39	Brown
8	3,4-Epoxy 6-methylcyclohexane-carboxylic acid	Unox 201	Union Carbide	16	20	Brown
9	Epoxy resin	Ferro 909	Ferro Corp	0, 5, 9, 11, 15, 24	0, 2, 3, 5, 8, 13, 21, 30	Violet

Table 5.11 Approximate R$_f$ x 100 values and colours obtained for epoxy plasticisers and stabilisers

Development on Silica Gel G with (A) 1,1,1-trichloroethane - dichloromethane (3:1) and (B) 1,1,1-trichloroethane – dichloromethane - methyl ethyl ketone (75:25:2) as solvent; indicator: sulfuric acid - anisaldehyde

No.	Sample	Trade name	Manufacturer	R_f x 100		Colour
				A	**B**	

Table 5.11 Continued...

Development on Silica Gel G with (A) 1,1,1-trichloroethane - dichloromethane (3:1) and (B) 1,1,1-trichloroethane – dichloromethane - methyl ethyl ketone (75:25:2) as solvent; indicator: sulfuric acid - anisaldehyde

No.	Sample	Trade name	Manufacturer	R_f x 100 A	R_f x 100 B	Colour
10	Epoxy resin	Synpron 473	Synthetic products	0, 2, 5, 9, 11, 15, 23	0, 2, 5, 8, 14, 21, 30	Violet, blue
11	Epoxy resin	Mark 224	Argus	0, 3, 5, 7, 9, 11, 15, 23	0, 2, 4, 5, 8,10, 13, 16, 20, 24, 30	Violet, yellow, brown, rose
12	Di(2-ethylhexyl) phthalate	Kodaflex DOP	Eastman	56	66	Rose
13	Di(2-ethylhexyl) azelate	Plastolein 9058	Emery	43	60	Rose
14	Tri(2-ethylhexyl) trimellitate	Morflex 510	Pfizer	53	71	Rose

Reproduced from J.G. Kreiner, Journal of Chromatography *[82]*

5.8 Amine and Phenolic Antioxidants and Antidegradants, Guanidines and Accelerators in Rubber

In the compounding of rubber formulations, many types of additives are used, some of which, such as antiozonants, are not usually included in polymer formulations. One of the earliest and most comprehensive procedures for the examination of vulcanisates was published by Zijp [114] in 1956. He subjected extracts of the vulcanisates to various preliminary treatments after which the compounding ingredients or their residues were separated and identified using paper chromatography. Somewhat later, Gaczynski and Stephen [115] published a paper chromatographic method for the identification of the accelerators most commonly used in Poland at that time.

The analysis of vulcanisates was reviewed by Burger [116] and Aulder [117]. Aulder examined the various methods that had been used for the determination of antioxidants, antiozonants and accelerators with special emphasis on paper chromatography. He evaluated and developed the methods of Miksch and Prolss [118] and Zijp [114], and refined parts of their methods.

Kreiner and Warner [119] have reported on the use of TLC for the identification of certain rubber compounding ingredients including amine antioxidants and antiozonants, phenolic antioxidants, guanidines, accelerators and the amines derived from accelerators. Each of these groups was examined in an effort to determine the solvent and indicator systems most suitable for the separation and, hence, identification of the largest possible number of compounds in each of the above categories. As a result, the systems they chose should make it possible to identify most of the previously named types of compounding materials manufactured in the United States.

A 2:1 weight ratio of water and Silica Gel G was used to make the slurries for the layer preparation. The layers were dried for 1 hour at 110 °C in a forced air oven and cooled in a desiccator where they were stored until use.

The layer thickness was kept between 250 to 300 µm and the sample sizes in most instances were kept between 35 to 45 µg. In general, samples of 5 to 15 µg were used for this layer thickness. However, the variation in R_f values for their sample size range was found to be small and caused no problem in identification work. A larger sample size was, in fact, found to be more advantageous when working with unknown extracts. In the case of multicomponent materials, the sample size was increased to yield reasonable quantities of the components. Saturation of the developing tank atmosphere was ensured by placing filter paper wet with solvent on the tank walls. The development distance was 15 cm in all cases except for the guanidines which were developed through a distance 10 cm.

The development solvents and spray detection reagents used by Kreiner and Warner [119] for different types of rubber additives are summarised in **Table 5.12**.

Some typical separations achieved under these conditions are illustrated in **Figures 5.12-5.15**.

Various other workers have described methods for the determination of compounding ingredients in rubbers [4, 7, 8, 11, 19, 46, 120-125].

5.9 Miscellaneous Additives

TLC and IR spectroscopy (Romano and co-workers [126]) have been used to determine antistatic agents in PE, and lubricants and plasticisers in PVC.

Schröder [38] has reviewed work [25, 78, 127-137] carried out on the applications of TLC to plastics additives such as plasticisers [127-129, 135], stabilisers, antioxidants, UV absorbers, lubricants, antistatic agents and optical brighteners.

Table 5.12 Determination of rubber additives		
Type of rubber additive	Development solvents	Spray detection reagent
Amine antioxidants	Benzene – acetone – concentrated ammonium hydroxide (100:5:0.1)	4% Benzoyl peroxide in benzene
Amine hydrochlorides	*n*-Butanol – water – formic acid (5:1:1)	Ninhydrin
Phenolic antioxidants	Benzene	Buffered solution, 235 g Na tetraborate, 3.3 g NaOH then 0.1% methanolic dichloroquinone – chlorimide (2:6)
Guanidines	Acetone containing 1% concentrated ammonia	4% Sodium hypochlorite
Accelerators	Benzene - ethylacetate – acetone (100:5:1)	4% Hydrochloric acid spray, then 0.5% ninhydrin spray
Thiazoles	Benzene - ethylacetate – acetone (100:5:1)	5% bismuth nitrate in 0.1 N nitric acid
Reproduced from J.G. Kreiner and W.C. Warner, Journal of Chromatography [119]		
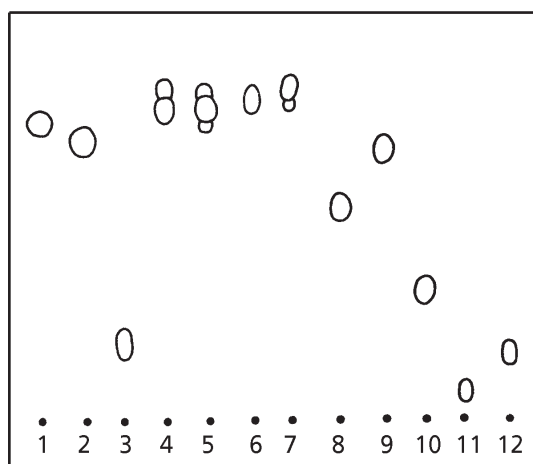
Figure 5.12 Separation of amine antioxidants and antiozonants by one-dimensional thin-layer chromatography. Solvent: benzene – acetone - concentrated ammonium hydroxide (100:5:0.1); development distance: 15 cm; indicator: 4% benzoyl peroxide in benzene. 1 = *N*-phenyl-1-naphthylamine; 2 = *N*-phenyl-2-naphthylamine; 3 = *p*-(*p*-tolylsulfonylamido)-diphenylamine; 4 = nonylated diphenylamines; 5 = octylated diphenylamines; 6 = octylated diphenylamines; 7 = octylated diphenylamines; 8 = 4,4-dimethoxydiphenylamine; 9 = 4-isopropoxydiphenylamine; 10 = 4′-isopropyl-aminodiphenylamine; 11 = *N, N*′-diisopropyl-*p*-phenylenediamine; 12 = N,N′-di-*sec*-butyl-*p*-phenylenediamine. *Reproduced from [119]*
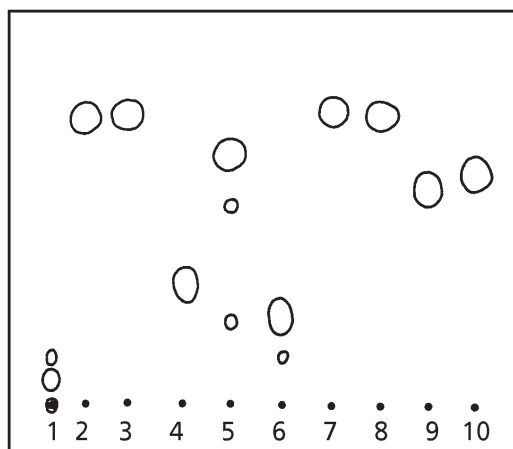
Figure 5.13 Separation of phenolic antioxidants by thin-layer chromatography. Solvent: benzene; development distance: 15 cm; indicators: (a) borate buffer; (b) 0.1% 2,6-dichloro quinonechlorimide in methanol. 1 = hydroquinone monobenzyl ether; 2 = 2,6-di-*tert*-butyl-phenol; 3 = 2,6-di-*tert*-butyl-4-methyl-phenol; 4 = 2,6-di-*tert*-butyl-α-methoxy-4-methyl-phenol; 5 = 2-α-methyl-cyclohexyl-4, 6-dimethyl-phenol; 6 = butylated hydroxyanisole; 7 = butylated hydroxy toluene; 8 = 4,4´-bis (2,6-di-*tert*-butyl-phenol); 9 = 2,2´-methylene-bis (4-methyl-6-*tert*-butyl-phenol); 10 = 2,2´-methylene-bis (4-ethyl-6-*tert*-butyl-phenol)
Reproduced from Kreiner and Warner, Journal of Chromatography [119]
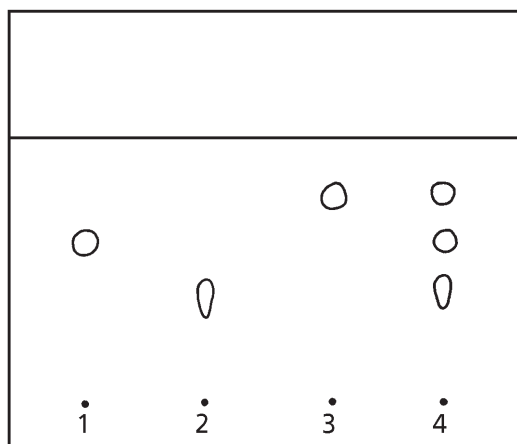
Figure 5.14 Separation of guanidines by thin-layer chromatography. Solvent: 1% concentrated, ammonium hydroxide in acetone; development distance: 10 cm; indicator 4% aqueous sodium hypochlorite. 1 = diphenylguanidine; 2 = di-*o*-tolylguanidine; 3 = triphenylguanidine; 4 = mixture
Reproduced from Kreiner and Warner, Journal of Chromatography [119]
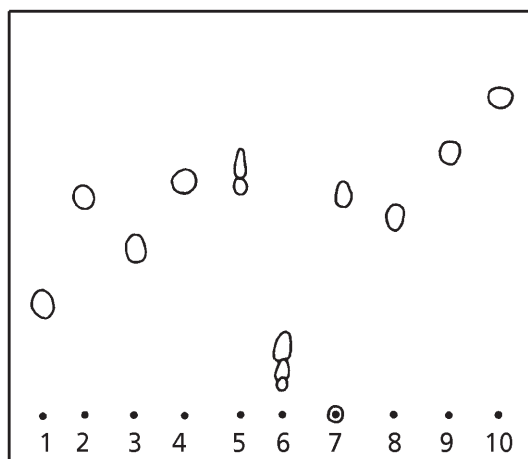
Figure 5.15 Separation of accelerators by thin-layer chromatography. Solvent: benzene - ethylacetate - acetone (100:5:1); development distance: 15 cm; indicators: (a) 4 N hydrochloric acid; (b) 0.5% ninhydrin in ethanol containing 10% acetic acid and 0.5% cadmium acetate. 1 = tetramethylthiuram monosulfide; 2 = tetrabutylthiuram monosulfide; 3 = tetramethylthiuram disulfide; 4 = tetraethylthiuram disulfide; 5 = dipentamethylenethiuram tetrasulfide; 6 = cyclic thiuram; 7 = piperidinium pentamethylene dithiocarbamate; 8 = zinc dimethyldithiocarbamate; 9 = zinc diethyldithiocarbamate; 10 = zinc dibutyldithiocarbamate
Reproduced f*rom Kreiner and Warner, Journal of Chromatography [119]*

The determination of various types of lubricants and plasticisers in PVC by TLC has been discussed by Hagen [103]. The types of compounds studied include paraffin oligomers, alkyl stearate, stearic acid and epoxystearic acid alkyl ester.

5.10 Combination of Thin-Layer Chromatography with Infrared Spectroscopy

Application of techniques such as IR and UV spectroscopy and MS to separated compounds isolated from a thin-layer plate has obvious advantages from the point of view of obtaining more reliable additive identifications. The relevant techniques comprise the following steps:

1. Removal of impurity materials from the plate coating before plate development to avoid migration of plate impurities to regions of the plate which during plate development coincide with the R_f values of separated additives.

2. Carrying out solvent development on the polymer extract.

3. Removal of gel bands containing separated additives from the development plate.

4. Extraction of pure separated polymer additives from separated adsorbent bonds.

5. Preparation of IR spectra of separated polymer additives.

6. Preparation of UV spectra of separated polymer additives.

5.10.1 Premigration of Plates

TLC grades of silica gel usually contain traces of organic impurities. If, during development of a chromatogram, these impurities migrate to regions of the plate which coincide with the R_f values of separated additives, then the impurities will interfere in the interpretation of the plate following spraying with aggressive detection reagents, such as concentrated sulfuric acid and antimony pentachloride, as the organic impurities in the adsorbent also react with these reagents and show up on the sprayed chromatograms. Also, the impurities absorb strongly in the UV region, especially below 250 nm. The adsorbent impurities do not have an appreciable adsorption in the IR region. Thus, concentrated chloroform or carbon disulfide extracts of Silica Gel G have a negligible adsorption over the whole IR region. As these impurities are extracted from the silica gel with organic solvents such as diethyl ether, ethanol, acetone, benzene, chloroform and many others, they could occur as contaminants in some of the fractions of separated additives isolated from the plate by solvent extraction of the gel and consequently interfere in the interpretation of the spectra of the additives, particularly in the case of additives which absorb below 250 nm in the UV. For this reason an identical blank chromatogram (only sample absent) should always be run in parallel with the sample chromatogram in order to check whether such interference effects exist.

It has been shown that the UV absorbing impurities in adsorbents are influenced by the nature of the migration solvent. Depending on the polarity of the migration solvent used, the impurities migrate to a greater or lesser extent up the plate towards the solvent front with the result that the lower part of the chromatogram nearer the baseline is cleared of impurities, and the impurities become concentrated in the upper section of the plate nearer the solvent front. Subsequently, when a section of the absorbent is removed and eluted with a further solvent to recover a separated compound, the amount of impurities contaminating the compound will depend on the location of the compound on the chromatogram (R_f value) and contamination may range from negligible to substantial. The extent to which this redistribution of impurity occurs will be influenced by a number of factors, including the type of adsorbent, the particular impurities present, and the migration solvent used.

In circumstances where slow moving compounds are being separated, the impurities may move away from the polymer additives towards the solvent front and thus not interfere in the subsequent examination of the separated compounds. This behaviour leads to a convenient method, described next, for moving the impurities beyond the section of the chromatogram to be used for the separation of polymer additives by migrating the chromatogram with appropriate washing solvents before applying and migrating the sample mixture. If this premigration washing covers a longer distance on the plate than is to be used in the sample migration then it is possible to move interfering impurities out of the way.

The following procedure has been found to be particularly suitable for the premigration of adsorbent impurities from thin-layer plates prior to the use of the plates for separation of polymer additives. In the case of silica gel at least, methyl alcohol is the recommended solvent and is much superior to *n*-hexane. Methanol is poured into a glass tank with a ground glass lid [3] to a depth of 1-2 cm and the walls of the tank are lined with sheets of filter paper dipping into the solvent. The tank is left for 30-60 minutes in a draught-free area until the interior has become saturated with solvent vapour. The coated 20 cm x 20 cm plate is then supported vertically in the methanol layer and left until solvent has ascended to the top of the plate (presaturation of the tank facilitates the development of migratory matter in a straight line and speeds up the chromatographic process). The plate is then removed from the tank, conditioned at 120 °C (for 30 minutes) and the top 5-10 cm of adsorbent containing the impurities scraped off with a sharp instrument and thrown away, leaving the remainder of the adsorbent coating free from impurities. A second solvent treatment of the plate can be carried out, but is rarely needed. Plates should be used as soon as possible after activation, but if a delay is inevitable then they should be stored in a desiccant box containing silica gel.

Plates prepared in this way are virtually free from UV and IR absorbing impurities and may be used with confidence for interference-free separations of polymer additives.

Premigrated plates should always be reactivated by heating for 30 minutes at 120 °C immediately prior to use in the chromatography of polymer extracts.

Kirchner and co-workers [138] and Stanley and co-workers [139] used descending solvent migration from the top edge to the bottom edge of the plates, for removal of adsorbent impurities. This provided effective adsorbent cleaning with little attention. The solvent and migrating impurities are continually removed from the lower edge of the chromatogram and the process continued indefinitely. This method is recommended when substantial numbers of chromatoplates are to be used because it is effective and needs little attention.

Brown and Benjamin [140] have suggested a similar technique in which the direction of washing is across the chromatogram. Their description is sketchy but apparently solvent

flow is maintained across the chromatogram and off the edge as their photographs of developed chromatograms show no concentrated impurity zone along the edge.

5.10.2 Removal of Separated Compounds from the Plate

Examination of the plates under UV light and by the application of general and specific spray reagents as described in the previous section will usually provide full information regarding the R_f values in different development solvents of the various components of the original additive mixture applied to the plate and, possibly some information regarding the types of compounds present.

It is emphasised here that, in order to avoid 'missing' any sample components it is highly advisable to apply the sample location techniques described in the last section to chromatograms of the sample obtained using several plate materials such as silica gels and alumina, and with each adsorbent to use as wide a variety as possible of different types of development solvents.

The simplest method of removing the zones containing the separated compounds (after allowing solvent to evaporate from the plate) is to hold the plate vertically, its side resting on a sheet of paper and to scrape off the desired zone with a spatula. For substances which are not sensitive to oxidation, the zones may be sucked from the layer directly into an extraction thimble by using a small 'vacuum cleaner' [3] (**Figure 5.16**). Each separated adsorbent band can then be bottled off in 5 ml polythene tubes and retained for further examination.
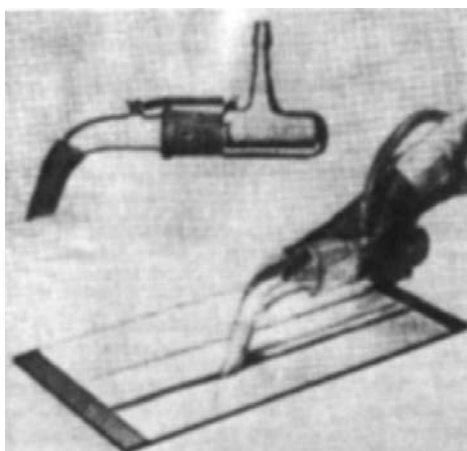
Figure 5.16 Direct transfer of the sample zones into an extraction thimble by the aid of a micro vacuum cleaner
Reproduced fFrom Stahl, Laboratory Practice [3]

5.10.3 Extraction of Pure Polymer Additives from Separated Adsorbent Bands

The separated portions of adsorbent, each, hopefully, containing a pure constituent of the original polymer extract, are now extracted with suitable solvents to isolate the additive preparatory to identification by physical and chemical methods.

Each portion of adsorbent is transferred from the storage bottle to a separate small sintered glass extraction thimble (**Figure 5.17**) and the organic compounds leached out with a suitable solvent such as anhydrous absolute ethanol, diethyl ether or methylene dichloride. This solvent must:

(i)   be a good solvent for the additive;

(ii) be sufficiently polar to desorb the additive from the absorbent (successive desorption with different solvents may be necessary at this stage);

(iii) have a low boiling point to facilitate subsequent removal of solvent and reduce to a minimum evaporation losses of any volatile sample constituents; and/or

(iv) not interfere in the subsequent spectroscopic examination of extracts.

Provided the desorption solvent is sufficiently powerful and polar, it should recover between 50 and 100% of the additive present in the silica gel fraction and provide sufficient material for examination by UV or IR spectroscopy or MS.

Table 5.13 shows the results obtained in some experiments carried out to determine the recovery of di-*n*-butyl phthalate (222 nm) and Ionox 330 (277 nm) adsorbing at shorter and longer UV wavelengths, respectively. These compounds were carried through the whole series of operations involving application of sample to a silica gel plate, solvent development, separation of adsorbent from the plate and, finally, solvent extraction of the compound from the adsorbent.

Ionox 330 has a low R_f value with cyclohexane:benzene (4:1) development solvent (**Table 5.13**) and hence, during solvent development, UV absorbing adsorbent impurities are swept well away from this compound to the solvent front. Premigration of the plate with methyl alcohol was unnecessary and therefore, not used prior to the application of Ionox 330 to the plate. Premigration of the plate with methanol before sample application was, however, carried out in the case of di-*n*-butyl phthalate. This was because this compound has a fairly high R_f value with the iso-octane:ethyl acetate (9:1) development solvent used, with consequent possible contamination of the di-*n*-butyl phthalate band with UV absorbing adsorbent impurities near the solvent front. It is seen from **Table 5.13** that satisfactory recoveries of both compounds were obtained by this procedure.

12 mm
I.D.

62 mm

Eluting solvent

Absorbent

No. 2 sinter disc

1-2 mm I.D.
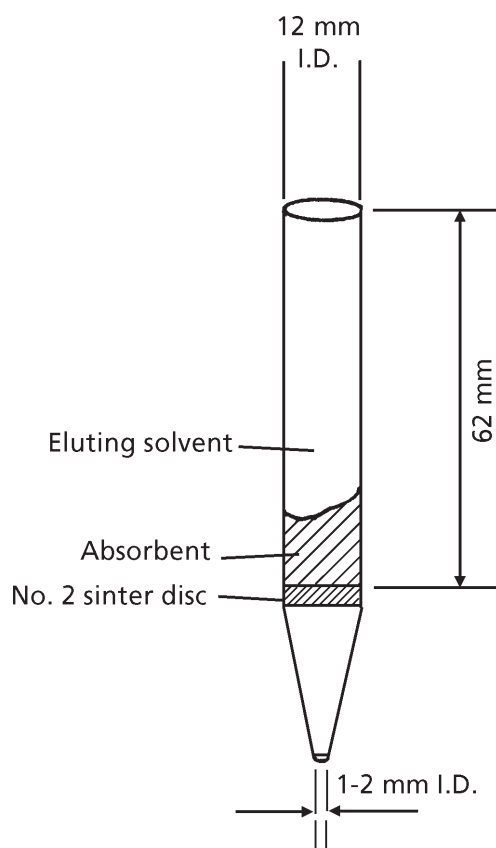
Figure 5.17 Filtration apparatus for extracting separated additives from adsorbent isolated
from thin-layer chromatography plates
Reproduced from Stahl, Laboratory Practice [3]

Millet and co-workers [141] have discussed in some detail rapid techniques for quantitatively recovering separated substances from thin-layer plates. They use a precision streaking device for applying the original sample to the plate. Following irrigation of the plate with development solvent, the substrate and separated components are picked up in vacuum collector tubes fashioned from sections in 5 mm borosilicate tubing. By varying the collector tube length and diameter, sample sizes ranging from micro to preparative can be handled.

Chromatographic elution of sample from the resulting powder columns isolated in the collector tubes is accomplished through transfer of a solvent from reservoir by means of a thread wick.

Table 5.13 Reproducibility of recovery of Ionex 330 and di-*N*-butyl-phthalate from a thin-layer plate (silica G gel G254)

Compound	Absorbance maximum, nm	Number of plates prepared	Sample size[†], µl	Sample concentration, % w/v	Development solvent	Plate drying time, h	Section of adsorbent removed from plate, R	Solvent used to desorb compound from adsorbent	Absorbtivity of standard solution of compound, l/g/cm	Recovery of compound 2[¶]	Standard deviation
Ionox 330	277	10	1	1	Cyclohexane: benzene (4:1)	18[§]	0.03–0.14	Methanol (extract made up to 1 ml)	8.0	100	1.2
Di-*n*-butyl-*p*-phthalate[‡]	22	5	1	5	Iso-octane: ethyl acetate (9:1)	18		Methanol (extract made up to 1 ml)	29.0	99.6	1.2

[†] *Applied by Hamilton PR600 repeating sample dispenser.*
[‡] *Plate premigrated once with methyl alcohol then reconditioned for 1 h at 120 °C before application of sample.*
[§] *To allow complete evaporation of benzene which would interfere in subsequent UV spectroscopy.*
[¶] *Based on the ratio of theoretical absorbtivity and absorbtivity of extract from thin-layer plate, methanol used as reference cell in all experiments.*
Reproduced from Stahl, Laboratory Practice [3]

5.10.4 Preparation of Infrared Spectra Separated Additives

It is now necessary to prepare IR spectra of the various portions, each containing a single polymer additive, isolated from the thin-layer plate.

McCoy and Fiebig [111] have developed a technique for obtaining IR spectra from 50 to 100 µg of components isolated from a thin-layer plate. This technique, described next, utilises an IR cavity micro cell.

The solvents used for the development of the plate must be volatile enough to be removed from the adsorbent by evaporation and the adsorbent itself must not contain impurities which will show a significant absorbance in the IR when treated as described next. In general, inorganic adsorbents, such as silica gel or alumina are satisfactory but blank determinations should be made to verify behaviour of each lot of adsorbent with solvents to be used. About 100 µg of a separated component is optimum - smaller amounts will sometimes suffice depending upon how effectively it is eluted and transferred.

The solid adsorbent is transferred to the elution column (**Figure 5.18**) and packed firmly and evenly on top of the glass wool pad. The solvent is then removed from the capillary column by evaporation in a special assembly (see **Figure 5.19**).

(a) Pasteur type disposable pipette 23 cm length

(b) Pipette modified and ready for elution

(c) Capillary before evaporation

(d) Capillary after evaporation
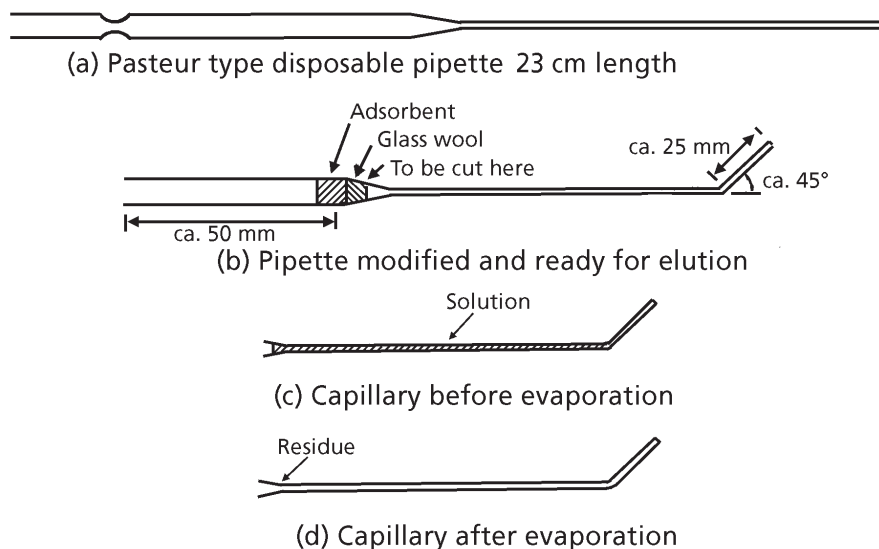
Figure 5.18 Steps in preparation and use of elution column used for fraction collecting: (a) Pasteur-type disposable pipette (23 cm length); (b) Pipette modified and ready for elution; (c) Capillary column before evaporation; (d) Capillary column after evaporation
Reproduced from McCoy and Fiebig, Analytical Chemistry, ACS [111]
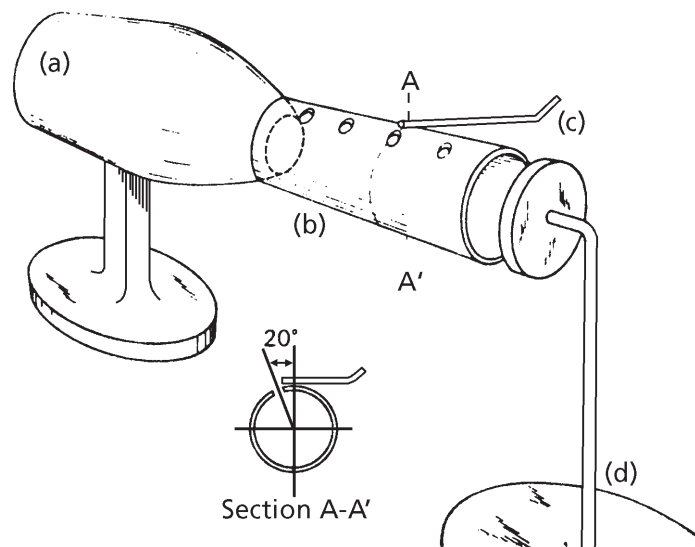
Figure 5.19 Apparatus for evaporation of solvent from capillaries prior to infrared spectroscopy. (a) Hair dryer; (b) Metal or glass tube a little larger in diameter than the air outlet of the hair dryer and 15 cm long. Drill four 0.65 cm holes, 2.5 cm apart in a straight line as shown. Mount with holes rotated 20° from the vertical as shown in Section A-A′; (c) Capillary containing liquid to be evaporated. Hold horizontal in a simple micromanipulator; (d) Moveable stand holding a solid disc of same diameter as tube which serves as a damper to adjust air flow out the side holes
Reproduced from McCoy and Fiebig, Analytical Chemistry, ACS [111]

The solid in the elution column is then extracted with a suitable IR grade spectroscopic solvent, usually carbon tetrachloride or carbon disulfide. The extract is then transferred to a ultra mass cavity cell (**Figure 5.20**).

The IR spectrum of the solvent solution can then be obtained by normal IR spectroscopic techniques.

Alternatively, especially if the compound is insoluble in the usual spectroscopic solvents, the solid can be dispersed in well-ground, solid, dry, potassium bromide using a dental mixing machine and the mixture pressed into a 1 mm thick, 5 mm diameter disc. This disc can then be mounted in a cardboard or plastic holder and used to prepare a spectrum.

Quartz microcell

The Ultracell Co., Emerson, N.J., 2 mm inside width, code 518-120.

Bevel edges to 30° included angle

54 mm

Mask with pin

Make from 1.5 mm brass sheet, bevel edges of slot from side with pin to leave sharp edges of dimensions shown on other side. Hand file outside edges as necessary for snug, sliding fit in groove of cell holder. Blacken with dull enamel or ink.

2 mm slot (centred) bevel from this side

10 mm
2.5 mm
1.5 mm
8 mm
12 mm

1 cm cell holder

Applied Physics Corp., Monrovia, Calif., Part. No. 1443150, ribs on top not shown.

Figure 5.20 Microcell, mask and cell holder used in ultraviolet spectroscopy
Reproduced from McCoy and Fiebig, Analytical Chemistry, ACS [111]

5.10.4.1 Examples of Identification of Additives by Combined Thin-layer Chromatography / Infrared Spectroscopy

An attempt was made to identify unequivocally three polymer components by comparing their IR spectra with those of authentic specimens of the suspected compounds. Chloroform solutions (1 ml) containing 15-30 mg of the polymer extract and of authentic UV 531 and Ionol CP, were applied along the edge of three 20 cm x 20 cm plates and the chromatograms developed using 40/60 petroleum spirit:ethyl acetate (9:1 *v/v*). The three UV adsorbing bands on each plate were then marked off and the silica gel corresponding to these zones removed from the plate and the additive extracted from each portion of gel with anhydrous diethyl ether. After removing the ether, the residues were intimately mixed

with dry potassium bromide and small discs prepared for IR spectroscopy. As a control a further blank chromatogram was developed, omitting the addition of a chloroform solution of sample. The gel from this plate corresponding in R_f value and area to the 0.6 and 0.8/0.85 R_f bands observed in the polymer extract, were isolated and ether extracted. **Figures 5.21** and **5.22** show the IR spectra in the 2.5 to 5 nm region of the authentic additives (direct spectrum (a) and spectrum after separation on the plate (b)), the blank run (c) and the corresponding extract of the polymer (d, e). The spectra (a) and (b) of authentic UV 531 are identical as are spectra (a) and (b) in the case of Ionol CP, i.e., it is valid to compare the spectra of these additives after chromatography with their direct IR spectra, indicating that contact with silica gel does not produce any structural alternation of these substances. Also, the blank spectra in **Figure 5.21** and **5.22** show that only minor IR absorptions due to plate impurities occur at 6.1 nm (water), and 8-10, 10.5, 13 nm (silica gel) and 7.2 nm (grease from glassware). These absorptions would not interfere in the interpretation of the additive's spectra.

Comparison of **Figures 5.21(b)** and (**d**) reveals that the compound at an R_f of 0.6 is identical or very similar to UV 531. The light stabiliser in the polymer extract is certainly a substituted benzophenone, although it may differ from UV 531 in the length of the alkoxy substituent, which is known to have little or no influence on the IR spectrum of compounds of this class.
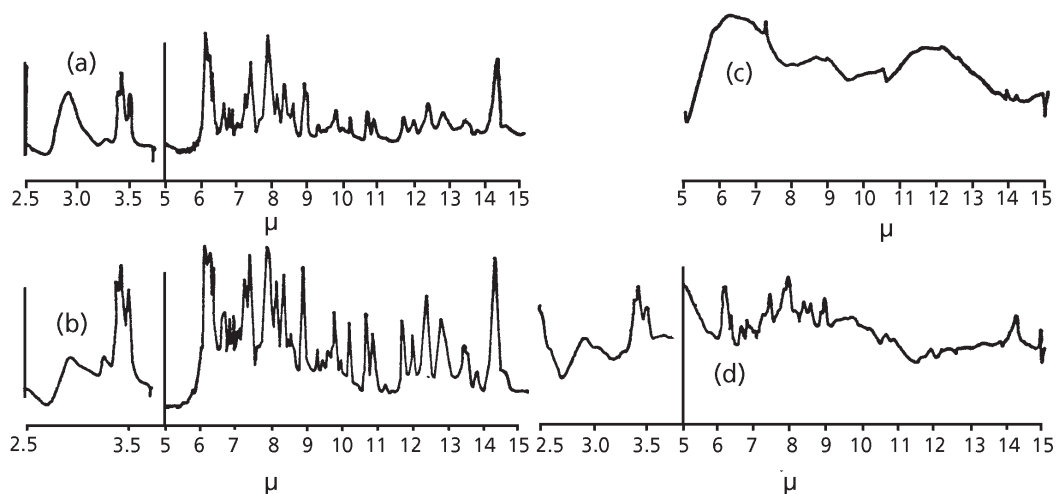
Figure 5.21 Infrared spectrum of UV 531 (2-hydroxy-4-*n*-octoxy benzophenone) isolated from a polyolefin (potassium bromide discs)
From: Author's own files
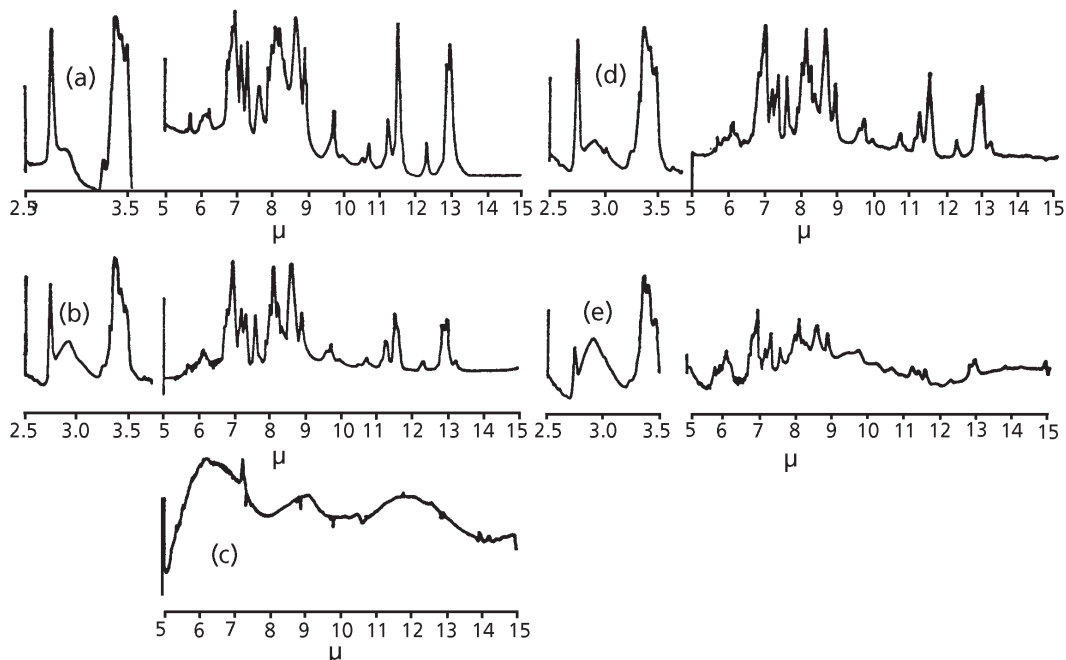
Figure 5.22 Infrared spectrum of Ionol and its degredation product isolated from a polyolefin (potassium bromide discs)
From: Author's own files

Comparison of **Figures 5.22(b)** and (**d**) confirms that the compound with an R_f of 0.85 in the polymer extract is Ionol CP, and comparison of (d) and (e) shows that the component of the polymer extract at R_f 0.8 has a spectrum very similar to that of authentic Ionol CP, suggesting that it is a breakdown product produced, presumably, by partial degradation of Ionol CP during polymer processing.

A further example concerns the identification of additives in a sample of PS. Preliminary TLC on silica gel of an extract of the polymer revealed the presence of four additives with R_f values of 0.0, 0.45, 0.8 and 0.9. Obviously, the substance that had not migrated has a high affinity for silica gel and, in fact, a very polar solvent combination (1:1 *v/v* chloroform:ethanol) was needed to desorb this compound. The other three, less polar compounds were easily desorbed from the adsorbent bands with chloroform. The separated extracts were weighed and infrared spectra prepared to provide the following identification (**Table 5.14**).

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Table 5.14 Identification of additives in polystyrene		
R_f	% in polymer	Type of additive
0.0	1.5	$RCON{\textstyle <}{(CH_2)_2\,OOCR \atop (CH_2)_2OH}$
0.45	0.5	⬡— COO Ph di cyclohexyl / COO Ph phthalate
0.8	2.0	$RCOOR^1$ Alcohol ester of saturated fatty acid (R-alkyl)
0.9	2.5	C_nH_{2n+2} Higher molecular weight paraffin
Source: Author's own files		

5.10.5 Preparation of UV Spectra of Separated Additives

After chromatography, the chromatogram is air-dried as necessary to remove residual migration solvent. If UV transparent solvents have been used that will not interfere with subsequent measurements, only a few minutes are needed to dry the adsorbent enough for the next step. When the solvent itself would subsequently interfere in UV spectroscopy, thorough removal by evaporation is necessary - several hours may be required. The chromatogram is illuminated with a UV light (253.7 nm) and the locations of the separated compounds which are visible as dark or fluorescing spots on the fluorescent background are marked. The areas are marked a little larger than those on which sample can be seen, if possible, to be more certain of including all of the compound. At this stage, compounds that absorb in the visible spectrum can be seen directly and need not be exposed to the UV light.

The amount of sample required for the preparation of a UV spectrum depends on the absorptivity of the particular compound. 10 µg of a compound having an absorptivity of 10 l/g-cm will give an absorbance reading of 0.1 when dissolved in 1 ml of solvent and measured according to this procedure.

The absorbance of the solution is measured at the desired wavelength or its spectrum is recorded using small volume micro cells. Either air or the elution solvent may be used as the reference. Blank determinations which are carried through the entire procedure, including chromatography, should always be made and measured or recorded. It is important that the sections of adsorbent eluted for the blanks come from chromatograms prepared and handled in the same manner as the sample chromatogram and that they represent the same areas and locations of adsorbent. This is necessary because impurities, if present, are not distributed uniformly on the chromatogram. Removal of impurities from the region of the adsorbent layer to be used for the sample separation by washing the layer prior to

migration of the sample using the methanol premigration technique described earlier is a convenient and effective method of reducing blank absorption.

When quantitative determinations are desired using this technique, it is necessary to know or to determine the absorptivities of the particular compounds. This is done by preparing and measuring solutions of known concentration of the pure compounds. It is also advisable to chromatograph known amounts of the pure compounds to verify the applicability of the technique to the particular compounds. This is recommended because unexpected errors can occur if compounds have enough volatility to escape from the adsorbent or are unstable and change during the chromatography and drying.

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6

Paper Chromatography

Wheeler [1] has reviewed the available literature on the applications of paper chromatography in the examination of polymers for antioxidants (**Table 6.1**). He points out that, as most antioxidants are highly polar, they cannot be efficiently separated on normal paper except by the use of highly polar mobile phases. Consequently reversed-paper chromatography [2-5] or acetylated papers [6-9] have been used to reduce the effects of 'tailing'. Various workers have discussed the determination of antioxidants in rubber extracts [10-14].

The detection spray reagents generally used for antioxidants are either diazotised amines [7, 15] which form coloured products with amines and phenols, or are oxidising agents, since the oxidation products of antioxidants are generally highly coloured [8, 9, 16, 17]. Sometimes the sample solution is treated with the colouring reagent first, and the coloured products are then chromatographed [6, 18, 19] but multiple spots can be obtained from a single antioxidant in this way as has been demonstrated by Auler [20].

The work of Zijp is a major contribution to paper chromatographic methods. He devised a comprehensive scheme for the systematic identification of antioxidants and accelerators [8, 9, 17, 21].

In the part of this scheme relating to antioxidants he uses acetylated paper and two solvent systems, one for basic and one for phenolic acidic constituents. Identification was based mainly on the R_f value of each constituent and on the colours produced by various spray reagents (**Tables 6.1** and **6.2**).

Auler [20] in his detailed survey on the analysis of antioxidants and accelerators was able to reproduce Zijp's work, and in addition, he applied the same solvent systems to circular paper chromatography with satisfactory results.

Williamson's work [7] is based on that of Zijp, but employs different solvent systems. Before the chromatography he evaporates the sample extract to dryness at 80 °C and dissolves the residue in 96% ethanol. Controlled additions of strontium chloride and ammonia solutions are made to precipitate out fatty acid and other impurities which

Table 6.1 Paper chromatographic separation of amine antioxidants					
Acetylated paper, Mobile phase: benzene:methanol (1:1). Spray reagent: 4% benzoyl peroxide in benzene					
Systematic name	Trade name	Colour of reaction product	Identification limits before/after chromatographic separation, µg		R_f values
1 Phenyl-α-naphthylamine	Neozone A Nonox A Alterungsschutzmittel PAN	Light yellow	5	10	0.64
2 Phenyl-β-naphthylamine	Neozone D Nonox D Alterungsschutzmittel PBN	Blue-grey	5	20	0.64
3 Diphenyl-*p*-phenylenediamine	JZF	Yellow-orange	< 1	2	0.56
4 Phenyl-cyclohexyl-*p*-phenylenediamine	Alterungsschutzmittel 4010	Yellow	< 1	10	0.73
5 Di-β-naphthyl-*p*-phenylenediamine	Agerite White Santowhite CI Nonox CI Alterungsschutzmittel DNP Antioxidant 123	Pink	1	5	0.55 (Tailing)
6 *p*-Isopropoxydiphenylamine	e.g. in Agerite Hipar, a mixture of 2, 3 and 6	Yellow-brown	-	-	0.73
7 *p, p′*-Dimethoxy-diphenylamine	e.g. in Thermoflex A, a mixture of 2, 3 and 7	Brown-pink	-	-	0.68
8 *p*-(*p*-Tolyl-sulfonylamino)-diphenylamine	Aranox	Brown-red	< 1	5	0.65
9 *p*-(*p*-Tolyl-sulfonylamino)-phenyl-*p*-tolylamine	MUF	Red	1	5	0.65
10 Mono- and diheptyldiphenylamine	Agerite Stalite	Green	-	-	0.81, 0.91
11 2, 4-Diamino-diheptyldiphenylamine	Oxynone	Brown	< 1	10	0.38
12 *p, p′* Diamino-phenylmethane	Tonox	Red-brown	2	40	0.50
13. Diphenyl-ethylenediamine	Stabilite	Red-brown	10	80	0.65
14. Di-*o*-tolyl-ethylene-diamine	Stabilite alba	Red-brown	10	80	0.67

Reproduced from J.W.H. Zijp, Recueil des Travaux Chimiques des Pays Bas, 1956, 75, 1155 [8]
R_f: ratio of the distance the substance moved to the distance the solvent moved

Table 6.2 Paper chromatographic separation of phenolic antioxidants					
Acetylated paper. Mobile phase: (1) Butyl acetate - pyridine - methanol - water (1:5:1:3) (2) Isopropanol - methanol - water (3:3:3) Spray reagents: (1) Tollen's reagent (2) Millon's reagent					
Systematic name	**Trade name**	**Identification before/after chromatographic separation (Tollen's reagent), μg**		R_f **values**	
				Mobile phase 1	**Mobile phase 2**
2,6-Di-*tert*-butyl-4-methylphenol	Ionol Deenax	10	80	0.60	0.44
2,2´-Methylene-bis-(4-methyl-6-*tert*-butylphenol)	2246	1	10	0.66	0.55
2,5-Di-*tert*-amyl-hydroquinone	Santovar A	1	40	0.69	0.53 T
2,5-Di-*tert*-butyl-hydroquinone	Santovar O	1	10	0.71	0.55 T
Hydroquinone-mono-benzylether	Agerite Alba	10	10	0.66	0.28 T
4,4´-Dihydroxybiphenyl	Alternungsschutzmittel DOD	1	2	0.77	0.43 T
4,4´-Thio-bis-(6-*tert*-butyl-3-methyl-phenol)	Santowhite crystals	10	40	0.71	0.63 T
4,4´-Thio-bis-(2,5-di-*tert*-amylphenol)	Santowhite L	10	40	0.58	0.70 T
4,4´-Butylidene-bis(6-*tert*-butyl-3-methylphenol)	Santowhite powder	10	40	0.69	0.73 T
T: tailing of the spot. *Reproduced from J.W.H. Zijp,* Recueil des Travaux Chimiques des Pays Bas, *1956,* **75,** *1155 [8]*					

are then removed by filtration and the clear filtrate examined for antioxidants by paper chromatography.

Delves [22] has described a procedure based on paper chromatography for the identification of nitrogen-containing antioxidants in synthetic aviation turbine oil formulations which, with minor modification could be applied to the analysis of plastics. His most successful solvent system for chromatography was dipropylene glycol (DPG) as the stationary phase and cyclohexane saturated with DPG as the mobile phase.

Whatman No. 1 paper was used for separation. A combination of methods was used to locate the separated antioxidants on the chromatogram. The chromatogram was first examined under UV radiation, when the compounds were detected either by their intense fluorescence or by absorption when they appeared as dark spots on the paper. The chromatogram was then sprayed with a 0.05% solution of *p*-nitrobenzenediazonium fluoborate in acetone to reveal those spots which formed azo dyes [23]. It was possible to detect as little as 2 μg of each antioxidant, and in some cases even less than 1 μg is detected.

The use of acetone as a location reagent solvent is advantageous, since it evaporates off the paper very quickly, thus a chromatogram is not wetted and is easy to handle.

Other reagents were tried by Delves [22]:

(a) A solution of bromine in carbon tetrachloride was found to detect phenothiazine as a blue-grey spot, 3,7-dioctylphenothiazine as a red-brown spot, and di-2-pyridylamine as a transient orange spot.

(b) If the antioxidant solutions were spotted directly on to an untreated paper, and then sprayed with a solution of tetracyanoethylene in benzene [24], coloured spots were formed similar to the azo dyes obtained with *p*-nitrobenzene-diazonium fluoborate. However, after solvent development of the antioxidants on paper impregnated with DPG, only phenothiazine was detected as a blue-green spot when sprayed with tetracyanoethylene reagent.

The R$_f$ values of the antioxidants and the effects observed under UV radiation and on spraying with *p*-nitrobenzenediazonium fluoborate are given in **Table 6.3**.

Davis and co-workers [25] separated antioxidants on Whatman NOAC 82 acetylated paper using ethanol - benzene - acetylacetone (10:10:1) as mobile phase and potassium-*p*-diazobenzene sulfonate as detection reagent. Korn and Waggon [26] separated urea based stabilisers on paper using propanol - methanol - water (2:1:1) migration and *p*-dimethyl-benzaldehyde detection.

Table 6.3 The paper chromatographic detection and identification of nitrogen containing antioxidants			
Antioxidants	Observation under ultraviolet radiation	Colour of azo dye	R_f values (23 °C)
Diphenylamine	Nil	Orange-red	0.55
Di-(*p*-octylphenyl) amine	Absorbs	Yellow	0.86
Phenothiazine	Fluoresces*	Pink	0.19
3,7-Dioctylphenothiazine	Absorbs	Brown-yellow	0.82
N-Phenyl-α-naphthylamine	Fluoresces	Mauve	0.57
N-Phenyl-β-naphthylamine	Fluoresces	Mauve	0.43
Di-2-naphthylamine	Fluoresces	Mauve	0.34
Di-2-pyridylamine	Fluoresces	Nil	0.22
*: At low concentrations phenothiazine is best detected as a dark spot against a white paper background. Reproduced from R.B. Delves, Journal of the Institute of Petroleum [22]			

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7 Supercritical Fluid Chromatography

Unlike paper and thin-layer chromatography (TLC; Chapters 5 and 6) techniques in which very little new work has been published since the 1970's, supercritical fluid chromatography (SFC) is a rapidly expanding area.

Until recently the chromatographer has had to rely on either gas chromatographic (GC) or high performance liquid chromatography (HPLC) for separations, enduring the limitations of both [1]. Lee Scientific has created a new dimension in chromatography, one which utilises the unusual properties of supercritical fluids. With the new technology of capillary supercritical fluid chromatography (CSFC) the chromatographer benefits from the best of both worlds - the solubility behaviour of liquids and the diffusion and viscosity properties of gases. Consequently, CSFC offers unprecedented versatility in obtaining high-resolution separations of difficult compounds.

Beyond its critical point, a substance can no longer be condensed to a liquid, no matter how great the pressure. As the pressure increases, however, the fluid density approaches that of a liquid. Because solubility is closely related to density, the solvating strength of the fluid assumes liquid-like characteristics. Its diffusivity and viscosity, however, remain. SFC can use the widest range of detectors available to any chromatographic technique. As a result, CSFC has already demonstrated a great potential in application to polymer additives.

SFC is now one of the fastest growing analytical techniques. The first paper on the technique was by Klesper and co-workers [2], but SFC did not catch the analyst's attention until Novotny and co-workers [3] published the first paper on CSFC.

Most supercritical fluid chromatographs use carbon dioxide as the supercritical eluent, as it has a convenient critical point of 31.3 °C and 7.3 MPa. Nitrous oxide, ammonia and n-pentane have also been used. This allows easy control of density between 0.2 ml/g and 0.8 ml/g and the utilisation of almost any detector from liquid chromatography (LC) or GC.

CSFC utilises narrow (50 µm or 100 µm id) columns of between 3 and 20 m in length. The internal volume of a 3 m x 50 µm id column is only 5.8 µl. SFC operates at pressures from 10.3 MPa to beyond 41 MPa. To allow injections of about 10-50 µl to be introduced to a capillary column, an internal loop LC injector (Valco Institute Switzerland) has been used with a splitter which is placed after the valve to ensure that a smaller volume was introduced onto the column (**Figure 7.1**). This method works well for compounds which are easily soluble in carbon dioxide at low pressures. Good reproducibility is attained for CSFC using a direct injection method without a split restrictor.

This method utilised a rapidly rotating internal loop injector, which remains in-line with the column for only a short period of time. This then gives a reproducible method of injecting a small fraction of the loop onto the column. For this method to be reproducible the valve must be able to switch very rapidly to put a small slug of sample into the column. To attain this, a method called timed-split injection was developed (Lee Scientific). For timed split to operate it is essential that helium is used to switch the valve, air or nitrogen cannot provide sharp enough switching pulses. The injection valve itself must have its internal dead volumes minimised. Dead volumes prior to the valve allow some of the sample to collect prior to the loop, effectively allowing a double slug of sample to be injected which appears at the detector as a very wide solvent peak.
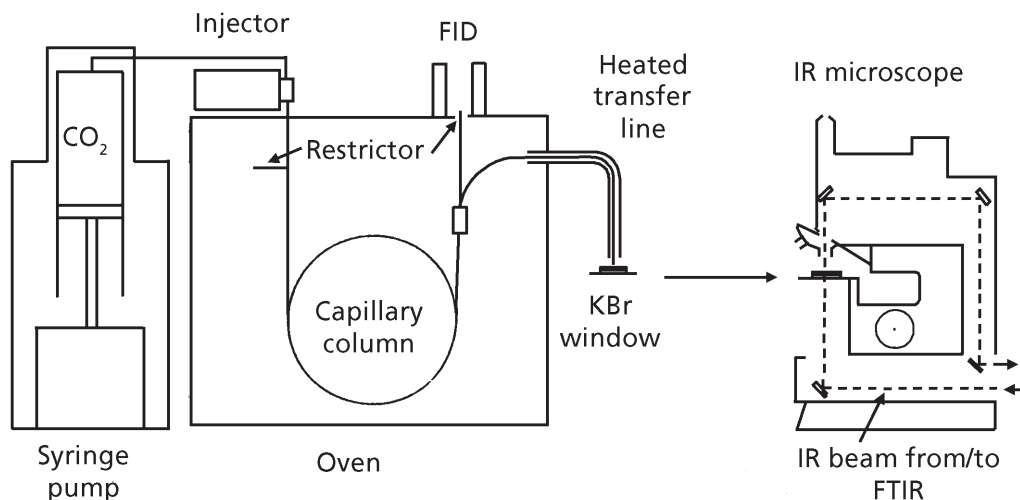
Figure 7.1 Major instrumental components of SFC/FTIR system using an FTIR microscope accessory. *From: Author's own files*

SFC uses detectors from both LC and GC. A summary of detection systems used in SFC has been documented (Later and co-workers [4]).

One of the most commonly used detection systems is the electron capture detector, a sensitivity down to about 50 pg minimum detection limit on a column has been obtained [5].

A paper has been published showing the use of the photoionisation detector (Sim and co-workers [6]. The photoionisation detector is to a certain extent specific in that only compounds that can be ionised by a ultraviolet (UV) lamp will give a response. The solvents used were dichloromethane and acetonitrile, both of which should have little response in the photoionisation detector. However, a clear sharp solvent peak was observed.

The amount detected by this system (0.3 pg on column) was below the level which could have been determined using a flame ionisation detector. Initial indications show that the photoionisation detector may be a very useful detector for people who wish to detect lower levels on the SFC and cannot concentrate their sample.

A sulfur chemiluminescence detector (Sievers Research Inc., Colorado, USA) has been investigated. Good sensitivities and chromatograms have been shown for standards and real samples. This detector shows no response to carbon dioxide and gives low picogram sensitivities for a wide range of sulfur compounds.

Upnmoor and Brunner [7] evaluated a packed column SFC with a light scattering detector using a mobile phase of carbon dioxide modified with methanol for the chromatography of polymer additives. Moulder and co-workers [8] transferred eluent fractions from a packed capillary size exclusion chromatographic (SEC) column using a solvent vented interface to an open tubular CSFC column. The system was evaluated for the analysis of polymer additives.

7.1 Antioxidants

SEC suffers from poor resolution and low sensitivity [5], while GC is limited by the high molecular weight and polar nature of many antioxidants and light stabilisers, which are designed to be reactive and so decompose when exposed to heat [9]. HPLC the most widely used instrumental method also has limitations [10-12]. HPLC lacks a simple sensitive universal detector that is compatible with all liquid mobile phases. UV or fluorescence detectors, which are commonly used, require that additives have a chromophoric moiety, while the universal refractive index detector only functions under isocratic conditions. As a result, Vargo and Olson have coupled HPLC with mass spectrometry (MS) for this type of application by using a moving belt interface [13].

The chemical similarity of many additives and the limited chromatographic efficiency of packed columns, even when employing special column packing and gradient schemes is still a major problem with HPLC methods. CSFC with carbon dioxide as the mobile phase is especially well suited to high-resolution separation of nonvolatile, thermally labile, high molecular weight, or moderately polar compounds and should therefore be the method of choice for analysing polymer additives [14]. It can also be coupled to a variety of detectors including the universal flame ionisation detector (FID) [15, 16]. The compressibility of carbon dioxide above its critical temperature and pressure is considerable, and densities similar to liquids can be achieved at moderate temperatures. Thus density programming can effectively control the solvating power of the supercritical fluid and thereby control selectivity.

A further advantage of supercritical carbon dioxide is its volatility on decompression. Fourier transform infrared (FTIR) micro spectrometry can therefore be coupled to SFC with ease as there is no significant interference from the mobile phase [17, 18]. With this technique, each eluate is directly deposited from the end of a restrictor onto a small area of an infrared (IR)-transparent support as the mobile phase evaporates away. The support is then positioned in an IR microscope, which serves as a beam condenser, matching the IR beam size to the area that the sample occupies (typically 200 μm in diameter). In this way IR spectra can be collected from nanogram levels of each deposited eluate. The information yielded by combining the separation power of CSFC with the identification power of FTIR micro spectrometry greatly increases the possibility of elucidating the structures of unknown compounds.

Raynor and co-workers [19, 20] evaluated CSFC for polymer additive characterisation. They showed that high-resolution CSFC was an efficient separation technique for the qualitative analysis of chemical additives in polymers. Twenty-one compounds varying in chemical composition and, molecular mass from 225 to 1178 were separated on a non-polar capillary column by using carbon dioxide as the mobile phase. A polypropylene (PP) extract is analysed to exemplify the method and highlight the limitation of using retention time data for identifying unknown compounds. The use of FTIR as a detector provides unique spectroscopic information for identification purposes. For this application, CSFC is coupled to FTIR by using a microscope accessory and a solvent elimination interface. Polymer additives that elute from the column pass through a capillary restrictor and are deposited onto a potassium bromide window, which is subsequently positioned in the IR microscope for analysis. As there is no significant interference from the mobile phase, good quality spectra can be obtained from samples deposited at levels in the order of 100 ng.

Figure 7.2 is a chromatogram obtained for a synthetic mixture of the additives identified in **Table 7.1** and **7.2**, and **Figure 7.3** is a chromatogram obtained for a diethyl ether extract of a commercial PP sample which shows that it contains Tinuvin 440, Irgafos 168 and Irganox 1010.
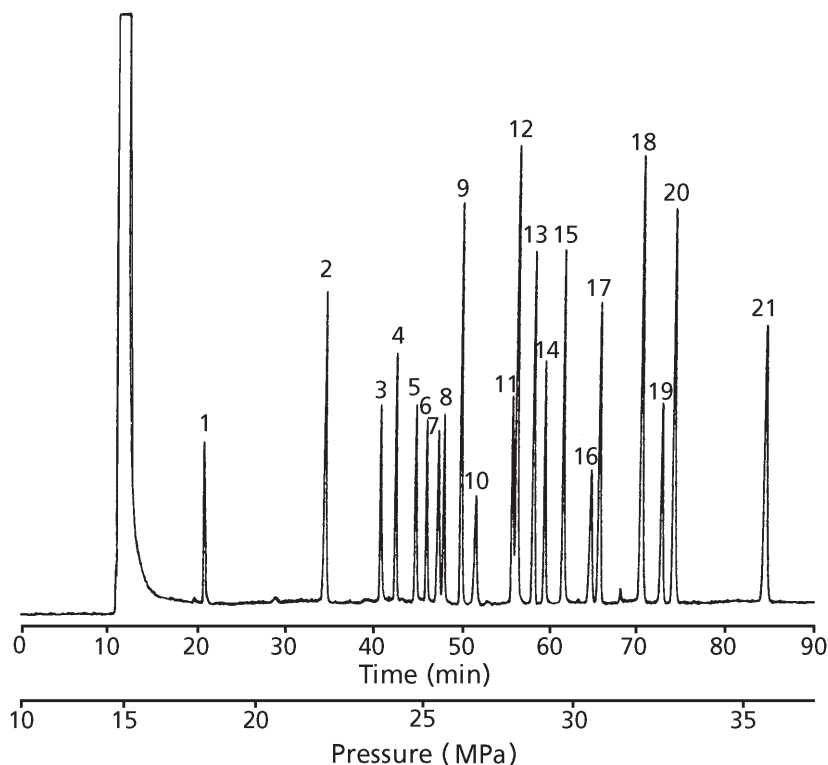
Figure 7.2 Supercritical fluid chromatogram of polymer additives listed in **Tables 7.1**
and **7.2**. Conditions: 10 m x 50 µm id fused-silica capillary column, crosslinked
methylpolysiloxane stationary phase (0.25 µm film thickness); carbon dioxide mobile phase
at 140 °C; 15 – 35 MPa at 0.3 MPa/min after an initial 12 minutes isobaric period;
20 ng/component introduced onto the column
Reproduced from Raynor and co-workers, ACS [19]

Reliance on retention time data can result in erroneous identifications. For this reason
Raynor and co-workers [19, 20] used SFC-FTIR interfacing as described by Pentoney and
co-workers [17] to ensure positive identifications.

Hunt and co-workers [21] used SFC to extract additives in polyvinylchloride (PVC).
The extraction time, temperature and pressure were varied in order to determine the
optimum supercritical fluid extraction (SFE) conditions. The effects of the particle size of
the sample and the addition of methanol to the extraction fluid were also investigated.
The separation and quantification of individual components in the PVC extracts were

Table 7.1 Polymer additives separated by capillary SFC
Peak No.	Trade name	Chemical name	RMM	Peak No. Figure
1	Topanol OC	2,4,6-Tri-*tert*-butylphenol	262	10
2	Tinuvin P	2-(2-Hydroxy-5-methylphenyl)-2*H*-benzotrizole	225	11
3	Tinuvin 292	Bis(1-methyl-2,2,6,6-tetramethylpiperidinyl) sebacate	506	
4	Tinuvin 320	2-(2-Hydroxy-3,5-di-*tert*-butylphenyl)-2*H*-benzotriazole	323	
5	Tinuvin 326	2-(3-*Tert*-butyl-2-hydroxy-5-methylphenyl)-2*H*-5-chlorobenzotriazole	316	
6	Tinuvin 328	2-(2-Hydroxy-3,5-di-*tert*-amylphenyl)-2*H*-benzotriazole	351	
7	Chimasorb 81	2-Hydroxy-4-*n*-octyloxybenzophenone	326	
8	Erucamide	*Cis*-13-docosenamide	351	
9	Tinuvin 770	Bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate	478	
10	Tinuvin 440	8-Acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro(4,5)decane-2,4-dione	436	
11	Irgafos 168	Tris(2,4-di-*tert*-butylphenyl)phosphite	647	
12	Tinuvin 144	2-*Tert*-butyl-2-(4-hydroxy-3,5-di-*tert*-butylbenzyl)[bis(methyl-2,2,6,6-tetramethyl-4-piperidinyl)]dipropionate	685	
13	Irganox PS800	Dilauryl thiodipropionate	515	
14	Irganox 1076	Octadecyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	537	
15	Irganox MD1025	*N,N*-bis[1-oxo-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propane]hydrazine	553	
16	Irganox 245	Triethylene glycol bis-3-(3-*tert*-butyl-4-hydroxy-5-methylphenyl)propionate	587	
17	Irganox 1035	2,2-Thiodiethylene bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate]	643	
18	Irganox 3114	Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate	784	
19	Irganox PS802	Distearyl thiopropionate	683	

Table 7.1 Cont'd...				
Peak No.	Trade name	Chemical name	RMM	Peak No. Figure
20	Irganox 1330	1,3,5-Tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene	726	
21	Irganox 1010	Pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate	1178	
RMM: *relative molecular mass* Reproduced from: *M.W. Raynor and co-workers,* Analytical Chemistry [19]				
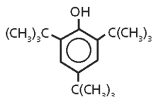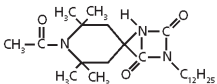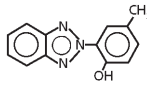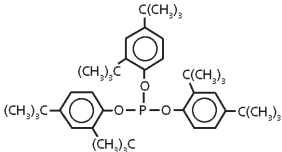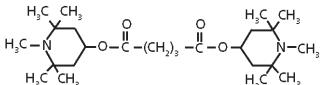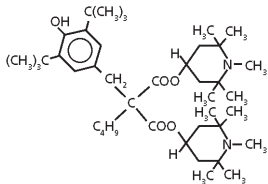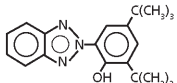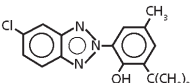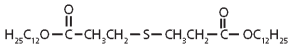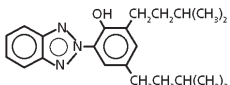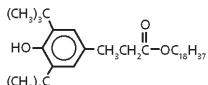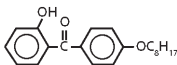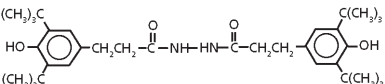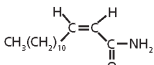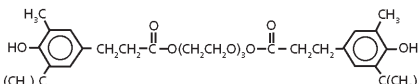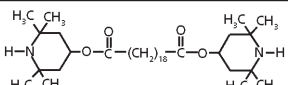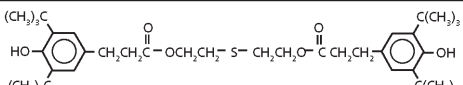
Table 7.2 Chemcal structures of polymer additives in order of elution			
Peak No.	Chemical structure	Peak No.	Chemical structure
1	*(structure)*	10	*(structure)*
2	*(structure)*	11	*(structure)*
3	*(structure)*	12	*(structure)*
4	*(structure)*		
5	*(structure)*	13	*(structure)*
6	*(structure)*	14	*(structure)*
7	*(structure)*	15	*(structure)*
8	*(structure)*	16	*(structure)*
9	*(structure)*	17	*(structure)*

Table 7.2 Continued...	
Peak No.	**Chemical structure**
18	
19	
20	
21	
Reproduced from: M.W. Raynor and co-workers, Analytical Chemistry *[19]*	

carried out off-line using packed column supercritical fluid chromatography (PSFC). This technique combined good resolution, rapid analysis times and linear calibrations over a wide range of additive concentrations. By using SFE, 29.2% m/m of the sample was extracted of which 66.7% m/m was di-isooctyl phthalate (DIOP). This compared with the existing liquid extraction method by which 30% m/m of the sample was extracted of which 67% was DIOP. The total extractions varied by 0.9% relative standard deviation (RSD) and the DIOP content varied by 1.2% RSD.

A chromatogram for the separation of di-iso-octylphthalate and Topanol CA in PVC extract is shown in **Figure 7.4**. The concentration of di-iso-octylphthalate the PVC is approximately 500 times that of Topanol CA.
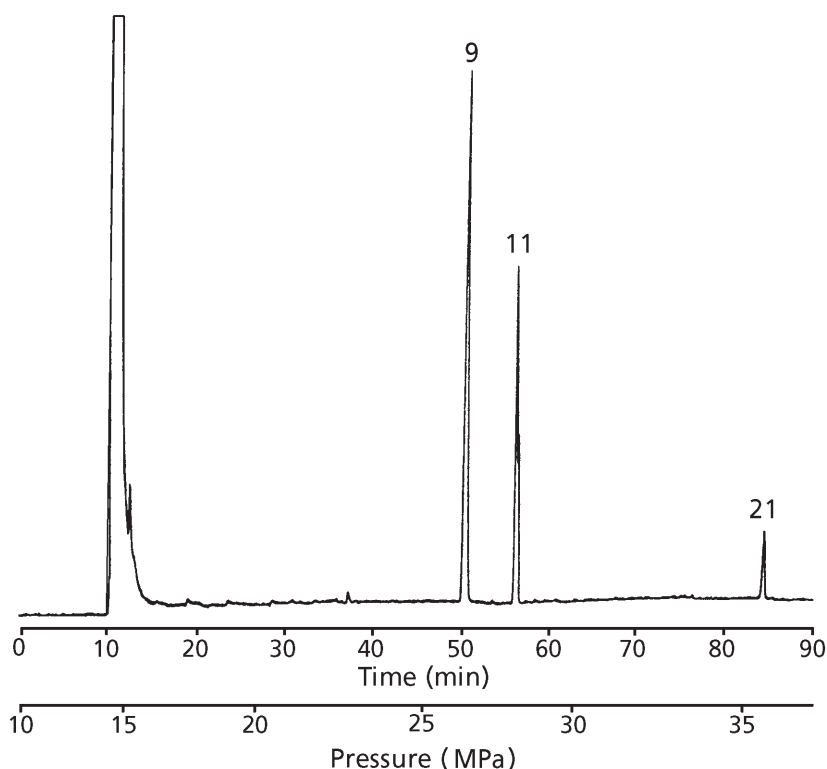
Figure 7.3 Supercritical fluid chromatogram of polymer additives (listed in **Tables 7.1** and **7.2**) extracted from a commercial PP sample. Conditions as in **Figure 7.2**. [19]

Hunt and co-workers [21] concluded that extraction of the major, volatile components in PVC with a moving stream of supercritical CO_2 is a fast, reproducible alternative to liquid extraction. Total solute extraction efficiencies of over 95% compared with liquid extraction are obtainable for extraction times of 15-20 minutes with a flow rate of 5 ml/min at temperatures above 80-90 °C and at pressures above 30-40 MPa. The results obtained are reproducible and there is no significant gain in extraction from utilising longer extraction times.

SFE chromatography has also been used in the determination of erucamide and antioxidants in polyethylene (PE) [22], butylated hydroxyl toluene, Isonox 129 and Irganox 1010 in PE [23], and PP [23], antioxidants and UV stabilisers in food packages [24] and secondary antioxidants such as distearyl thiodipropionate and phosphonites in polyolefins [25].
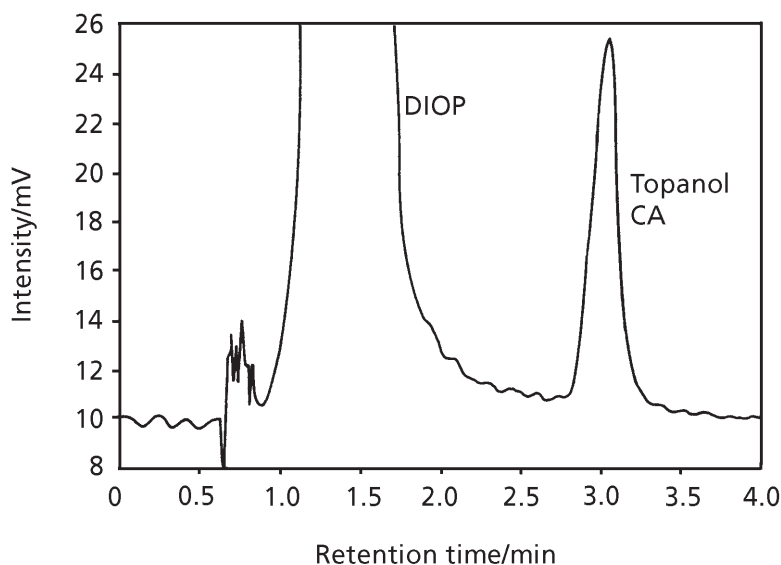
Figure 7.4 PSFC trace of PVC extract. Column: Spherisorb ODS-1, 250 x 4.6 mm id; mobile phase: 10-17% methanol – CO_2; oven temperature 45 °C; pressure: 10 MPa; flow rate: 4.0 ml/min; and UV detector wavelength: 275 nm
Reproduced from Hunt and co-workers RSC [21]

7.2 Oligomers

Ute and co-workers [26] used preparative SFC followed by thermal analysis to separate isotactic and syndiotactic monomethyl-methacrylate oligomers from 19-mer and 29-mer.

Figure 7.5(a) shows an SFC curve of the isotactic-polymethylmethacrylate (PMMA) (degree of polymerisation (DP) = 28.6, M_w/M_n = 1.15) prepared with t-C_4H_9MgBr. The oligomer components from 10-mer to 59-mer separated completely. The amount of the sample injected on the silica gel column was 50 mg (100 µl of 50 *w/v*% acetone solution). SFC separation of the methylmethacrylate (MMA) oligomer with a DP of 9.9 was performed.

The fractions from 19-mer to 28-mer (**Figure 7.5a**) were collected several times. The delay of the timing for the fractionation was estimated as approximately 1.0 seconds from the flow rate and the volume of the connecting path between the detector and the back pressure regulator (160 µl). The fraction of 25-mer obtained was analysed by SFC under the same conditions (**Figure 7.5b**). The fraction showed an elution peak at the original position, accompanied by some small peaks due to the lower DP components. Then, the fraction was subjected to the SFC again, and the pure component giving a single peak
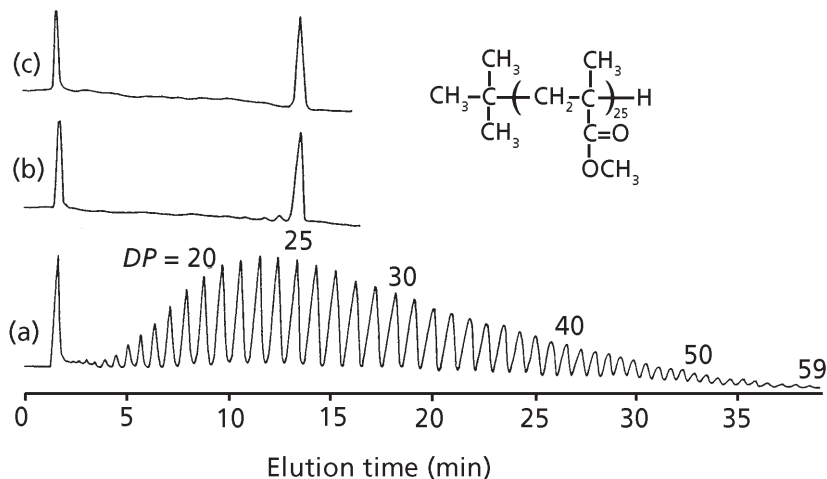
Figure 7.5 SFC traces of the isotactic PMMA (DP = 28.6, M_w/M_n = 1.15) (a) the crude 25-mer isolated from the PMMA (b) and the 25-mer purified by the repeated fractionation of (b) and (c)
Reproduced from Ute and co-workers, Polymer Bulletin [26]

in the chromatogram could be isolated (**Figure 7.5c**). In a similar manner, several tens or hundreds milligrams of the pure oligomers from 19-mer to 28-mer were obtained, individually.

Willian and Lilly [27] also used SFC carbon dioxide mobile phase with FID to monitor the separation of MMA oligomers and polymer additives.

Takeuchi and Saito [28] used semi-micro SFC with gradient elution to separate oligomers from PMMA, polystyrene (PS) and polymethyl phenyl siloxane. Temperature programmed elution gave good separation of low molecular weight oligomers while gradient elution gave good resolution over a broad range of oligomer molecular weights.

SFE coupled to SFC gave good separation of low molecular weight oligomers and additives occurring in PP, polyethylene terephthate (PET) and polyamides [29].

SFC has also been used to separate oligomers of polyethylene oxide [30], polycaprolactone [30], poly-2-vinyl-pyridine [30], epoxy pre-polymers, PS [31, 32] and poly-2-vinyl naphthylene [31, 32].

Several other workers have discussed the application of SFC to the determination of additives in PE and PP [23, 33-44].

7.3 Supercritical Fluid Chromatography-Mass Spectrometry (SFC-MS)

Van Leuken and co-workers [45] have discussed the optimisation of capillary SFC-MS using a standard direct introduction technique capillary interface for the determination of additives in polymers.

The technique has also been applied to the determination of oligomers in PET [46, 47].

Bücherl and co-workers [48] has described an integral restrictive interface with jet separation for coupling capillary column SFC with carbon dioxide mobile phase with high resolution mass spectrometry.

Fatty acids esters and polymer additive with a wide range of masses could be determined. An FID was used in parallel with the mass spectrometer.

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8 Headspace Analysis - Volatiles

Headspace GLC analysis is a method used to monitor a vapour over a polymeric matrix. It is a very effective technique, but may require more time and effort than direct injection. This method can be performed manually, when a vial containing the monomer is heated, an equilibrium is established, for volatile compounds between the sample and the headspace above it. Because no dissolution step is required, sample viscosity problems and loss of response due to dilution are eliminated. Automated headspace analysis units are available from instrument manufacturers, as well as multiple extraction systems. Any analytically useful headspace method must obey Henry's law:

$$P_B = \kappa X_B \qquad\qquad (8)$$

where P_B is the partial pressure of solute B (in solvent A), κ is the proportionality constant and X_B is the mole fraction of solute B.

8.1 Volatiles

There are two basic principal methods of headspace analysis in polymers. In one method a solution of the polymer is examined, in the other method solid polymer is examined directly. When working with polymer solutions, headspace equilibrium is more readily obtained than the solid approach and the calibration procedure is simplified.

In the solid polymer approach the residual monomer is partitioned between the headspace and the polymer phase. The monomer concentration in the head space is determined and the original concentration in the polymer is calculated. Since polymer standards of known monomer content are not readily available, the headspace monomer concentration must be related to the original concentration in the polymer either by assuming 100% diffusion of the constituent into the head space or through equilibrium calculations utilising Henry's Law and the appropriate partition coefficient. Berens [1] determined this coefficient for the vinyl chloride-PVC system and applied this to the determination of vinyl chloride in PVC resin powder. Equilibration of residual vinyl chloride with the headspace occurred within one hour when PVC powder was heated to 90 °C.

A good example of the solution approach is that of Crompton and Myers [2] who carried out gas chromatographic analyses out on solutions of polystyrene in the presence of internal standards. To avoid interferences in the analysis, it is essential for the solvent and the internal standard to have retention times different from those of the volatile compounds being determined in the polymer. Application of the volatiles apparatus described by Crompton and Myers [2] to a polystyrene provides a rapid means of determining the retention time of the volatile compounds present in the polymer, enabling a suitable solvent and internal standard to be selected for the subsequent quantitative analysis by solution procedures.

Mixtures of iso-pentane and *n*-pentane are commonly used as expanding agents in expandable grades of polystyrene. An available procedure for doing this involved the gas chromatographic analysis of a solution of the polymer in propylene oxide in the presence of 2,2-dimethyl butane as an internal standard. This method is entirely satisfactory for analysing grades of expandable polystyrene in which it is known that iso-pentane and *n*-pentane are the only expanding agents present. However, if other types of expanding agent have been used in the polymer formulation then it is possible that, under the selected conditions, their retention times might coincide with those of propylene oxide or 2,2-dimethyl butane, with the result that the analysis would be invalidated.

Figure 8.1 shows a chromatogram of the volatiles liberated by an expanded polystyrene after heating at 200 °C for 15 minutes under helium. Superimposed on the chromatogram is the solvent peak which would be present if the analysis were carried out on a solution of the polymer in propylene oxide. In addition to *n*-pentane and iso-pentane, the sample contains lower concentrations of several C_6 and C_7 hydrocarbons, all of which originate as impurities in the pentanes used in the polystyrene formulation. One of these hydrocarbons is 2,2-dimethyl butane. Hence, the presence of this substance must be allowed for by using an alternative internal standard. The chromatogram also shows that although propylene oxide would not interfere with the determination of most of the components, the *n*-hexane and one of the C_7 hydrocarbons would be completely obscured and could not be determined. For a complete analysis by a solution procedure it was therefore necessary to select a solvent which is eluted later than propylene oxide. Benzene was found to be suitable.

Crompton and Myers [2] used the solid polymer approach in their simple and inexpensive apparatus for liberating both existing volatiles and those produced by thermal degradation from polymers by heating at temperatures up to 300 °C, in the absence of solvent, prior to their examination by gas chromatography. The technique avoids the disadvantages resulting from the use of extraction or solution procedures.

The apparatus illustrated in **Figure 8.2** consists of a glass ignition tube, supported as shown in a Wade 6.25 mm diameter brass coupling nut, covered with a silicone rubber
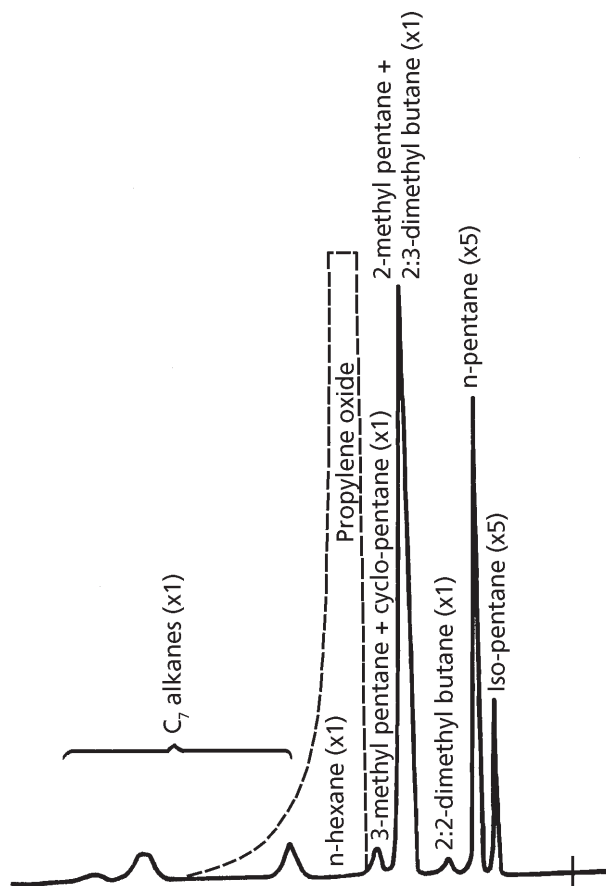
Figure 8.1 Gas chromatogram of expanding agents liberated from expendable PS at 200 °C for 15 minutes in helium. Chromatographed on 3 m x 5 mm id, 25% di-*n*-butyl phthalate on 44/60 celite aqt 40 °C and 50 ml/min helium flow, with thermal conductivity detection
*Reproduced from Crompton and Myers, Plastics and Polymers [2]*

septum and sealed with a Wade 6.25 mm brass stop-end body. The stop-end body has two 1 mm diameter holes drilled through the cap. The whole unit is placed in a slot in a cylindrical copper block (7.5 cm long x 5 cm diameter) which is heated by two (240 V, 85 W) cartridge heaters and controlled at temperatures up to 300 °C from a variable transformer. The temperature is measured with a thermocouple capable of accurately measuring temperatures in the 100-300 °C temperature range with a maximum error of ±5%. The thermocouple is inserted in the slot adjacent to the ignition tube; it has been
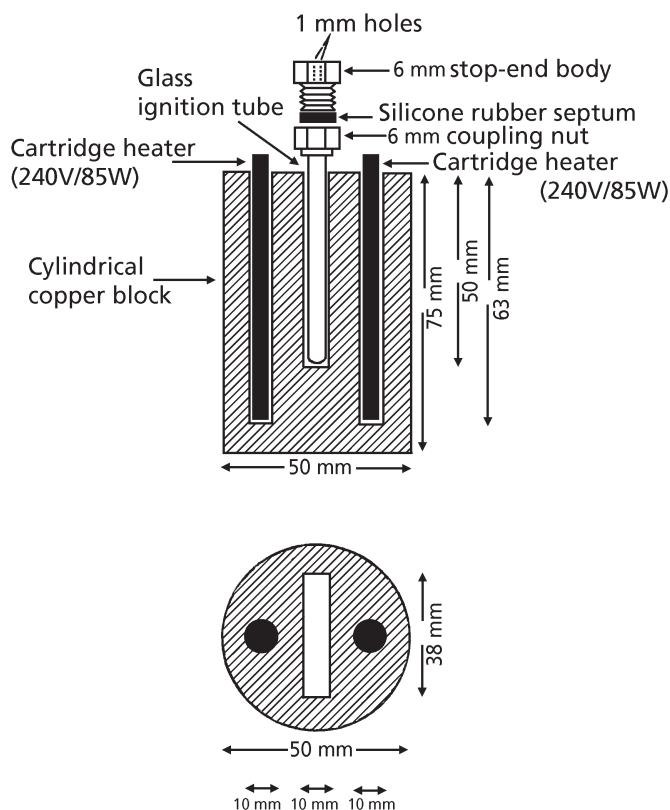
Figure 8.2 Apparatus for liberating volatiles from polymers
Reproduced from Crompton and Myers, Plastics and Polymers [2]

shown that under these conditions the thermocouple records the true temperature of the contents of the tube. The provision of a slot in the copper block enables more than one ignition tube to be heated simultaneously if required.

Polyethylene is not appreciably soluble in organic solvents, and the determination of existing volatile impurities cannot be conveniently carried out by the analysis of solutions of the polymer. Many organic solvents will extract such volatiles from polyethylene, but these are likely to be lost during the solvent-removal stage prior to gas chromatographic analysis. A further problem is that extraction procedures cannot be used for investigating those volatiles that are not inherently present but are produced only when the polymer is heated. The following examples illustrate the use of the method for examining both types of volatiles released from polyethylene.

The above technique was used to study the effect of temperature on the nature of the volatiles released, and to investigate this polyethylene was heated for 15 minutes in air at 125, 150, 175 and 200 °C and the volatiles were analysed by gas chromatography (see **Figure 8.3**).

These observations suggest that between 125 and 200 °C there is some thermal degradation of the polymerisation solvent to C_2-C_4 hydrocarbons.

These results led to the conclusion that the major volatile components of this polyethylene were due to residual polymerisation solvent. Also that when examining polyethylene for existing volatiles, it is necessary to use is low a temperature as possible for liberating the volatiles if thermal degradation is to be avoided. A temperature of 125 °C appeared to be suitable.

In **Figures 8.4 A** to **E** are shown gas chromatograms of volatiles obtained when polystyrenes from two different manufacturers were heated at 200 °C for 15 minutes under helium. All the samples liberated the same range of aromatic hydrocarbons, these differing only in their
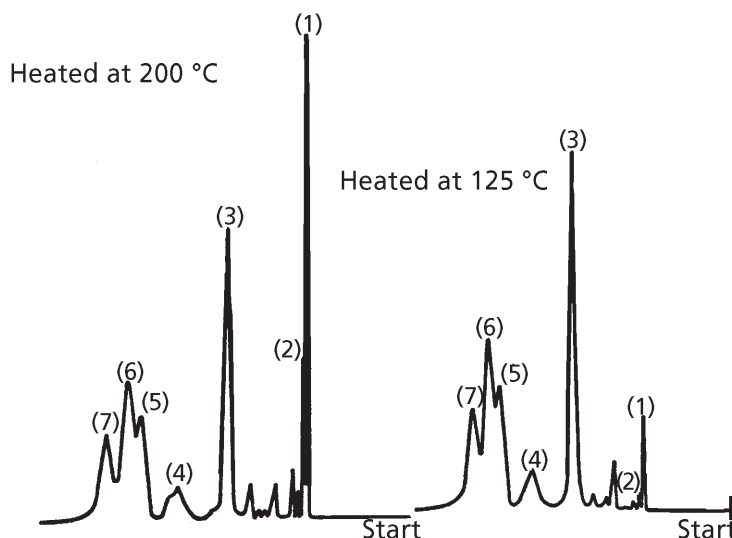
Figure 8.3 Gas chromatogram of volatiles liberated from PE heated at different temperatures for 15 minutes in air. Chromatographed on 60 m x 1.5 mm id dibutyl phthalate coated copper column at 30 °C and 100 ml/min helium flow, with flame ionisation detection
Reproduced from Crompton and Myers, Plastics and Polymers [2]

309
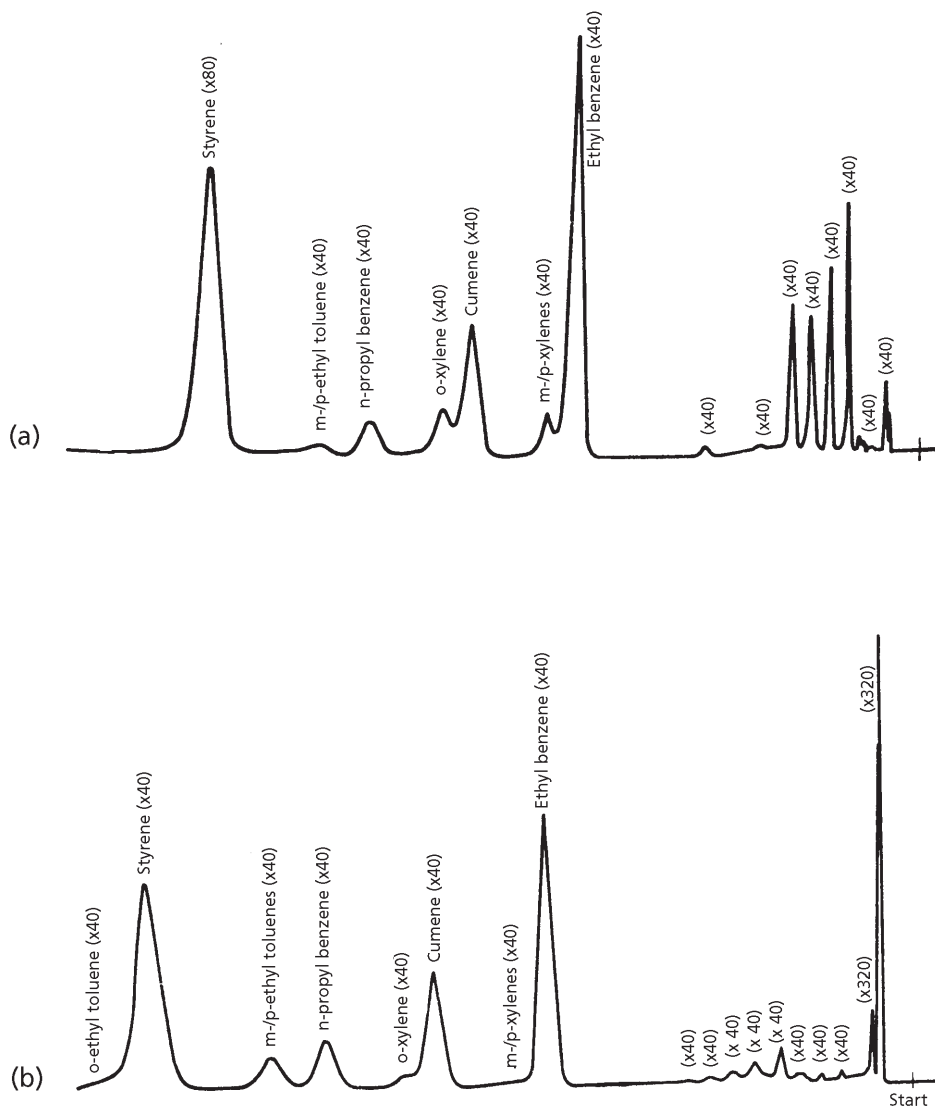
Figure 8.4 Gas chromatogram of volatiles liberated from different PE heated at 200 °C for 15 minutes in helium. Chromatographed on 4.5 m x 4.7 mm id, 10% Carbowax 15-20M on 60-72 Celite at 90 °C and 100 ml/min helium flow, with flame ionisation detection
Reproduced from Crompton and Myers, Plastics and Polymers [2]
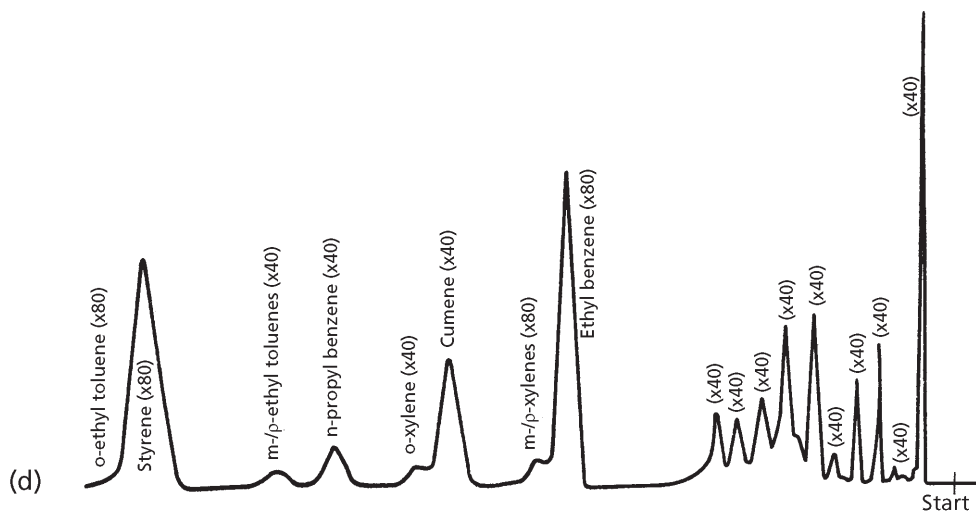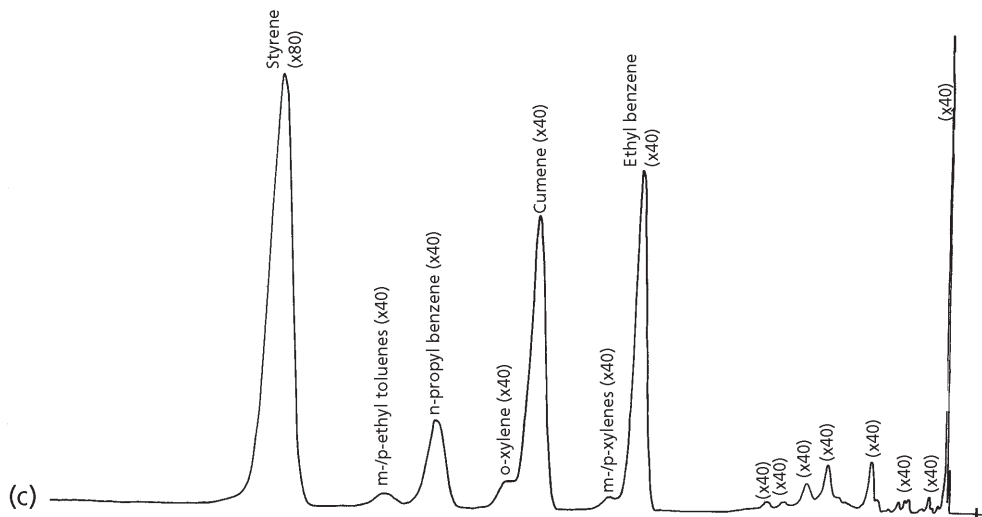
Figure 8.4 Continued...
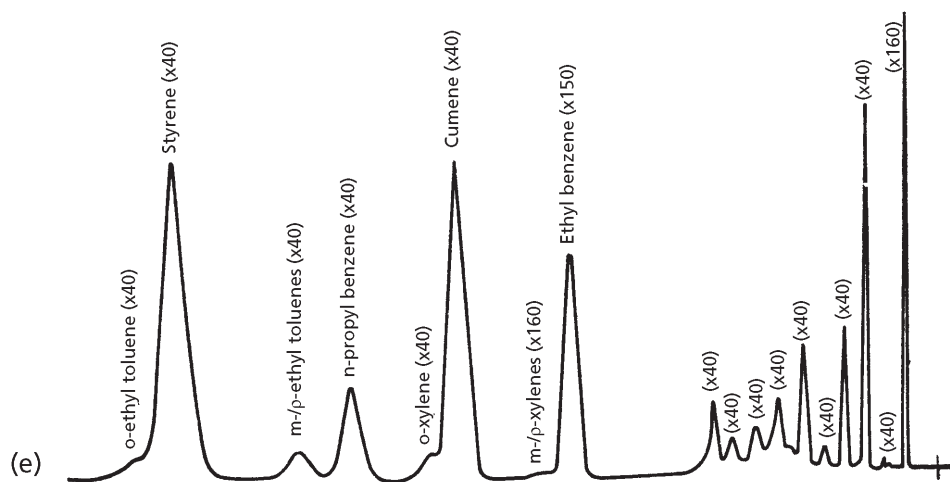
Figure 8.4 Continued...

relative concentrations. However, the non-aromatic hydrocarbon material, eluted from the gas chromatographic column prior to ethyl benzene, shows marked differences from sample to sample. The results do show the value of the technique for detecting differences in the volatiles liberated by polystyrenes produced by different manufacturers.

Hagman and co-workers [3] and Schmidt and co-workers [4] used dynamic headspace analysis to study volatiles in polypropylene-polyethylene copolymers and PVC and polyethylene terephthalate. In the latter method [3], volatiles from PET and PVC were collected and separated by open tubular GC. Other solid polymer headspace methods discussed include hexane, tridicane and butylated hydroxytoluene in polypropylene [5], vinyl chloride, vinyl acetate, acetaldehyde and water in vinyl and acrylic polymers and polyolefins [6], ethyl acetate and toluene in laminated polyolefins [7], miscellaneous volatiles in polymers [8] and solvents retained in plastic films [9-12].

Gadelle and co-workers [13, 14] used a Hewlett Packard headspace sampler (HP-19395A) connected to a Hewlett Packard gas chromatograph (HP5890) equipped with a capillary column and a flame ionisation detector to determine benzene, chlorobenzene, toluene and xylene in ethylene oxide propylene oxide triblock copolymers. The headspace sampler consists of a valve and loop system to inject a vapour sample of a known volume (1 µl) into the gas chromatograph. Peak areas are then determined by a Hewlett Packard integrator (HP 3393A).

Basically, 10 ml sample vials containing various concentrations of polymers and organic solutes are prepared. Sets of calibration standards (water and organic only) are prepared the same way. Samples were equilibrated at constant temperature (25 °C) in a shaker bath for at least 48 hours. Equilibration times of 12, 24, and 48 hours yielded the same results.

8.2 Monomers

The solution headspace approach is applicable to a much wider range of samples than the solid approach. When working with sample solutions, headspace equilibrium is more readily attained and the calibration procedure is simplified. The sensitivity of the solution method depends upon the vapor pressure of the constituent to be analysed and its solubility in the solvent phase. Vinyl chloride, butadiene, and acrylonitrile, are readily transferred from polymer solutions into the headspace by heating to 90 °C. The headspace/solution partitioning for these constituents is not appreciably affected by changes in the solvent phase (namely, addition of water) since the more volatile materials favour the headspace at 90 °C. Less volatile monomers such as styrene (bp = 145 °C) and 2-ethylhexyl acrylate (bp = 214 °C) may not be determined using headspace techniques with the same sensitivities realised for the more volatile monomers. By altering the composition of the solvent phase to decrease the monomer solubility, the equilibrium monomer concentration in the headspace can be increased. This resulted in a dramatic increase in the detection sensitivity for styrene and 2-ethylhexyl acrylate.

The more volatile monomers vinyl chloride, butadiene, and acrylonitrile can be determined by dissolution of the polymer and analysis of the equilibrated headspace above the polymer solution. By this method it was possible to determine vinyl chloride and butadiene at the 0.05 ppm level and acrylonitrile down to 0.5 ppm. The injection of water into polymer solutions containing styrene and 2-ethylhexyl acrylate monomers prior to headspace analysis greatly enhanced the detection capability for these monomers making it possible to determine styrene down to 1 ppm and 2-ethylhexyl acrylate at 5 ppm. Incorporation of polymer into the calibration standards compensates for the effect which the polymer matrix has upon the equilibrium partitioning of the monomer between the solution and head space. The relative precision and error in the determination of these monomers near the quantitation limit was found to be less than 7%.

Other monomers that have been determined by solution headspace methods include styrene in polystyrene [15-23], vinyl chloride in PVC [24] and by the solid polymer approach volatiles in ethylene-propylene co-polymers [25], styrene and *o*-xylene in polystyrene.

A modified headspace gas chromatographic method has been described for the determination of free methylmethacrylate monomer in contact lenses regardless of their

method of production. This method allowed supervision of the quality of a lens of unknown origin within 15 minutes and the test was used to evaluate production tests of new polymerisation initiators [26].

8.3 Oligomers

Styrene and styrene oligomer have been determined in polystyrene equilibrated headspace analysis in amounts down to 0.29 mg/kg [27].

8.4 Miscellaneous

Headspace sampling and GC have been used to quantitatively follow the thermal oxidation of a low molecular weight hydroxyl-terminated polybutadiene [26]. Rate studies using this simple, efficient technique revealed an induction period for the oxidation followed by self-catalysed oxidation. The rate for this latter step was quickly controlled by the diffusion of oxygen into the polymer.

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9 Thermal Methods

Two thermal methods have been extensively studied in recent years, pyrolysis-gas chromatography (Py-GC) - mass spectrometry (MS) and evolved gas analysis involving infrared spectroscopy (IR) - MS, thermogravimetry and differential scanning calorimetry (DSC).

9.1 Pyrolysis-Gas Chromatography-Mass Spectrometry

Py-GC employing various detection systems is the technique usually used to qualitatively and quantitatively analyse major components and low-level additives in polymers [1-3]. The technique utilises thermal energy to break down polymers to monomers and small oligomers. The mixture of pyrolysis products is directly passed into a gas chromatograph (GC) for separation. However, there are numerous low-level co-monomers and additives that may not be appropriately separated at the same time as the major monomers. These low-level co-monomers and additives frequently appear with poor peak shape under the chromatographic conditions established for analysis of the major monomers hence the interest in combining this technique with MS (such as a polar additive in a non-polar capillary column). Additionally, these peaks may have been overlooked because they exist as converted products in the chromatogram after the pyrolysis-induced reaction (such as vinyl acetate converted to acetic acid).

Ogawa and co-workers [4] used Py-GC-MS to analyse the components of ozone deteriorated nitrile-butadiene rubber sheet containing additives. There were three peaks related to the quinoline antioxidant in the program. They noted that the mechanical strength of the sheet became zero when the antioxidant level reached 50% of its original level.

Franich and co-workers [5] described two simple methods using internal standards for the quantitative analysis of 2,6-di-*tert*-butyl-4-methylphenol (butylated hydroxytoluene, BHT) antioxidant in samples of solvent-formulated liquid adhesive and in cured polychloroprene adhesive films. Because only very small samples of cured adhesive could be taken from articles or components without substantially detracting from the product, the methods were developed to use minimal quantities of cured adhesive. The Py-GC method required

less than 1 mg of adhesive for analysis. The extraction method required less than 100 mg. A satisfactory correlation ($r = 0.8$) was obtained between the two methods. Recovery of BHT by extraction from cured Neoprene adhesive was better than 90%. Using 2,6-di-*tert*-butylphenol as internal standard, the error for the Py-GC analysis method was 10%, while that of the extraction method was 1%.

The 9-16 minute retention time window of a typical Py-GC analysis of polychloroprene adhesive is shown in **Figure 9.1**. **Figure 9.1a** shows the chromatogram of a standard adhesive containing 2 parts of BHT per hundred parts of chloroprene, and newly
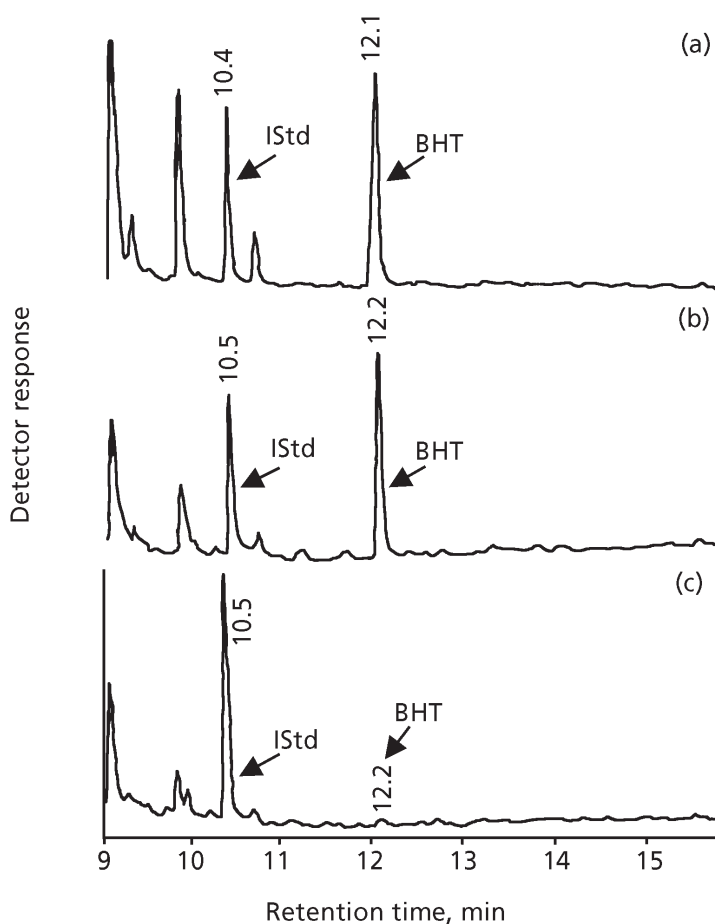
Figure 9.1 Pyrolysis gas chromatograms of: (a) a newly formulated adhesive, (b) a well-performing adhesive and (c) a failed adhesive showing resolution of internal standard and BHT peaks
Reproduced from Franich and co-workers RSC [5]

cured on adherend substrate. **Figure 9.1b** is the chromatogram of a well-performing adhesive, showing high peel strength and ample (1.63 parts of BHT per hundred parts of polychloroprene) residual antioxidant, while **Figure 9.1c** is the chromatogram resulting from the analysis of adhesive that has failed in service. The other peaks in the pyrolysis chromatogram were products from thermal rearrangement of polychloroprene [1-chloro-4(1′-chloroethenyl)cyclohex-1-ene], and from the coumarone-indene resin (a mixture of compounds such as indene, 7-methylindene, and their dimers). The error determined for analysis of test samples in triplicate using the Py-GC method was 10% (18% for samples containing 0.01% BHT), with a limit of detection of 0.01%.

In contrast to the Py-GC method, the extraction method showed only two peaks in the chromatogram, for the internal standard (10.4 min) and the BHT (12.2 min). The resolution and integration facility of the peaks were excellent.

Wang and co-workers [6] used a Py-GC technique for the qualitative analysis of fumaric acid and itaconic acid as low-level monomers polymerised with other major monomers in emulsion styrene maleic anhydride co-polymers. In order for fumaric acid and itaconic acid to be detected through pyrolysis, the acids are derivatised with primary amines such as methylamine and ethylamine to form a cyclic imide. The detection of derivatised fumaric acid and itaconic acid was accomplished by atomic emission detection. The structures of the derivatisation-pyrolysis products were elucidated by MS.

Figure 9.2 shows a Py-GC-MS, pyrogram (total ion current (TIC)) of a 50:50 styrene/maleic acid co-polymer standard.

Wang and co-workers [7] have described pyrolysis with a trapping scheme to determine low levels of acrylic acid and methacrylic acid in emulsion pyrolysis. The advantages of this scheme are flexibility of the choice of trapping solvents, sample accumulation and the option of choosing the separation technique after trapping. The trapped pyrolysate was in this case, separated by GC-MS. Single ion monitoring is necessary to catch the peak as many other low level fragments are also present.

Van Lieshout and co-workers [8] have adopted a high temperature programmable, temperature vapourisation injector for use as a multi-step thermal desorption programmed Py-GC to study polymer mixtures. They analysed a complex mixture of polymers and additives using this method.

The Py-GC-MS technique has also been applied to identification of polar monomers in polyacrylate co-polymers [9], acrylamide monomer in emulsion co-polymers [10], unsaturated acids in acrylic co-polymers [11].
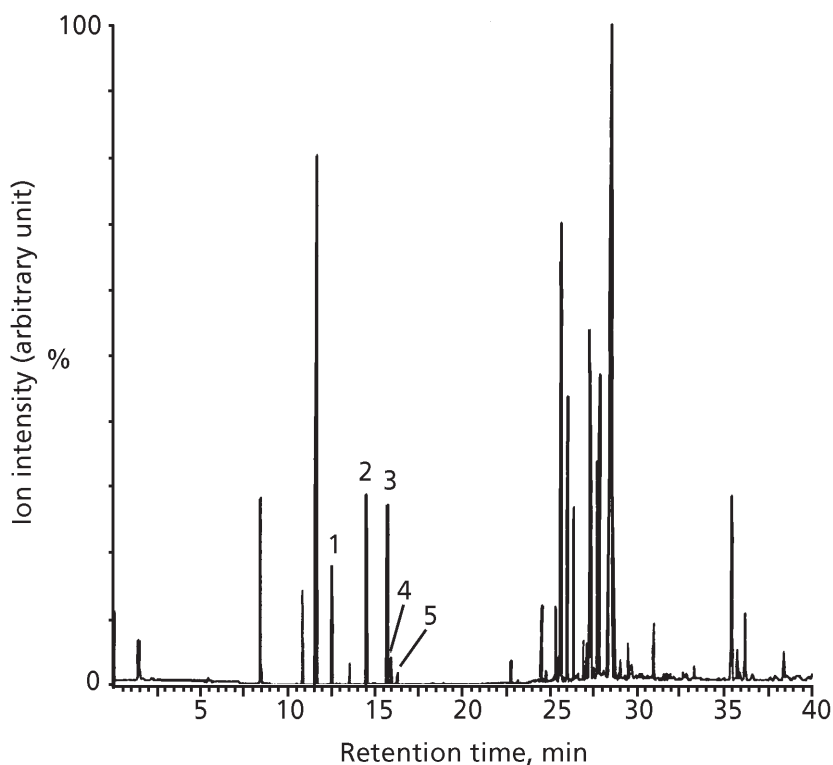
Figure 9.2 Pyrolysis – gas chromatography – mass spectrometry TIC pyrogram of styrene/maleic acid (50:50) copolymer standard
Reproduced from Wang and co-workers ACS [7]

Application of Py-GC-MS has been reviewed by Geissler [12], Meyer-Dulheuer and co-workers [13] and workers at Shindzu-Volkswagen [14, 15]. One of these papers [15] lists additive fragment spectra for 174 additives.

9.2 Evolved Gas Analysis

Evolved gas analysis (EGA) involving coupling of a GC to a MS has been used to identify volatile products formed on heating polystyrene [16-19].

Keen and co-workers [20] used EGA to monitor the evolution of additives from rubber and polymers in order to evaluate the effectiveness of encapsulated BHT antioxidant from polyisoprene. The technique involves the coupling of a thermogravimetry mass spectrometry with oxidative DSC.

Mechanisms of antioxidant action have been described elsewhere [21]. **Schemes 9.1** and 9.**2** give some indication of reactions involved.

In selecting or designing antioxidants for practical situations, problems of loss of antioxidant by both chemical and physical processes may be encountered.

Chemical loss of antioxidant can occur during processing as the antioxidant behaves in the intended way by stabilising the base polymer. Moreover, if the base polymer is to be crosslinked, the antioxidant may become consumed by interfering with the crosslinking reactions. The net result is that the concentration of antioxidant in the base polymer is reduced, and so the service life of the product is shortened.

Physical loss of antioxidant can occur during processing of the polymer if the antioxidant is sufficiently volatile at the fabrication temperature. Another effect is that antioxidants may diffuse to the surface, or those which are soluble in molten polymers may become insoluble at service temperatures and may separate out preferentially on the surface. This

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Initiation:
$$RH + X = R\cdot + Y \ (X = \text{photon or } O_2)$$

Propagation:
$$R\cdot + O_2 = RO_2$$
$$RO_2\text{-} + RH = R\cdot + ROOH$$

Chain branching:
$$ROOH = RO\cdot + \text{-}OH$$
$$ROOH + RH = RO\cdot + R\cdot + H_2O$$
$$2ROOH = RO\cdot + RO_2\cdot + H_2O$$

Further reactions of RO· and ·OH
$$RO\cdot + RH = R\cdot + ROH$$
$$\cdot OH + RH = R\cdot + H_2O$$

Termination
$$\text{two radicals} = \text{non-radical product(s)}$$
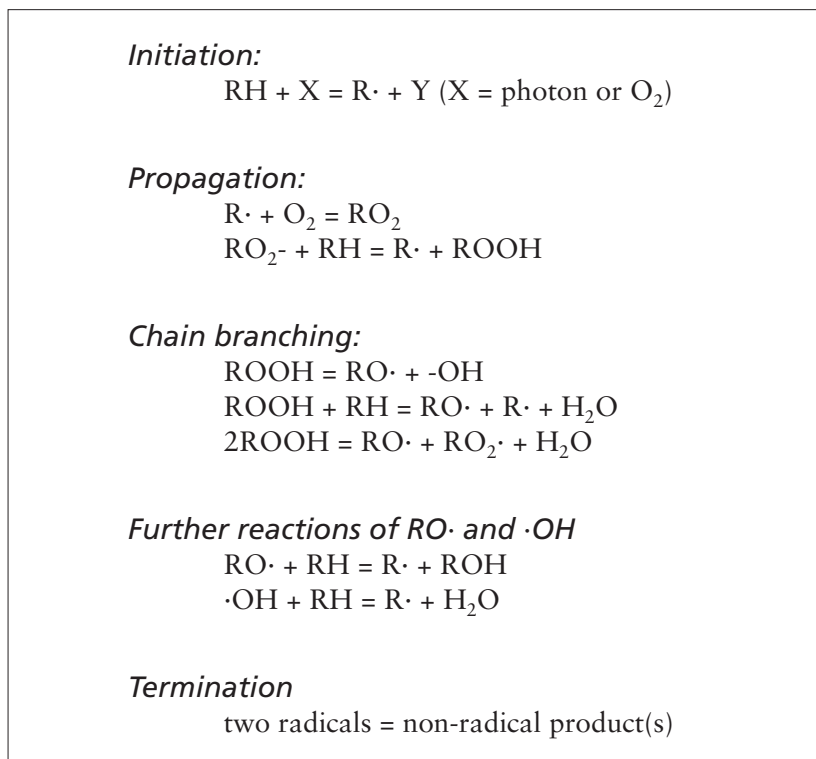
Scheme 9.1 Basic mechanism of oxidation

Example: a 'hydrogen donor' oxidation stabiliser. Such stabilisers act principally by competing with the polymer for the RO_2- radicals involved in the oxidation chain process.

If the antioxidant is represented as AOH, then:

$$RO_2\cdot + AOH = ROOH + AO\cdot \qquad\qquad (1)$$

The $AO\cdot$ radical is generally resonance stabilised, but this is sufficiently reactive to terminate an active $RO_2\cdot$ radical:

$$RO_2\cdot + AO\cdot = ROOAO \qquad\qquad (2)$$

AOH can also react with other species present, for example:

$$R\cdot + AOH = RH + AO\cdot \qquad\qquad (3)$$

$$RO\cdot + AOH = ROH + AO\cdot \qquad\qquad (4)$$

$$ROOH + AOH = RO\cdot + H_2O + AO\cdot \qquad\qquad (5)$$
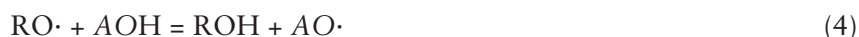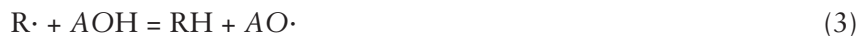
Reactions 3 and 4 also contribute to antioxidant activity. Reaction 5 is undesirable, but is not significant for well designed antioxidants.

Scheme 9.2 An example of antioxidant action

phenomenon is known as 'blooming', and subsequent loss of antioxidant then occurs from the polymer surface by evaporation. Finally, if the polymer is in contact with appropriate solvents during service, these may lead to the loss of soluble antioxidants by leaching.

Keen and co-workers [20] adopted an approach for overcoming these difficulties involving encapsulation of the antioxidant in an alginate matrix.

Thermogravimetric apparatus (Perkin-Elmer TGS-2) coupled to a quadrupole mass spectrometer (Balzers QMG-511) was used for this work. The coupling was via a heated glass-lined steel capillary and a needle valve. The basic approach [22] is illustrated in **Figure 9.3** which indicates the great advantage of this method i.e., that the signals on the weight loss curve can be interpreted in terms of specific products involved.

The mass spectrum of BHT is given in **Figure 9.4**. The most abundant fragment ion is that at *m/z* 205. The TG-MS curves are shown in **Figure 9.5**, which it can be seen that the TG curve is a typical 'S'-shaped evaporation curve. It can be seen that, under these conditions, the rate of loss of BHT reaches a maximum at 100 ± 10 °C. Although 100% weight loss
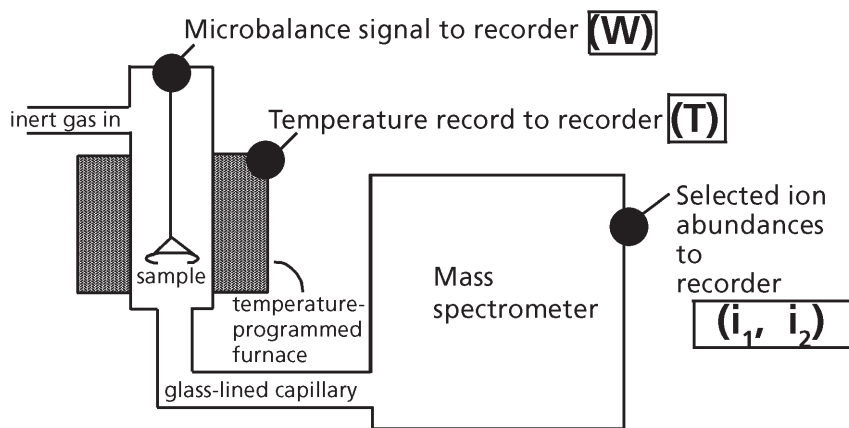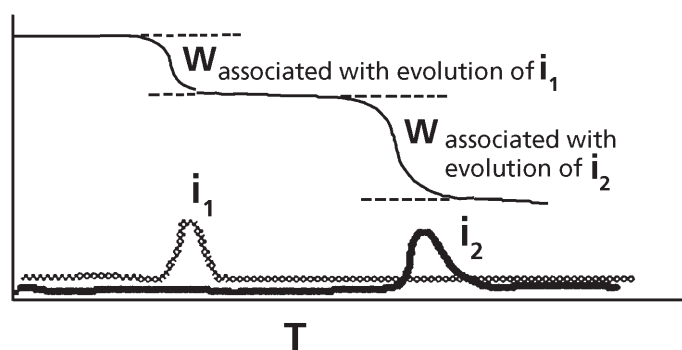
Figure 9.3 The principle of thermogravimetric (TG) mass spectrometry, as used in capsule retention studies: (a) equipment permitting weight loss at particular temperatures to be associated with characteristic ions (b) thermogram with ion abundance traces
Reproduced from Keen and co-workers, Polymer Degradation and Stability [20]

was observed at 110 ± 10 °C, the weight did not become zero due to buoyancy effects in the system [23]. Subsequently, the 205 and 220 peaks were used to characterise the BHT.

Examples of the corrected DSC curves at 112 °C of polyisoprene containing similar concentrations of un-encapsulated and encapsulated BHT are given in **Figure 9.6**. Despite the fact that these samples have been subjected to severe conditions likely to encourage loss of BHT, it can be seen from the curves that when there is encapsulated BHT there is
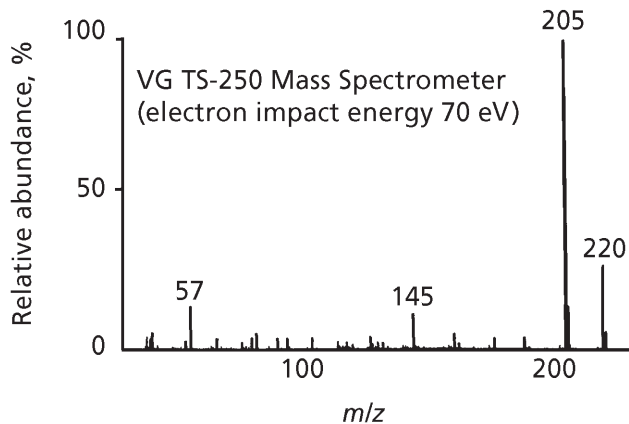
Figure 9.4 The mass spectrum of BHT, shown to illustrate the selection of characteristic ions for continuous ion monitoring. For this material, ions with *m/z* = 205 and 220 are suitable
Reproduced from Keen and co-workers, Polymer Degradation and Stability [20]
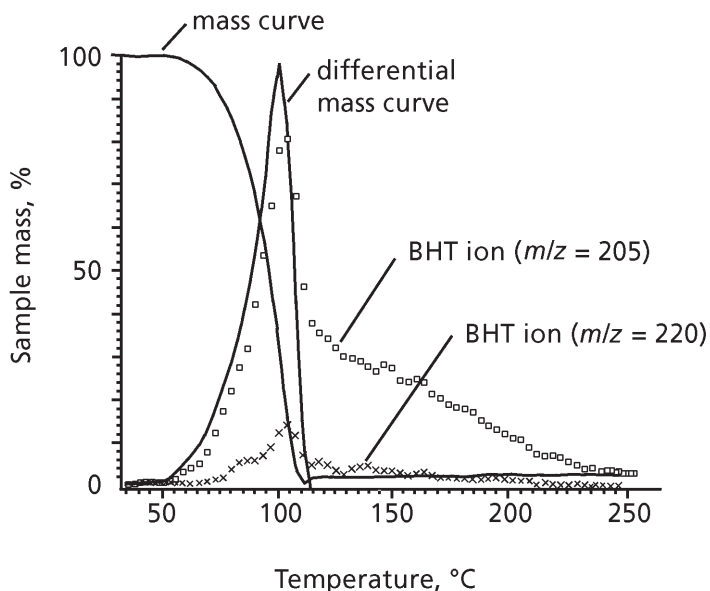
Figure 9.5 TG and DTG curves (continuous lines) for BHT subjected to the temperature programme in inert atmosphere. The points correspond to continuous MS monitoring of BHT fragment ions. These results show that BHT is lost at 100 °C under the conditions being used
Reproduced from Keen and co-workers, Polymer Degradation and Stability [20]
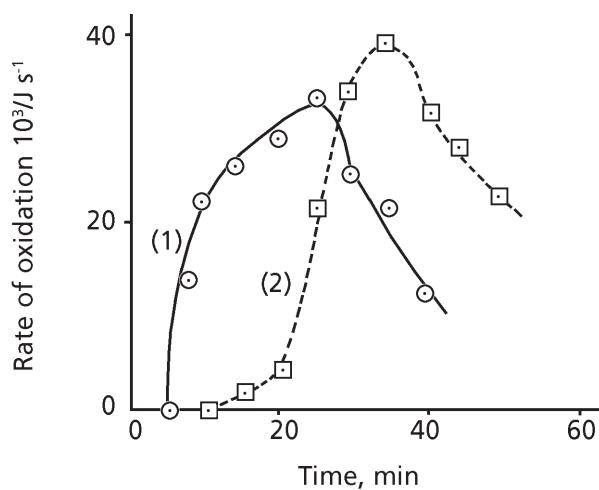
Figure 9.6 Oxidative DSC curves (corrected for evaporation) for (1) 1,4-cis polyisoprene with added BHT, and (2) 1,4-cis polyiosprene incorporating BHT capsules. These results show that encapsulation of the BHT increases the oxygen induction time (see also **Table 9.1**)
Reproduced from Keen and co-workers, Polymer Degradation and Stability [20]

Table 9.1 Oxygen induction times (OIT) from DSC measurements		
Sample	**Number**	**OIT/min**
Control	1	5 ± 1
Control	2	6 ± 1
Capsules	1	17 ± 2
Capsules	2	14 ± 2
Reproduced from F.E. Keen and co-workers, Journal of Polymer Degradation and Stability *[20]*		

an increased delay before the onset of oxidation. The estimated oxidation induction times from this work are given in **Table 9.1**.

Therefore, these results demonstrate that encapsulated BHT is a more effective antioxidant under these severe conditions than free BHT.

Bertin and co-workers [23] used a combined thermogravimetric analysis (TGA)/Fourier transform infrared spectroscopy (FTIR) technique to obtain accurate real time qualitative

and quantitative data for thermal decomposition of polymers. These workers used it to study interactions between an additive and a filler (talc). This technique allowed these workers to bring to the fore a degradation phenomenon of additive by talc, and this phenomenon depended on the structure and chemical composition of talc. Furthermore, this procedure was also shown to be suitable for the analysis of degradation of other additives by talc.

The weight loss of pure Irganox 1010 which was obtained, ranged from 1% at temperatures between 0 and 320 °C thereafter weight mass steadily increased until at 350-450 °C it reached 95%. By mathematical analysis of the weight loss curve, the rate of decomposition is about 44% in the first stage and 55% in the second one.

The FTIR spectra of these two fractions indicate the following composition for the two stages:

> *Stage 1* Isobutylene
> *Stage 2* Phenol, carbon dioxide, aromatic compounds

Figure 9.7 shows results of the TGA experiments for the mixture talc A - Irganox 1010, the curve denoted 1 is for pure talc and curve 2 for the mixture talc - Irganox 1010.
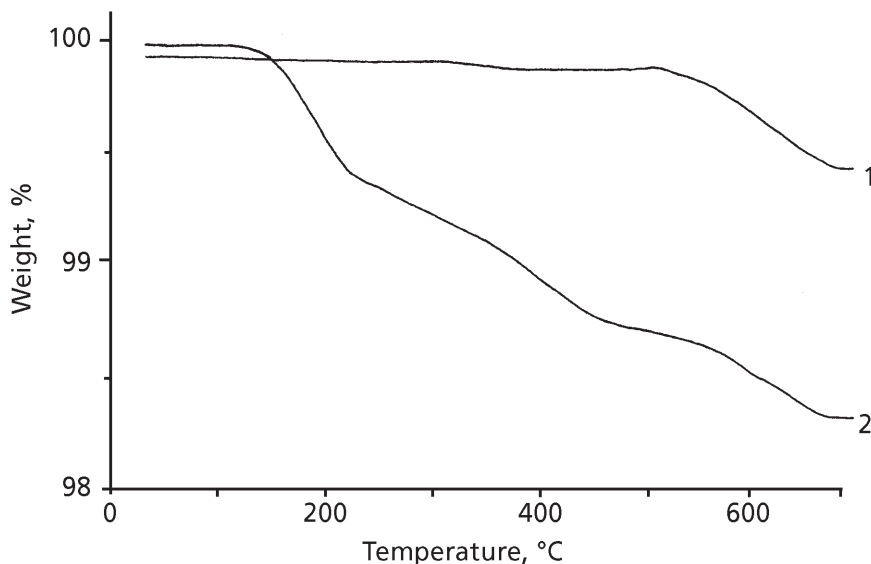
Figure 9.7 Curves of TGA experiments for talc A: 1 – pure talc A; 2 – mixture of talc A/Irganox 1010
Reproduced from Bertin and co-workers, European Polymer Journal [23]

For the pure talc the weight loss was very low, 0.45-1.8% for pure talcs heated to 500-700 °C due to loss of water only. For mixtures of talc and Irganox 1010 three stages of degradation were identified (**Table 9.2**).

The volatile products identified by MS were:

> *Stage 1* Isobutylene, phenol, carbon dioxide
> *Stage 2* Isobutylene, phenol, carbon dioxide
> *Stage 3* Water

Similar results were obtained in studies on talc-Irganox 1010 filled polypropylene.

Techniques such as this can obviously provide much valuable information on additive degradation occurring in polymers at elevated temperatures.

Barnes [24] showed that evolved gas analysis techniques when linked to mass spectrometry are very useful for determining residual volatile additive and/or their degradation products.

Groenewoud and de Jong [25] used combinations of TG, FTIR-MS, the quantitive determination of evolved component with boiling points up to 250 °C and such techniques have been applied to determine volatiles released by heating polyvinylchloride [26] and polyimide/polytetrafluroethylene [27].

Several qualitative and quantitive techniques have been evolved to characterise blowing agents in polymers. These methods include EGA [28-30], differential thermal analysis (DTA) [31, 32] and TGA [31, 32]. The EGA technique limitations are well-described by Jaafer and Sims [28] where rate of gas evolved is dependent on type of additive and

Table 9.2 Results of TGA experiments for talc/additive mixture			
Stage of degradation	Talc A	Talc B	Talc C
(1) Initial temperature (°C)	152	215	210
Weight loss (%)	0.7	0.55	0.40
(2) Initial temperature (°C)	350	500	310
Weight loss (%)	0.7	2	0.5
(3) Initial temperature (°C)	560	572	550
Weight loss (%)	0.4	2	0.85
Reproduced from D. Bertin and co-workers, European Polymer Journal *[23]*			

average particle size of the additive. Also, when the azo concentration is below 5%, the measurement accuracy is poor due to the low volume of gas evolved.

Fortunately, it is often possible to assay thermodynamically a chemical blowing agent in commercial resins without extracting it. In the past, the thermal analysis techniques have been used only for the qualitative analysis of the chemical blowing agents. DTA [31, 32] and DSC [28, 33, 34] have been used to determine the decomposition temperature and whether the process is endothermic or exothermic. TGA has been widely used as a means for assessing the thermal stability and onset of decomposition points of blowing agents. The disadvantage of TGA is that further complications may arise due to the presence of other additives in the formulation. Surprisingly until the work of Prasad and Shanker [35], DSC has not been exploited for the quantitive analysis of the chemical blowing agents in foam formulations. It is known that the decomposition of azo is an exothermic process [34] and that the heat of decomposition can be measured quantitatively by the DSC. Thus, in principle, its concentration can be estimated from the total heats of decomposition.

Prasad and Shanker [35] describe a method for determining the concentration of azo in various carrier resins using the DSC technique and compare the DSC results with those obtained by the EGA methods.

The heats of decomposition studies were carried out on the Perkin-Elmer DSC-4 and DSC-7 differential scanning calorimeters. The thermal scan shown in **Figure 9.8** illustrates the type of result DSC technique yields. **Figure 9.8** shows the thermal decomposition scan for a sample that contains 30% azo dispersed in low-density polyethylene (LDPE). The endothermic peak at 115 °C is due to the melting of LDPE and the exothermic peak at about 222 °C is due to the decomposition of azo.

Normalised DSC curves as a function of azodicarbondimide (azo) blowing agent concentration are shown in **Figure 9.9**, which clearly shows that the magnitude of the exothermal curve (i.e., its area) increases with the azo concentration.

Figure 9.9 demonstrates that the relative heat of decomposition strongly depends on the amount of azo compound present in a given sample. Therefore, in principle, the DSC data can be used to construct a calibration plot of the azo concentration against the relative heat of decomposition, ΔH_d. Once a calibration plot has been established, routine samples run under the same conditions can simply be compared to the standard curves to measure the actual amount of azo compound present in unknown foam concentrate samples.

Table 9.3 shows that there is a reasonably good agreement between the DSC and the results obtained by the EGA technique. Other types of additives in commercial formulation do not seem to influence DSC results. Hence, the DSC technique can be successfully applied to actual, complete foam formulations and can provide direct, quantitative information on the percentage azo content.
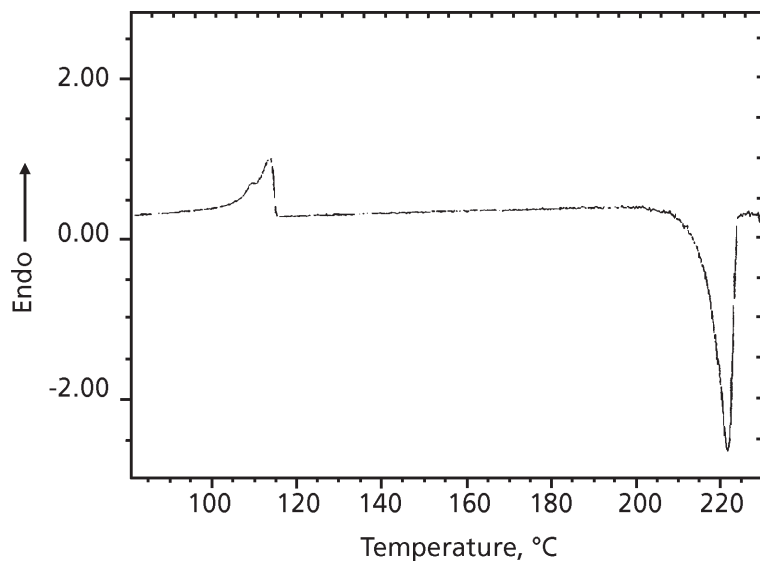
Figure 9.8 Typical DSC heating scans of azo dispersed in LDPE. The endothermic peak is due to the melting of LDPE. The exothermic peak is due to the decomposition of azo
Reproduced from Prasad and Shanker, Cellular Polymers [35]
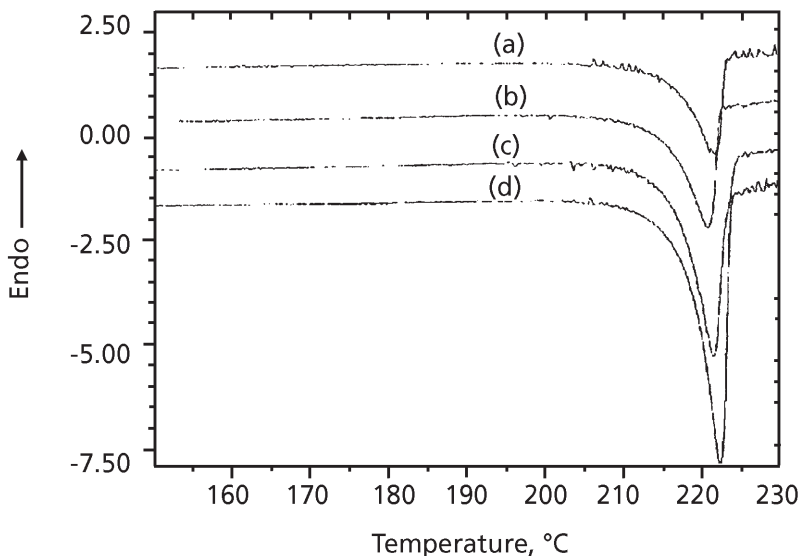
Figure 9.9 Normalised DSC scans showing the change in the exothermic peak area as a function of % azo. (a) sample B (15% azo), (b) sample C (25% azo) (c) sample E (30% azo) and (d) sample F (36% azo)
Reproduced from Prasad and Shanker, Cellular Polymers [35]

Sample	Decomposition temperature, °C		% Azo Target	% Azo DSC	% Azo EGA
	Peak	Range			
A	222.5	200-226	10	9.3 ± 0.5	8.5 (10.3)
B	222.5	198-228	15	14.7 ± 0.8	14.8
C	221.8	202-228	20	20.1 ± 0.6	19.6
D	222	198-227	25	25.1 ± 1	24.8
E	220	197-228	30	30.4 ± 1.3	30.4
F	223	200-228	36	34.1 ± 0.8	38.3 (36.6)
G	222.0	195-227	24	26.0 ± 1.2	25.6 (23.8)
H	220.0	195-225	30	30.3 ± 1.4	30.9 (29.4)
I	194.0	174-208	10	6.2 ± 0.6	6.1 (6.6)
J	199.0	172-208	20	16.8 ± 1.2	16.5 (14.6)
K	174.0	160-180	20	20.0 ± 0.9	20.5
L	220.0	195-225	30	24.3 ± 1.7	24.8
M	222.0	195-225	30	30.9 ± 0.3	29.2 (32.6)
N	166.0	147-173	20	20.4 ± 1.6	-
O	219.0	197-225	17	15.8 ± 1.1	-
P	240.0	195-280	2.5	3.2 ± 0.6	-

Table 9.3 Composition of the DSC and EGA results of control and commercial samples

The numbers in parentheses represent results of duplicate runs by EGA
±: The 95% confidence limit value measured by DSC in 5 replicates
Reproduced from A. Prasad and M. Shanker, Cellular Polymers *[35]*

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10 Determination of Water

Whilst it is not an additive, for completeness, the determination of water in polymers is briefly discussed here.

Jeffs [1] has developed a versatile gas chromatographic unit (GC), described next, for the determination of water and other volatiles in vinyl, acrylic and polyolefin polymer powders.

The instrument is shown diagrammatically in **Figure 10.1**, and consists essentially of a sample tube, forming an external loop, connected to a GC. This loop can be isolated and the sample heated to the required temperature. After an initial heating period the volatile constituents liberated from the sample are 'flushed' on to the chromatographic column by a flow of carrier gas through or over, the sample, and the required components are separated and determined quantitatively. A pneumatic switch valve, located in the chromatographic oven to prevent the condensation of volatile constituents within the valve, and a split heater mounted on a horizontal travel in a plane at right angles to the sample tube are essential parts of the apparatus. The instrument is semi-automatic.

The apparatus shown in **Figure 10.1** is fitted with katharometer and flame-ionisation detectors (FID). Although only one detector is necessary for any one specific method, e.g., a katharometer for the determination of water in polymer powder, it is invaluable to have both available (with separate recorders) to establish the conditions, i.e., in the above case to ensure that no organic components are being eluted at the same time as water, and thus contributing to the peak measurement. **Figure 10.2** shows chromatograms obtained simultaneously from the katharometer and the FID on a partially dried polyvinyl chloride powder.

Maltese and co-workers [2] describe a GC procedure for determining moisture in polypropylene in which water was removed from the polymer *in vacuo* (molten sample), or in a stream of dry nitrogen at a pressure of 400 Pa (granular sample), and was then determined by Karl Fischer titration.
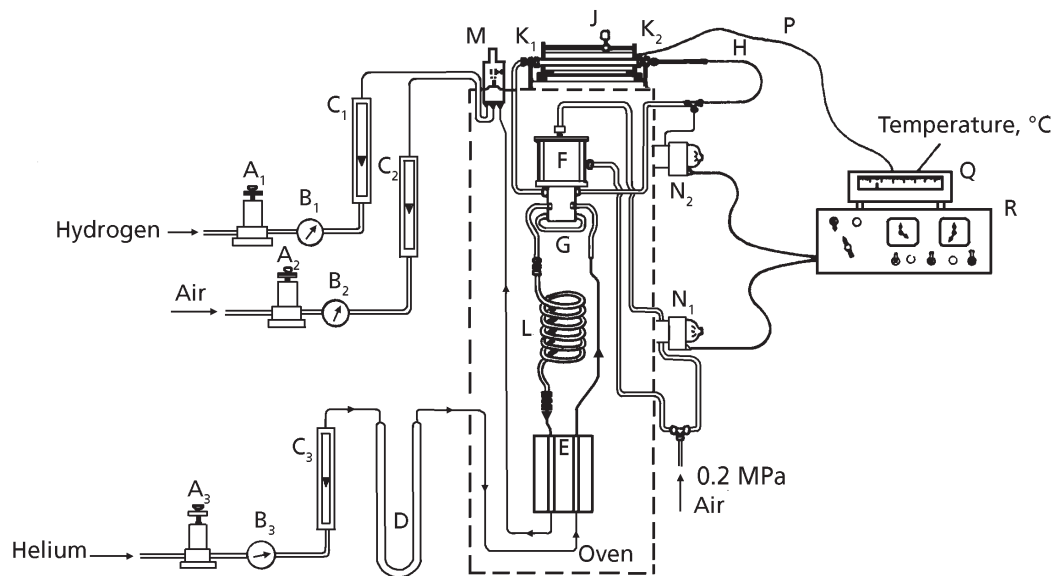
Figure 10.1 Details of general purpose instrument for GC determination of water and volatiles in polymers
Reproduced from Jeffs, RSC [1]

A_1, A_2 and A_3 = Edwards VPC pressure controller
B_1, B_2 and B_3 = Pressure gauges 0 to 0.2 MPa
C_1, C_2 and C_3 = Rotameter-type flow gauges
D = Clear plasticised PVC tubing (1.5 m x 6.4 mm bore), packed with copper sulfate crystals, $CuSO_4.5H_2O$, > 44 mesh
E = Katharometer
F = Pneumatic sample valve
G = Internal loop
H = External loop made in part of 18 gauge stainless-steel capillary tubing
J = Sample split heater
K_1 and K_2 = Straight reducing couplings, captive seal type for 9.5 to 6.4 mm od tubing
L = Chromatographic column
M = Flame ionisation detector
N_1 and N_2 = Electrically actuated 3-port pilot valves
P = Nickel – chromium/nickel – aluminium
Q = Electronic temperature controller, proportional type
R = Sample-valve, time-delay unit, containing three synchronous timers and a semi-conductor, proportional energy controller for the sample heater
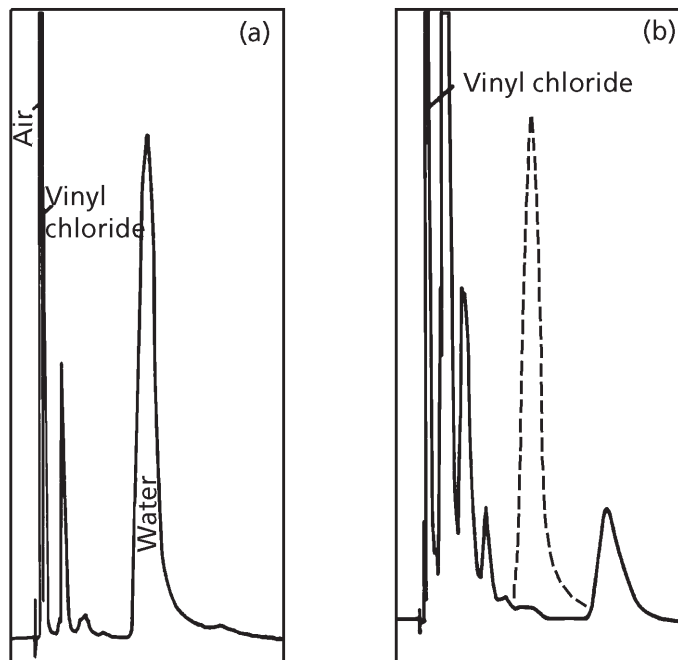
Figure 10.2 Gas chromatogram obtained simultaneously with (a) katharometer and (b) flame ionisation detectors on a partially dried PVC powder. In (b) the dotted line represents the portion of the water peak as transposed from (a)
Reproduced fromFrom Jeffs, RSC [1]

Kallos and Tou [3] have described a hollow drill mass spectrometric interface technique for the determination of water and volatiles in solid epoxy resins.

Other work on the determination of water in polymers includes water in anionic resins [4] and polyethylene terephthalate [5] by Karl Fischer titration, water in polyesters [6] and in polyamides [6, 7], aqueous polymers [7-9] and in polyesters [10].

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11 Determination of Metals

Different techniques have evolved for trace metal analysis of polymers. Generally speaking, the techniques come under two broad headings:

- *Destructive techniques:* these are techniques in which the sample is decomposed by a reagent and then the concentration of the element in the aqueous extract determined by a physical technique such as atomic absorption spectrometry (AAS; Section 11.1.1), graphite furnace atomic absorption spectrometry (GFAAS; Section 11.1.2), cold vapour atomic absorption spectrometry (CVAAS; Section 11.1.4), Zeeman atomic absorption spectrometry (ZAAS; Section 11.1.5), inductively coupled plasma atomic emission spectrometry (ICP-AES; Sections 11.1.6 and 11.1.8), visible spectrometry (Section 11.1.13), or polarographic or anodic scanning voltammetric techniques (Section 11.1.14).

- *Non-destructive techniques:* these include techniques such as X-ray fluorescence (XRF; Section 11.2.1) and neutron activation analysis (NAA; Section 11.2.2), in which the sample is not destroyed during analysis.

Detection limits achievable by various atomic spectroscopy techniques are reviewed in **Table 11.1**.

11.1 Destructive Techniques

11.1.1 Atomic Absorption Spectrometry

11.1.1.1 Theory

Since shortly after its inception in 1955, AAS has been the standard tool employed by analysts for the determination of trace levels of metals. In this technique a fine spray of

Table 11.1 Guide to analytical values for IL spectrometers (IL 157/357/457/451/551/951/Video 11/12/22/S11/S12 Atomic Absorption Spectrophotometers®, IL Plasma-1 00/-200/-300 ICP Emission Spectrometers)

Element	Wavelength (nm)		AAS Lamp current (mA)	Flame AAS		Furnace AAS (IL755 CTF Atomiser)			ICP
	AAS	ICP		Sensitivity[2] (μg/l)	Detection limit (μg/l)	Sensitivity[2]	(μg/l)	Detection limit (ug/l)	Detection limit (ug/l)
Aluminium (Al)[1]	309.3	396.15	8	400	25	4.0	0.04	0.01	10
Antimony (Sb)	217.6	206.83	10	200	40	8.0	0.08	0.08	40
Arsenic (As)	193.7	193.70	8	400	140[3]	12	0.12	0.08	30
Barium (Ba)[1]	553.5	455.40	10	150	12	4.0	0.04	0.04	0.5
Beryllium (Be)[1]	234.9	313.04	8	10	1	1.0	0.01	0.003	0.1
Bismuth (Bi)	223.1	223.06	6	200	30	4.0	0.04	0.01	35
Boron (B)[1]	249.7	249.77	15	9,000	700	-	-	-	3
Cadmium (Cd)	228.8	214.44	3	10	1	0.2	0.002	0.000	1.5
Calcium (Ca)	422.7	393.37	7	50	2	1.0	0.01	0.01	0.2
Calcium[1]	422.7	-	7	1	1	-	-	-	-
Carbon (C)	-	193.09	-	-	-	-	-	-	40
Cerium (Ce)	-	413.77	-	-	-	-	-	-	40
Caesium (Cs)	852.1	455.53	10	150	20	-	-	-	-
Chromium (Cr)	357.9	205.55	6	40	3	4.0	0.04	0.004	3
Cobalt (Co)	240.7	238.89	8	50	4	8.0	0.08	0.008	3
Copper (Cu)	324.7	324.75	5	30	1.8	4.0	0.04	0.005	1

Table 11.1 Continued...

Element	Wavelength (nm)		AAS Lamp current (mA)	Flame AAS		Furnace AAS (IL755 CTF Atomiser)			ICP
	AAS	ICP		Sensitivity[2] (µg/l)	Detection limit (µg/l)	Sensitivity[2] (µg/l)	(µg/l)	Detection limit (ug/l)	Detection limit (ug/l)
Dysprosium (Dy)[1]	421.2	353.17	8	600	60	-	-	-	4
Erbium (Er)[1]	400.8	337.27	8	400	40	50	0.5	0.3	3
Europium (Eu)	-	381.97	-	-	-	-	-	-	2
Gadolinium (Gd)[1]	368.4	342.25	9	13,000	2,000	1,600	16	8	4
Gallium (Ga)	287.4	294.36	5	400	50	5.2	0.05	0.01	15
Germanium (Ge)[1]	265.1	209.43	5	800	50	40	0.4	0.1	20
Gold (Au)	242.8	242.80	5	100	6	5.0	0.05	0.01	10
Hafnium (Hf)[1]	307.3	339.98	10	14,000	2,000	-	-	-	5
Holmium (Ho)[1]	410.4	345.60	12	660	60	90	0.9	0.7	1
Indium (In)	303.9	325.61	5	180	30	11	0.11	0.02	15
Iridium (Ir)[1]	208.8	224.27	15	1,500	500	170	1.7	0.5	8
Iron (Fe)	248.3	238.20	8	40	5	3.0	0.03	0.01	2
Lanthanum (La)[1]	550.1	333.75	10	22,000	2,000	58	0.58	0.5	2
Lead (Pb)	217.0	220.35	5	100	9	4.0	0.04	0.007	25
Lithium (Li)	670.8	670.78	8	16	1	4.0	0.04	0.01	2[5]
Lutetium (Lu)	-	261.54	-	-	-	-	-	-	0.2

Table 11.1 Continued...

Element	Wavelength (nm)		AAS Lamp current (mA)	Flame AAS		Furnace AAS (IL755 CTF Atomiser)			ICP
	AAS	ICP		Sensitivity[2] (µg/l)	Detection limit (µg/l)	Sensitivity[2]	(µg/l)	Detection limit (ug/l)	Detection limit (ug/l)
Magnesium (Mg)	285.2	279.55	3	3	0.3	0.07	0.0007	0.0002	0.1
Manganese (Mn)	279.5	257.61	5	20	1.8	1.0	0.01	0.0005	1
Mercury (Hg)	253.7	253.65	3	2,500	140	40	0.4	0.2	12
Molybdenum (Mo)[1]	313.3	202.03	6	200	25	12	0.12	0.03	4
Neodymium (Nd)[1]	492.5	401.23	10	5,000	700	-	-	-	8
Nickel (Ni)	232.0	221.65	10	60	5	20	0.2	0.05	4
Niobium (Nb)[1]	334.9	309.42	15	12,000	2,000	-	-	-	6
Osmium (Os)[1]	290.9	225.59	15	1,000	90	270	2.7	2	0.6
Palladium (Pd)	247.6	340.46	5	140	20	13	0.13	0.05	13
Phosphorus (P)	213.6	213.62	8	125,000	30,000	4,900	49	20	16
Platinum (Pt)	265.9	214.42	10	1,000	50	80	0.8	0.2	16
Potassium (K)	766.5	766.49	7	10	1	0.4	0.004	0.004	30[5]
Praseodymium (Pr)[1]	495.1	390.84	15	20,000	2,000	-		-	20
Rhenium (Re)	346.1	221.43	15	8,000	800	1,000	10	10	6
Rhodium (Rh)	343.5	343.49	5	200	2	20	0.20	0.1	8

Table 11.1 Continued...

Element	Wavelength (nm)		AAS Lamp current (mA)	Flame AAS		Furnace AAS (IL755 CTF Atomiser)			ICP
	AAS	ICP		Sensitivity[2] (µg/l)	Detection limit (µg/l)	Sensitivity[2]	(µg/l)	Detection limit (ug/l)	Detection limit (ug/l)
Rubidium (Rb)	780.0	-	10	30	2	-	-	-	-
Ruthenium (Ru)	349.9	240.27	10	800	400	-	-	-	8
Samarium (Sm)[1]	429.7	359.26	10	3,000	500	-	-	-	8
Scandium (Sc)[1]	391.2	361.38	10	100	20	-	-	-	0.5
Selenium (Se)	196.0	196.03	12	300	80[3]	8.0	0.08	0.05	30
Silicon (Si)[1]	251.6	251.61	12	800	60	60	0.60	0.6	6
Silver (Ag)	328.1	328.07	3	30	1.2	0.5	0.005	0.001	3
Sodium (Na)	589.0	589.59	8	3	0.4	0.4	0.004	0.004	7
Strontium (Sr)	460.7	407.77	12	80	6	1.8	0.018	0.01	0.2
Tantalum (Ta)[1]	271.5	240.06	15	10,000	800	-	-	-	13
Tellurium (Te)	214.3	214.28	7	200	30	7.0	0.07	0.03	20
Terbium (Tb)[1]	432.7	350.92	8	3,300	1,000	-	-	-	3
Thallium (Tl)	276.8	276.79	8	100	30	4.0	0.04	0.01	27
Thorium (Th)	-	283.73	-	-	-	-	-	-	8
Thulium (Tm)	-	313.13	-	-	-	-	-	-	0.9
Tin (Sn)[1]	235.5	189.99	6	1,200	90	7.0	0.07	0.03	30

Table 11.1 Continued...

Element	Wavelength (nm)		AAS Lamp current (mA)	Flame AAS		Furnace AAS (IL755 CTF Atomiser)			ICP
	AAS	ICP		Sensitivity[2] (µg/l)	Detection limit (µg/l)	Sensitivity[2] (µg/l)	(µg/l)	Detection limit (ug/l)	Detection limit (ug/l)
Titanium (Ti)[1]	364.3	334.94	8	900	60	50	0.50	0.3	1
Tungsten (W)[1]	255.1	207.91	15	5,000	500	-	-	-	14
Uranium (U)[1]	358.5	263.55	15	100,000	7,000	3,100	31	30	70
Vanadium (V)[1]	318.5	309.31	8	600	25	40	0.40	0.1	3
Ytterbium (Yb)	398.8	328.94	5	80	-	1.3	0.01	0.01	1
Yttrium (Y)[1]	410.2	371.03	6	1,800	200	1,300	13	10	0.7
Zinc (Zn)	213.9	213.86	3	8	1.2[3]	0.3	0.003	0.001	2
Zirconium (Zr)[1]	360.1	343.82	10	10,000	2,000	-	-	-	2

[1] *Nitrous oxide - acetylene flame (AAS)*
[2] *Sensitivity is concentration (or mass) yielding 1% absorption (0.0044 absorbance units)*
[3] *With background correction*
[4] *Furnace AAS concentration values are based on cuvette capacity of 100 µl*
[5] *Requires use of red-sensitive photo multiplier tube*
ICP: Inductively coupled plasma
Source: Author's own files

the analyte is passed into a suitable flame, frequently oxygen - acetylene or nitrous oxide - acetylene, which converts the elements to an atomic vapour. Through this vapour is passed radiation at the right wavelength to excite the ground state atoms to the first excited electronic level. The amount of radiation absorbed can then be measured and directly related to the atom concentration: a hollow cathode lamp is used to emit light with the characteristic narrow line spectrum of the analyte element. The detection system consists of a monochromator (to reject other lines produced by the lamp and background flame radiation) and a photomultiplier. Another key feature of the technique involves modulation of the source radiation so that it can be detected against the strong flame and sample emission radiation.

This technique can determine a particular element with little interference from other elements. It does, however, have two major limitations. One of these is that the technique does not have the highest sensitivity. The other is that only one element at a time can be determined. This has reduced the extent to which it is currently used.

11.1.1.2 Instrumentation

Increasingly, due to their superior intrinsic sensitivity, the AAS currently available are capable of implementing the graphite furnace techniques. Available suppliers of this equipment are listed in Appendix 1.

Figures 11.1(a) and (**b**) show the optics of a single-beam flame spectrometer (Perkin Elmer 2280) and a double-beam instrument (Perkin Elmer 2380).

11.1.2 Graphite Furnace Atomic Absorption Spectrometry

11.1.2.1 Theory

The GFAAS technique, first developed in 1961 by L'vov, was an attempt to improve the detection limits achievable. In this technique, instead of being sprayed as a fine mist into the flame, a measured portion of the sample is injected into an electrically heated graphite boat or tube, allowing a larger volume of sample to be handled. Furthermore, by placing the sample on a small platform inside the furnace tube, atomisation is delayed until the surrounding gas within the tube has heated sufficiently to minimise vapour phase interferences, which would otherwise occur in a cooler gas atmosphere.

The sample is heated to a temperature slightly above 100 °C to remove free water, then to a temperature of several hundred degrees centigrade to remove water of fusion and
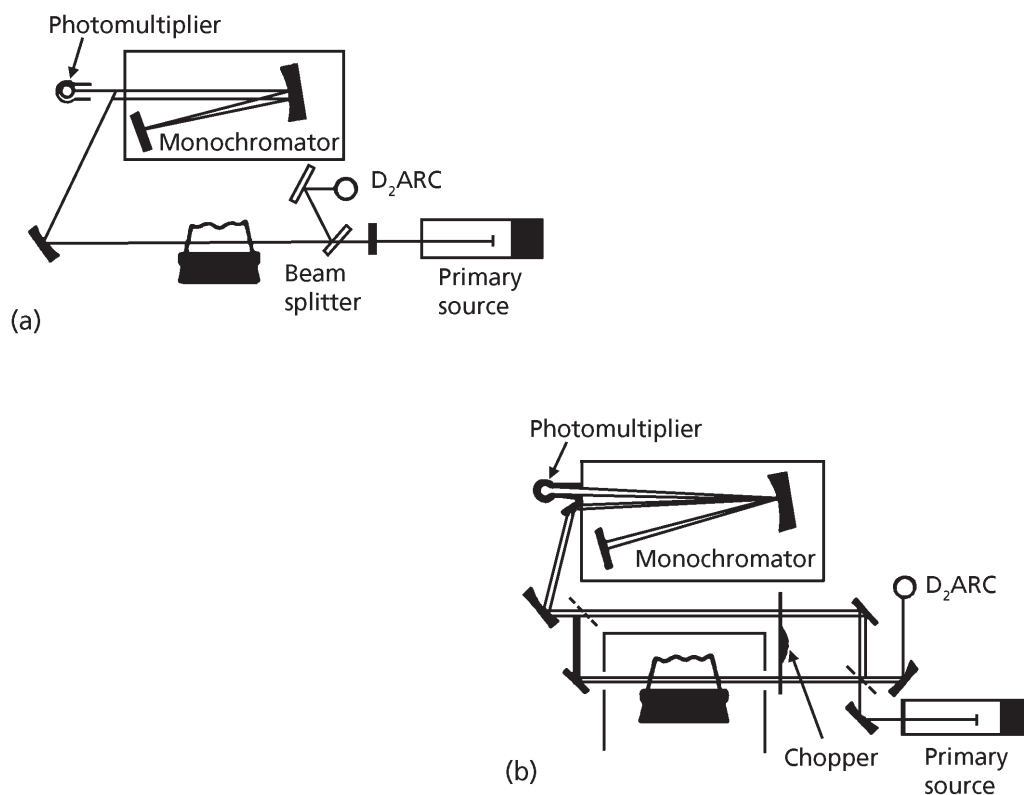
Figure 11.1 (a) Optics Perkin-Elmer Model 2280 single beam atomic absorption spectrometer; (b) Optics Perkin-Elmer Model 2380 double beam atomic absorption spectrometer
Source: Author's own files

other volatiles. Finally, the sample is heated to a temperature near to 1000 °C to atomise it and the signals produced are measured by the instrument.

The problem of background absorption in this technique is solved by using a broad-band source, usually a deuterium arc or a hollow cathode lamp, to measure the background absorption independently and subsequently to subtract it from the combined atomic and background signal produced by the analyte hollow cathode lamp. By interspersing the modulation of the hollow cathode lamp and 'background corrector' sources, the measurements are performed apparently simultaneously.

Graphite furnace techniques are about one order of magnitude more sensitive than direct injection techniques. Thus lead can be determined down to 50 µg/l by direct AAS and down to 5 µg/l using the graphite furnace modification of the technique.

11.1.2.2 Instrumentation

The instrumentation is dealt with in Appendix 1.

11.1.3 Atom Trapping Technique

The sensitivity difference between direct flame and furnace atomisation has been bridged via the general method of atom trapping proposed by Watling [1]. A silica tube is suspended in the air - acetylene flame. This increases the residence time of the atoms within the tube and therefore within the measurement system. Further devices such as water-cooled systems that trap the atom population on cool surfaces and then subsequently release them by temporarily halting the coolant flow are sometimes employed. The application of atom-trapping AAS to the determination of lead and cadmium has been discussed by Hallam and Thompson [2].

11.1.4 Vapour Generation Atomic Absorption Spectrometry

11.1.4.1 Theory

In the past certain elements, e.g., antimony, arsenic, bismuth, germanium, lead, mercury, selenium, tellurium and tin, were difficult to measure by direct AAS [3-8].

A novel technique of atomisation, known as vapour generation via generation of the metal hydride, has been evolved, which has increased the sensitivity and specificity enormously for these elements [5-7]. In these methods the hydride generator is linked to an AAS (flame graphite furnace) or inductively coupled plasma-optical emission spectrometer (ICP-OES) or an inductively coupled plasma mass spectrometer (IPC-MS). Typical detection limits achievable by these techniques range from 3 µg/l (arsenic) to 0.09 µg/l (selenium).

This technique makes use of a property that these elements exhibit, i.e., the formation of covalent, gaseous hydrides that are not stable at high temperatures. Antimony, arsenic, bismuth, selenium, tellurium, and tin (and to a lesser degree germanium and lead) are volatilised by the addition of a reducing agent like sodium tetrahydroborate(III) to an

acidified solution. Mercury is reduced by stannous chloride to the atomic form in a similar manner.

11.1.4.2 Instrumentation

Automating the sodium tetrahydroborate system based on continuous flow principles represents the most reliable approach in the design of commercial instrumentation. Thompson and co-workers [9] described a simple system for multi-element analysis using an ICP spectrometer, based on the sodium tetrahydroborate approach. PS Analytical Ltd developed a reliable and robust commercial analytical hydride generator system, along similar lines, but using different pumping principles from those discussed by Pahlavanpour and co-workers [9].

A further major advantage of this range of instruments is that different chemical procedures can be operated in the instrument with little, if any, modification. Thus, in addition to using sodium tetrahydroborate as a reductant, stannous chloride can be used for the determination of mercury at very low levels.

The main advantage of hydride generation atomic absorption spectrometry for the determination of antimony, arsenic, selenium, and so on, is its superior sensitivity.

More recently, PS Analytical have introduced the PS A 10.003 and the Merlin Plus continuous flow vapour generation atomic absorption and atomic fluorescence spectrometers (AFS) [10-12]. These facilitate the determination of very low concentrations (ppt) of mercury, arsenic, and selenium in solution, enabling amounts down to 10-20 ppm of these elements to be determined in polymer digests.

11.1.5 Zeeman Atomic Absorption Spectrometry

11.1.5.1 Theory

The Zeeman technique, although difficult to establish, has an intrinsic sensitivity perhaps five times greater than that of the graphite furnace technique, e.g., a 1 µg/l detection limit for lead.

The Zeeman effect is exhibited when the intensity of an atomic spectral line, emission or absorption, is reduced when the atoms responsible are subjected to a magnetic field, nearby lines arising instead (**Figure 11.2**). This makes a powerful tool for the correction of background attenuation caused by molecules or particles that do not normally show

(a)

No
magnetic
field

ν_o

π

Normal
Zeeman
pattern

σ^- ν_o σ^+

(b)

No
magnetic
field

ν_o

π
Components

Anomalous
Zeeman
pattern

σ^- ν_o σ^+
Components   Components
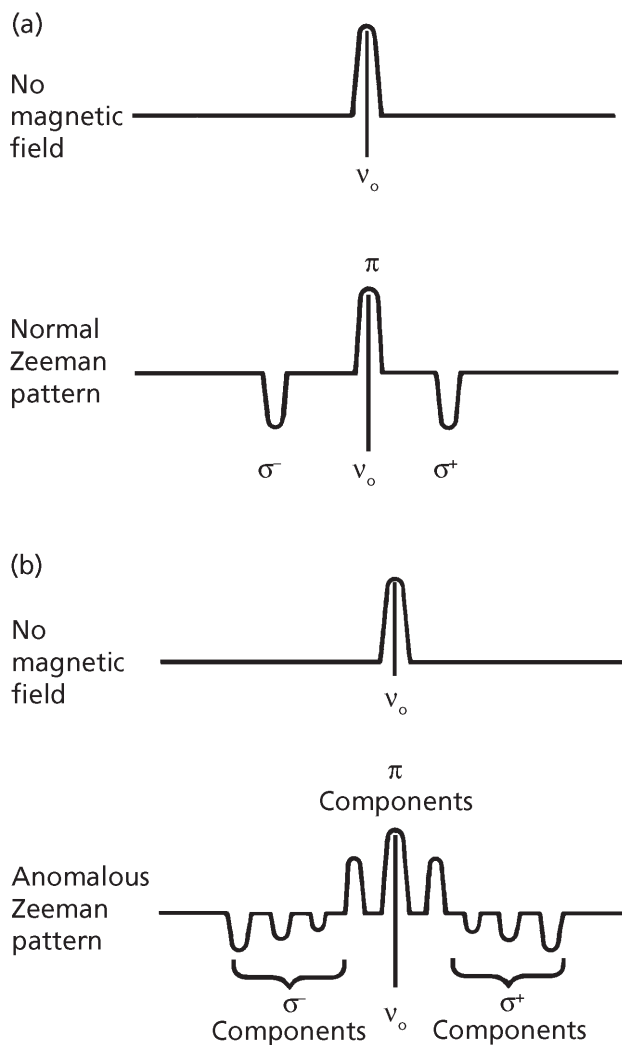
Figure 11.2 Zeeman patterns: (a) normal; (b) anomalous
Source: Author's own files

such an effect. The technique is to subtract from a 'field-off' measurement the average of 'field-on' measurements made just beforehand and just afterwards. The simultaneous, highly resolved graphic display of the analyte and the background signals on a video screen provides a means of reliable monitoring of the determination and simplifies methods development.

Determination of Additives in Polymers and Rubbers

The stabilised temperature platform furnace eliminates chemical interferences to such an extent that in most cases personnel- and cost-intensive sample preparation steps, such as solvent extractions, as well as the time-consuming method of additions are no longer required.

The advantages of Zeeman background correction are:

- Correction over the complete wavelength range.

- Correction for structural background.

- Correction for spectral interferences.

- Correction for high background absorptions.

- Single-element light source with no possibility of misalignment.

11.1.5.2 Instrumentation

The instrumentation for ZAAS is given in **Table 11.2** (see also Appendix 1).

Table 11.2 Available Zeeman atomic absorption spectrometers				
Supplier	**Model**	**Type**	**Hydride and mercury attachment**	**Autosampler**
Perkin Elmer	Zeeman 3030	Integral flame/graphite furnace	-	Yes
	Zeeman 5000	Fully automated integral flame/graphite furnace double-beam operation roll-over protection	Yes	Yes
Varian	SpectrA A30/40	Automated analysis of up to 12 elements; roll-over protection	-	Yes
	SpectrA A300/400	Automated analysis of up to 12 elements; roll-over protection	-	Yes

Figure 11.2 illustrates the operating principle of the Zeeman 5000 system. For Zeeman operation, the source lamps are pulsed at 100 Hz (120 Hz) while the current to the magnet is modulated at 50 Hz (60 Hz). When the field is off, both analyte and background absorptions are measured at the unshifted resonance line. This measurement directly compares with a 'conventional' atom and absorption measurement without background correction.

However, when the field is on, only the background is measured since the σ absorption line profiles are shifted away from the emission line while the static polariser, constructed from synthetic crystalline quartz, rejects the signal from the π components. Background correction is achieved by subtraction of the field-on signal from the field-off signal. With this principle of operation, background absorption of up to 2 absorbance units can be corrected most accurately even when the background shows a fine structure.

In assessing overall performance with a Zeeman effect instrument, the subject of analytical range must also be considered. For most normal class transitions, a component will be completely separated at sufficiently high magnetic fields. Consequently, the analytical curves will generally be similar to those obtained by standard AAS. However, for certain anomalous transitions some overlap may occur. In these cases, curvature will be greater and may be so severe as to produce double-valued analytical curves. **Figure 11.3**, which shows calibration curves for copper, illustrates the reason for this behaviour. The Zeeman pattern
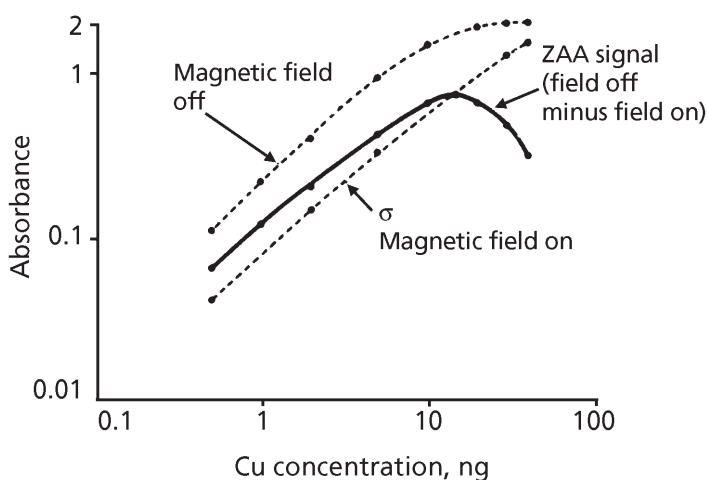
Figure 11.3 Copper calibration curves (324.8 mm) measured with the Zeeman 5000
Source: Author's own files

for copper (324.8 nm) is particularly complex due to the presence of hyperfine structures. The dashed lines represent the separate field-off and field-on absorbance measurements. As sample concentration increases, field-off absorbance begins to saturate as in standard AAS. The σ absorbance measured with the field-on, saturates at higher concentrations because of the greater separation from the emission line. When the increase in σ absorbance exceeds the incremental change in the field-off absorbance, the analytical curve, shown as the solid line, rolls over back towards the concentration axis. This behaviour can be observed with all Zeeman designs regardless of how the magnet is positioned or operated. The existence of roll-over does introduce the possibility of ambiguous results, particularly when peak area is being measured.

11.1.6 Inductively Coupled Plasma Atomic Emission Spectrometry

11.1.6.1 Theory

An inductively coupled plasma is formed by coupling the energy from a radiofrequency (1-3 kW or 27-50 MHz) magnetic field to free electrons in a suitable gas. The magnetic field is produced by a two- or three-turn water-cooled coil and the electrons are accelerated in circular paths around the magnetic field lines that run axially through the coil. The initial electron 'seeding' is produced by a spark discharge but once the electrons reach the ionisation potential of the support gas further ionisation occurs and a stable plasma is formed.

The neutral particles are heated indirectly by collisions with the charged particles upon which the field acts. Macroscopically the process is equivalent to heating a conductor by a radiofrequency field, the resistance to eddy current flow producing Joule heating. The field does not penetrate the conductor uniformly and therefore the largest current flow is at the periphery of the plasma. This is the so-called 'skin' effect and coupled with a suitable gas-flow geometry it produces an annular or doughnut-shaped plasma. Electrically, the coil and plasma form a transformer with the plasma acting as a one-turn coil of finite resistance.

If mass spectrometric (MS) determination of the analyte is to be incorporated, then the source must also be an efficient producer of ions.

Greenfield and co-workers [13] were the first to recognise the analytical potential of the annular ICP.

Wendt and Fassel [14], reported early experiments with a 'tear-drop'-shaped ICP but later described the medium power, 1-3 kW, 18 mm annular plasma now favoured in modern analytical instruments [15].

The current generation of ICP emission spectrometers provides limits of detection in the range 0.1-500 µg/l of metal in solution, a substantial degree of freedom from interferences, and a capability for simultaneous multi-element determination facilitated by a directly proportional response between the signal and the concentration of the analyte over a range of about five orders of magnitude.

The most common method of introducing liquid samples into the ICP is by using pneumatic nebulisation [16], in which the liquid is dispensed into a fine aerosol by the action of a high-velocity gas stream. The fine gas jets and liquid capillaries used in ICP nebulisers may cause inconsistent operation and even blockage when solutions containing high levels of dissolved solids, or particular matter, are used. Such problems have led to the development of new types of nebuliser, the most successful being based on a principle originally described by Babington (US patents). In these, the liquid is pumped from a wide-bore tube and then to the nebulising orifice by a V-shaped groove [17] or by the divergent wall of an over-expanded nozzle [18]. Such devices handle most liquids and even slurries without difficulty.

Two basic approaches are used for introducing samples into the plasma. The first involves indirect vaporisation of the sample in an electrothermal vaporiser, e.g., a carbon rod or tube furnace or heated metal filament as commonly used in AAS [19-21]. The second involves inserting the sample into the base of the ICP on a carbon rod or metal filament support [22, 23].

11.1.6.2 Instrumentation

Further details are given in Appendix 1.

There are two main types of ICP spectrometer systems. The first is the monochromator system for sequential scanning, which consists of a high-speed, high-resolution scanning monochromator viewing one element wavelength at a time.

Typical layouts are shown in **Figure 11.4**. **Figure 11.4(a)** shows a one-channel air path double monochromator design with a pre-monochromator for order sorting and stray light rejection and a main monochromator to provide resolution of up to 0.02 nm. The air path design is capable of measuring wavelengths in the range 190-900 nm. The wide wavelength range enables measurements to be performed in the ultraviolet (UV), visible, and near-infrared regions of the spectrum (allowing determinations of elements from arsenic at 193.70 nm to caesium at 852.1 nm).

A second design (**Figure 11.4(b)**) is a vacuum monochromator design, which gives measurements in the 160-500 nm wavelength range. The exceptionally low wavelength
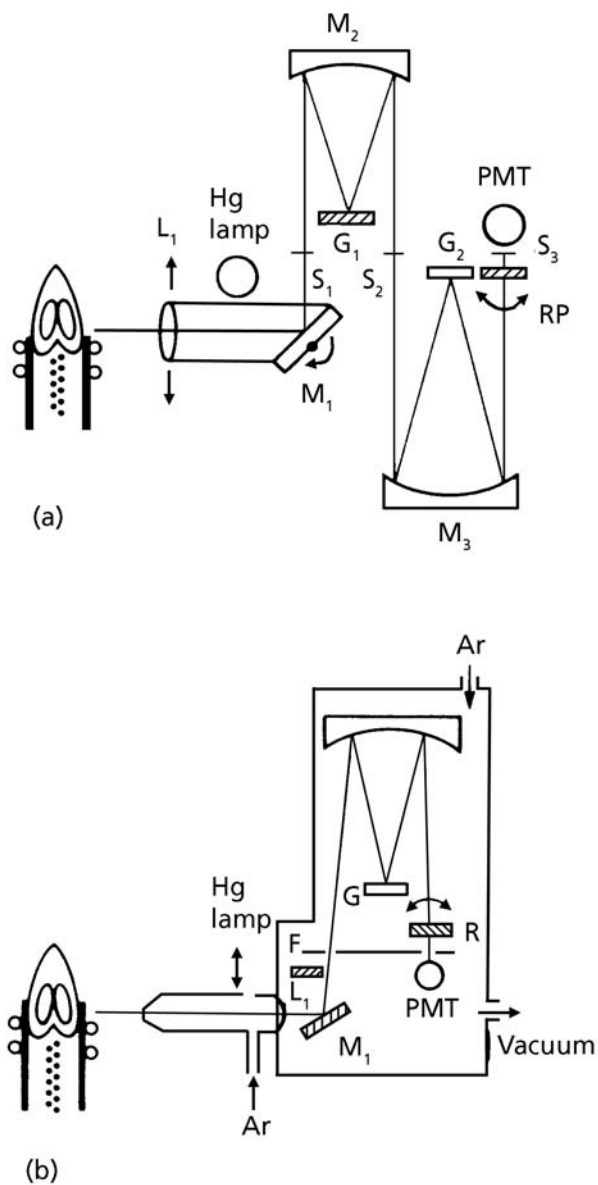
Figure 11.4 A double monochromator consisting of an air-path monochromator with a pre-monochromator for order sorting and stray light rejection to determine elements in the 190-900 nm range; (b) the vacuum UV monochromator – an evacuated and argon-purged monochromator to routinely determine elements in the 160 to 500 μm range
Source: Author's own files

range gives the capability of determining trace levels of non-metals such as bromine at 163.34 nm as well as metals at low UV wavelengths, such as the extremely sensitive aluminium emission line at 167.08 nm. Elements such as boron, phosphorus or sulfur can be routinely determined using interference-free emission lines.

The sequential instrument, equipped with either or both monochromators facilitates the sequential determination of up to 63 elements in turn, at a speed as fast as 18 elements per minute in a single sample. Having completed the analysis of the first sample, usually in less than a minute, it proceeds to the second sample, and so on.

The second main type of system is the polychromator system for simultaneous scanning. The polychromator systems scan many wavelengths simultaneously, i.e., several elements are determined simultaneously at higher speeds than are possible with monochromator systems. It then moves on to the next sample. A typical system is shown in **Figure 11.5**.

It is possible to obtain instruments that are equipped for both sequential and simultaneous scanning, e.g., the Labtam 8410.

11.1.6.3 Applications

Briseno and co-workers [24] quantified inorganic dopants in polypyrrole films by a combination of electrochemistry and ICP-AES.

11.1.7 Hybrid Inductively Coupled Plasma Techniques

11.1.7.1 Chromatography-Inductively Coupled Plasma

Direct introduction of a sample into an ICP produces information only on the total element content. It is now recognised that information on the form of the element present, or trace element speciation, is important in a variety of applications. One way of obtaining quantitative measurement of trace element speciation is to use the separation power of chromatography with the ICP as a detector. Since the majority of interesting trace metal speciation problems concern either nonvolatile or thermally unstable species, high-performance liquid chromatography (HPLC) becomes the separation method of choice. The use of HPLC as the separation technique requires the introduction of a liquid sample into the ICP with the attendant sample introduction problem.
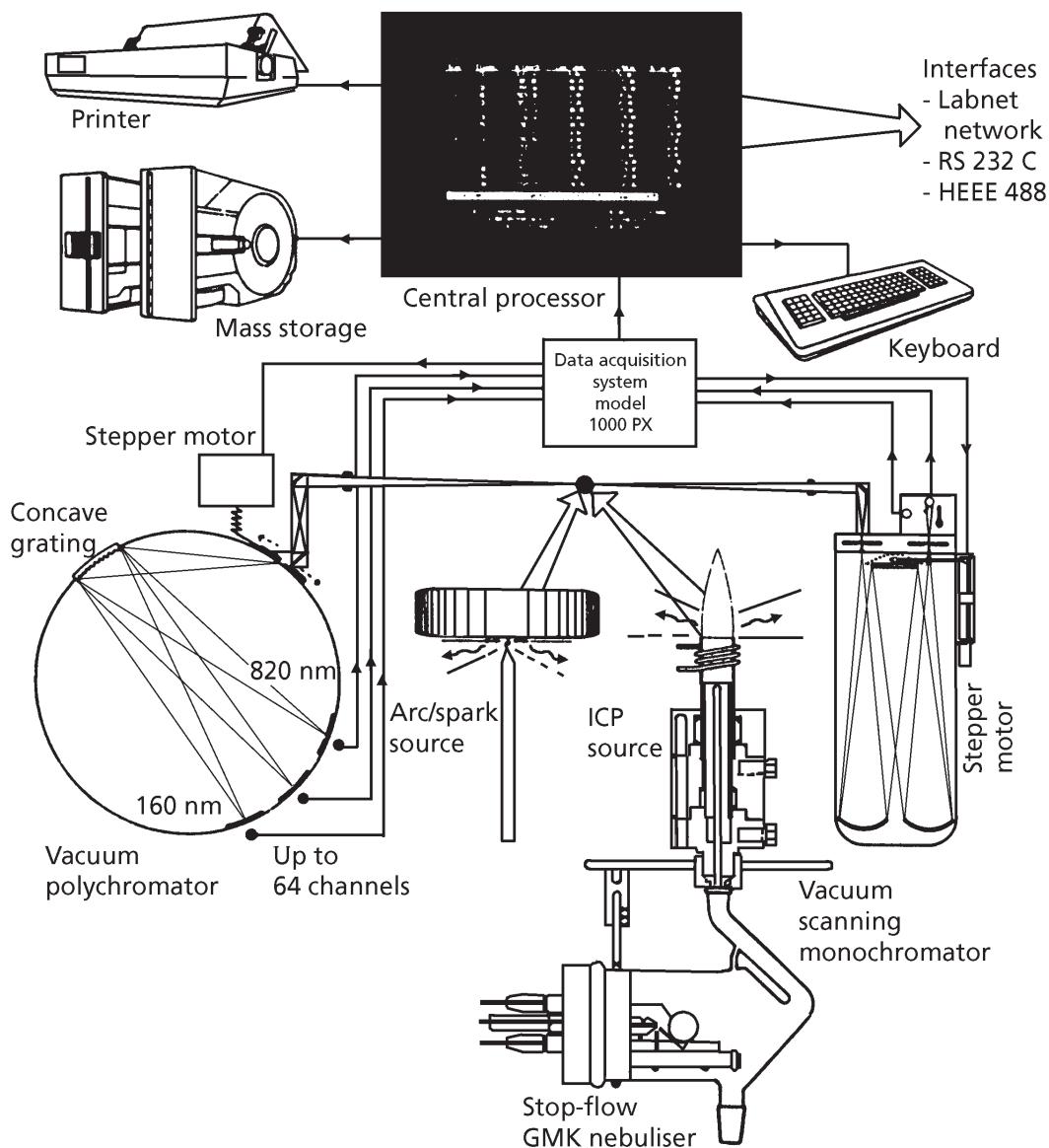
Figure 11.5 Polychromator system for inductively coupled plasma atomic emission
spectrometer
Source: Author's own files

11.1.7.2 Flow Injection with Inductively Coupled Plasma

In conventional ICP-OES, a steady-state signal is obtained when a solution of an element is nebulised into the plasma. In flow injection [25] a carrier stream of solvent is fed continuously through a 1 mm id tube to the nebuliser using a peristaltic pump, and into this stream is injected, by means of a sampling valve, a discrete volume of a solution of the element of interest. When the sample volume injected is suitably small a transient signal is obtained (as opposed to a steady-state signal which is obtained with larger sample volumes) and it is this transient signal that is measured. Very little sample dispersion occurs under these conditions, the procedure is very reproducible, and sample rates of 180 samples per hour are feasible.

11.1.7.3 Inductively Coupled Plasma with Atomic Fluorescence Spectrometry

Atomic fluorescence is the process of radiational activation followed by radiational deactivation, unlike atomic emission, which depends on the collisional excitation of the spectral transition. For this, the ICP is used to produce a population of atoms in the ground state and a light source is required to provide excitation of the spectral transitions. Whereas a multitude of spectral lines from all the accompanying elements are emitted by the atomic emission process, the fluorescence spectrum is relatively simple, being confined principally to the resonance lines of the element used in the excitation source.

The ICP is a highly effective line source with a low background continuum. It is optically thin - it obeys Beer's law - and therefore exhibits little self-absorption. It is also a very good atomiser and the long tail flame issuing from the plasma has such a range of temperatures that conditions favourable to the production of atoms in the ground state for most elements are attainable. It is therefore possible to use two plasmas in one system: a source plasma to supply the radiation to activate the ground state atoms and another to activate the atomiser. This AFS mode of detection is relatively free from spectral interference, the main drawback of ICP-OES. Good results have been obtained using a high power (6 kW) ICP as a source and a low-power plasma as an atomiser.

11.1.8 Inductively Coupled Plasma Optical Emission Spectrometry-Mass Spectrometry

11.1.8.1 Theory

ICP-MS uses the established ICP technique to break the sample into a stream of positively charged ions which are subsequently analysed on the basis of their mass. ICP-MS does not

depend on indirect measurements of the physical properties of the sample. The elemental concentrations are measured directly - individual atoms are counted giving the key attribute of high sensitivity. The technique has the additional benefit of unambiguous spectra and the ability to directly measure different isotopes of the same element.

The sample under investigation is introduced, most typically in solution, into the ICP at atmospheric pressure and a temperature of approximately 5725 °C. The sample components are rapidly dissociated and ionised and the resulting atomic ions are introduced via a carefully designed interface into a high-performance quadrupole MS at high vacuum.

A horizontally mounted ICP torch forms the basis of the ion source. Sample introduction is via a conventional nebuliser optimised for general-purpose solution analysis and suitable for use with both aqueous and organic solvents.

Nebulised samples enter the central channel of the plasma as a finely dispersed mist which is rapidly vaporised; dissociation is virtually complete during passage through the plasma core with most elements fully ionised.

Ions are extracted from the plasma through a water-cooled sampling aperture and a molecular beam is formed in the first vacuum stage and passes into the high-vacuum stage of the quadrupole mass analyser.

In an ICP-MS system, a compact quadrupole mass analyser selects ions on the basis of their mass-to-charge ratio, *m/e*. The quadrupole is a simple compact form of mass analyser which relies on a time-dependent electric field to filter the ions according to their mass-to-charge ratio. Ions are transmitted sequentially in order of their *m/e* with constant resolution, across the entire mass range.

11.1.8.2 Instrumentation

Several manufacturers, including VG Isotopes and Perkin Elmer, supply equipment for ICP-MS (see Appendix 1).

The Perkin Elmer Elan 500 instrument is designed for routine and rapid multi-element quantitative determinations of trace and ultra-trace elements and isotopes. The Elan 500 can determine nearly all of the elements in the periodic table with exceptional sensitivity.

The entire Elan 500 Plasmalok system is designed for simplicity of operation. A typical daily start-up sequence from the standby mode includes turning on the plasma and changing to the operating mode. After a brief warm-up period for the plasma, routine sample analysis can begin.

VG Isotopes Ltd., is another leading manufacturer of ICP-MS equipment. The special features of their VG Plasmaquad PQ2 includes a multi-channel analyser which ensures rapid data acquisition over the whole mass range. The multi-channel analyser facilities include 4096 channels, 300 m facility for spectral analysis, user-definable number of measurements per peak in peak jumping mode, and the ability to monitor data as they are acquired. A multi-channel analyser is imperative for acquiring short-lived signals from accessories such as flow injection, electrothermal vaporisation, laser ablation, and so on, or for fast multi-element survey scans (typically 1 minute).

A variant of the Plasmaquad PQ2 is the Plasmaquad PQ2 plus instrument. This latter instrument has improved detector technology which incorporates a multimode system that can measure higher concentrations of elements without compromising the inherent sensitivity of the instrument. This extended dynamic range system (**Table 11.3**) produces an improvement in the effective linear dynamic range to eight orders of magnitude. Hence, traces at the microgram per litre level can be measured in the same analytical sequence as major constituents.

This technique has been applied to the analysis of aqueous digests of polymers containing up to 2% solids.

Table 11.3 Dynamic ranges of various techniques	
Graphite furnace AAS	0.1 µg/l to 1 mg/l
Plasmaquad PQ2	0.1 µg/l to 10 mg/l
Inductively coupled plasma - atomic absorption spectrometry	10.0 µg/l to 1000 mg/l
Plasmaquad PQ2 plus	0.1 µg/l to 1000 mg/l
Reproduced with permission from TR Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, UK, 2006 [26]*	

11.1.8.3 Applications

Dobney and co-workers [27] have used laser ablation ICP-MS to determine various metals in polyolefins.

11.1.9 Pre-concentration Atomic Absorption Spectrometry Techniques

Detection limits can be improved still further in the case of all three techniques mentioned previously by the use of a pre-concentration technique [28]. One such technique that has

found great favour involves converting the metals to an organic chelate by reaction of a larger volume of sample with a relatively small volume of an organic solvent solution, commonly of diethyldithiocarbamates or ammonium pyrrolidone diethyldithiocarbamate. The chelate dissolves in the organic phase and is then back-extracted into a small volume of aqueous acid for analysis by either of the techniques mentioned previously. If 0.5-1 litre of sample is originally taken and 20 ml of acid extract is finally produced then concentration factors of 25-50 are thereby achieved with consequent lowering of detection limits. Needless to say, this additional step in the analysis considerably increases analysis time and necessitates extremely careful control of experimental conditions.

Microscale solvent extractions involving the extraction of 2.5 ml sample with 0.5 ml of an organic solvent solution of a chelate give detection limits for lead and cadmium by the Zeeman GFAAS method of 0.6 and 0.02 μg/l, respectively. This is equivalent to determining 1.2 ppm cadmium in polymers (assuming the digest of 10 mg of polymer is diluted to 20 ml).

11.1.10 Microprocessors

In recent years the dominating influence on the design and performance of AAS is that of the microprocessor. Even the cheapest instruments are expected to provide autosampling systems for both flame and furnace use and therefore a means of recording the data produced.

11.1.11 Autosamplers

Gilson and PS Analytical supply autosamplers suitable for automation of AAS and ICP. The Gilson autosampler can house up to 300 samples and is capable of operation 24 hours per day. PS Analytical supply 20- and 80-position autosamplers.

For many applications such as hydride analysis, conventional multi-element analysis, and repetitive analysis for major element quantification, conventional autosamplers are not sufficiently sophisticated. The PS Analytical twenty-position autosampler has been specifically developed to fill this void. It is easily interfaced to computer systems via a transistor-transistor logic interface.

11.1.12 Applications: Atomic Absorption Spectrometric Determination of Metals

11.1.12.1 Catalyst Remnants and Other Impurities

Two types of catalysts used in polymer manufacture are metallic compounds such as aluminium alkyls and titanium halides used in low-pressure polyolefin manufacture. As the presence of residual catalysts can have important effects on polymer properties it is important to be able to determine trace elements which reflect the presence of these substances.

11.1.12.2 Elemental Analysis of Polymers

Elements occurring in polymers and copolymers can be divided into three categories:

1. Elements that are a constituent part of the monomers used in polymer manufacture, such as nitrogen in acrylonitrile used in the manufacture of, for example, acrylonitrile-butadiene-styrene terpolymers.

2. Elements that occur in substances deliberately included in polymer formulations, such as, for example, zinc stearate.

3. Elements that occur as adventitious impurities in polymers. For example, during the manufacture of polyethylene (PE) by the low-pressure process, polymerisation catalysts such as titanium halides and organo-aluminium compounds are used, and the final polymer would be expected to, and indeed does, contain traces of aluminium, titanium, and chlorine residues.

The classic destructive techniques are generally based on one of three possible approaches to the analysis: (i) dry ashing of the polymer with or without an ashing aid, followed by acid digestion of the residue, alternatively acid digestion of the polymer without prior ashing, (ii) fusion of the polymer with an inorganic compound to effect solution of the elements, and (iii) bomb or oxygen flask digestion techniques.

Another method for avoiding losses of metals during ashing is the low-temperature controlled decomposition technique using active oxygen. This method has been studied in connection with the determination of trace metals in polyvinyl chloride (PVC), polypropylene (PP), and polyethylene terephthalate [29].

11.1.12.3 Trace Metals in Polymers

Sources of traces of metals in polymers are neutralising chemicals added to the final stages of manufacture to eliminate the effects of acidic catalyst remnants on polymer processing properties (e.g., hygroscopicity due to residual chloride ion). A case in point is high-density polyethylene (HDPE) and PP produced by the aluminium alkyl-titanium halide route which is treated with sodium hydroxide in the final stages of manufacture.

A technique that involves combustion of the polymer under controlled conditions in a platinum crucible, followed by dissolution of the residual ash in a suitable aqueous reagent prior to final analysis by spectrophotometry is of limited value. A quite complicated and lengthy ashing programme is necessary in this technique to avoid losses of alkali metal during ignition: 0-1 hour from start: heat to 200 °C; 1-2 hours from start: hold at 200 °C; 3-5 hours from start: heat to 450 °C; 5-8 hours from start: hold at 450 °C.

After ignition the residue is dissolved in warm nitric acid and made up to a standard volume prior to evaluation by flame photometry or AAS. Alternatively, the polymer is ashed overnight at 500 °C with sulfur and a magnesium salt of a long-chain fatty acid (Magnesium AC dope), and the ash mixed with twice its weight of carbon powder containing 0.1% palladium prior to emission spectrographic evaluation of the sodium/palladium 330.3/276.31 line pair.

The results in **Table 11.4** show clearly that flame photometry following dope ashing at 500 °C gives a quantitative recovery of sodium relative to results obtained by a non-destructive

Table 11.4 The effects of modification of ashing procedure on the flame photometric determination of sodium in polyethylenes					
Sodium by flame photometry, ppm					
Sample	By neutron activation	By emission spectrography	Original (ashed between 650 °C and 800 °C)	Dope ash at 500 °C	Direct ash at 500 °C
1	99, 96, 99	95	60, 76, 55	100	75
2	256, 247, 259	258, 259	160, 178, 271	225	208
3	343, 321, 339	339, 287	250, 312	282	265
4	213, 210, 212	218, 212	140, 196	210	191
5	194, 189, 192	209, 198	80, 158, 229	196	169
6	186, 191, 198	191, 191	96, 173	193	173
Reproduced with permission from T.R. Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, UK, 2006 [26]*					

method of analysis, i.e., NAA. Direct ashing without the magnesium ashing aid at 500 °C causes losses of 10% or more of the sodium while direct ashing at 800 °C causes even greater losses.

Dry ashing in platinum has been found to give reasonably good results in the determination of low concentrations of vanadium in an ethylene-propylene copolymer. A sample of 10 g of polymer is ashed in platinum by charring on a hot plate followed by heating over a Meker burner. Dilute nitric acid is added to the residue and any residue in the crucible dissolved by fusion with potassium persulfate. The vanadium is determined spectrophotometrically by the 3,3′-diaminobenzene method [30]. **Table 11.5** compares the results obtained by this method with those obtained by NAA, which in this case can be considered to be an accurate reference method. Good agreement is obtained between the results of the two methods for samples containing vanadium.

It has been shown in studies [31, 32] using a radioactive copper isotope that, when organic materials containing copper are ashed, losses of up to some 10% of the copper will occur due to retention in the silica crucible; this could not be removed by acid washing. Virtually no retention of copper in the silica crucible occurred, however, when copper was ashed under the same conditions in the absence of added organic matter. This was attributed to reduction of copper to the metal by organic matter present, followed by partial diffusion of the copper metal into the crucible wall. Distinctly higher copper concentrations are obtained for polyolefins by the procedure involving the use of a magnesium oxide ashing aid than are obtained without an ashing aid, or by the use of a molten potassium bisulfate fusion technique to take up the polymer ash.

Table 11.5 Vanadium (ppm)		
Sample	Dry ashing	Neutron activation
A	10.2	9.9 ± 0.2
B	14.0	14.1 ± 0.1
C	14.6	15.6 ± 0.3
D	0.5	0.14 ± 0.01
E	13.0	14.8 ± 0.2
F	0.9	0.27 ± 0.01
G	15.2	18. 8 ± 0.3
H	18.2	17.9 ± 0.3
Reproduced with permission from T.R. Crompton, The Polymer Reference Book, Rapra Technology, Shrewsbury, UK, 2006 [26]		

Henn [33] has reported on a flameless AAS technique with solid sampling for determining trace amounts of, chromium, copper and iron in polymers such as polyacrylamide with a detection limit of approximately 0.01 ppm.

AAS is a useful technique for the determination of traces of metals in polymers. Generally, the polymer is ashed at a maximum temperature of 450 °C: 0.1 hour from start: heat to 200 °C; 1-3 hours from start: hold at 200 °C; 3-5 hours from start: heat to 450 °C; 5-8 hours from start: hold at 450 °C. The ash is digested with warm nitric acid prior to spectrometric analysis. The detection limits for metals in polymers achieved by this procedure are given in **Table 11.6**.

Certain elements (such as arsenic, antimony, mercury, selenium, and tin) can, after producing the soluble digest of the polymer, be converted to gaseous metallic hydrides by reaction of the digest with reagents such as stannous chloride or sodium borohydride:

$$As_2O_3 + 3SnCl_2 + 6HCl = 2AsH_3 + 3H_2O + 3SnCl_4$$

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2$$

$$6H_2 + As_2O_3 = 2AsH_3 + 3H_2$$
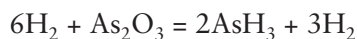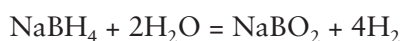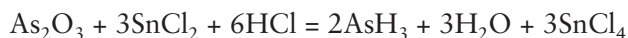
These hydrides can be determined by AAS. To illustrate, let us consider a method developed for the determination of trace amounts of arsenic in acrylic fibres containing antimony oxide fire-retardant additive [34]. The arsenic occurs as an impurity in the antimony oxide additive and, as such, its concentration must be controlled at a low level.

In this method a weighed amount of sample is digested with concentrated nitric and perchloric acids and digested until the sample is completely dissolved. Pentavalent arsenic

Table 11.6 Analytical conditions for metals in polymers					
Element	Wavelength, nm	Band pass	Operating range (in polymer), ppm	Detection limit (in polymer), ppm	Concentration of standard solution, ug/l
Iron	248.3	0.3	5	0.57	500
Manganese	279.5	0.5	1.25	0.03	250
Chromium	357.9	0.5	2.5	0.03	500
Cadmium	228.8	1.0	0.5	0.015	50
Copper	324.7	1.0	1.25	0.045	250
Lead	217.0	1.0	5	0.15	1250
Nickel	232.0	0.15	2.5	0.07	500
Zinc	213.9	1.0	0.5	0.015	125
Reproduced with permission from L. Henn, Elsevier Science [33]					

in the sample is then reduced to trivalent arsenic by the addition of titanium trichloride dissolved in concentrated hydrochloric acid:

$$As^{5+} + 2Ti^{3+} = As^{3+} + 2Ti^{4+}$$
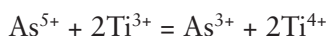
The trivalent arsenic is then separated from antimony by extraction with benzene, leaving antimony in the acid layer. The trivalent arsenic is then extracted with water from the benzene phase. This solution is then extracted with a mixture of hydrochloric acid, potassium iodide, and stannous chloride to convert trivalent arsenic to arsine (AsH_3), which is swept into the AAS. Arsenic is then determined at the 193.7 nm absorption line. Recoveries of between 96 and 104% are obtained by this procedure in the 0.5-1.0 μg arsenic range, with a detection limit of 0.04 ppm.

The results for the arsenic obtained with various acrylic fibre samples containing antimony oxide are given in **Table 11.7**. Antimony, present as the trioxide, has been accurately determined in a concentrated hydrochloric acid extract of PP powder [35].

Table 11.7 Results for the determination of arsenic in acrylic fibres containing antimony oxide				
Sample no.	Supplier	Content of Sb_2O_5*, %	No. of determinations	Arsenic content, ppm
1	A	5.1	4	50 ± 1
2	A	5.1	3	84 ± 4
3	A	4.5	2	94 ± 7
4	A	4.6	5	10.3 ± 0.5
5	A	5.0	5	4.1 ± 0.2
6	B	3.0 (Sb_2O_3)	3	45 ± 0
7	C	-	2	180 ± 11
8	C	-	4	103 ± 6
9	D	2.4 (Sb_2O_3)	2	8.5 ± 0.5
10	E	1.0 (Sb_2O_3)	4	3.2 ± 0.1
11	-	Sb_2O_5 50 mg + acrylic fibre (no Sb) 1 g	2	0.47 ± 0.03
12	-	Sb_2O_5 50 mg + acrylic fibre (no Sb) 1 g	1	0.08
* Even when antimony(III) was present in acrylic fibres (samples 6, 9 and 10), antimony(III) was easily and completely oxidised to antimony(V) by the wet digestion with a mixture of nitric, perchloric and sulfuric acids. Hence, arsenic in acrylic fibres containing antimony(III) oxide could be determined as well as that in acrylic fibre samples containing antimony(V) oxide by this method. Reproduced with permission from T. Korenaga, Royal Society of Chemistry [34]				

11.1.12.4 Pressure Dissolution

Pressure dissolution and digestion bombs have been used to dissolve polymers for which wet digestion is unsuitable. In this technique the sample is placed in a pressure dissolution vessel with a suitable mixture of acids and the combination of temperature and pressure effects dissolution of the sample. This technique is particularly useful for the analysis of volatile elements that may be lost in an open digestion.

11.1.12.5 Microwave Dissolution

More recently, microwave ovens have been used for polymer dissolution. The sample is sealed in a Teflon bottle or a specially designed microwave digestion vessel with a mixture of suitable acids. The high-frequency microwave temperature (~100-250 °C) and increased pressure have a role to play in the success of this technique. An added advantage is the significant reduction in sample dissolution time [36, 37].

11.1.12.6 Equipment for Sample Digestions

• *Dissolution Acid Digestion Bombs*

Inorganic and organic materials can be dissolved rapidly in Parr acid digestion bombs with Teflon liners and using strong mineral acids, usually nitric and/or *aqua regia* and, occasionally, hydrofluoric acid. Perchloric acid must not be used in these bombs due to the risk of explosion.

For nitric acid, 200 °C (80 °C above the atmospheric boiling point) and 0.7 MPa can be achieved in 12 minutes and for hydrochloric acid 153 °C (43 °C above the atmospheric boiling point) and 0.7 MPa can be obtained in 5 minutes. The aggressive digestion action produced at the higher temperatures and pressures generated in these bombs results in remarkably short digestion times, with many materials requiring less than one minute to obtain a complete dissolution, i.e., considerably quicker than open-tube wet ashing or acid digestion procedures. Several manufacturers supply microwave ovens and digestion bombs (Parr Instruments, CEM Corporation, Prolabo).

• *Oxygen Combustion Bombs*

Combustion with oxygen in a sealed Parr bomb has been accepted for many years as a standard method for converting solid combustible samples into soluble forms for chemical analysis. It is a reliable method whose effectiveness stems from its ability to treat samples quickly and conveniently within a closed system without losing any of the sample or its combustion products. Sulfur-containing polymers are converted to soluble forms and

absorbed in a small amount of water placed in the bomb. Halogen-containing polymers are converted to hydrochloric acid or chlorides. Any mineral constituents remain as ash but other elements such as arsenic, boron, mercury, nitrogen and phosphorus, and all of the halogens are recovered with the bomb washings. In recent years the list of applications has been expanded to include metals such as beryllium, cadmium, chromium, copper, iron, lead, manganese, nickel, vanadium and zinc by using a quartz liner to eliminate interference from trace amounts of heavy metals leached from the bomb walls and electrodes [38-40].

Once the sample is in solution in the acid and the digest diluted to a standard volume, the determination of metals is completed by standard procedures such as AAS, ICP-OES, or any of the techniques listed in Sections 11.1.1 to 11.1.8.

11.1.12.7 Techniques for Sample Digestion

Table 11.8 shows results obtained for the digestion in closed vessels of 1 g samples digested (a) in 20 ml of 1:1 nitric acid:water or (b) in 5 ml of concentrated nitric acid and 3 ml of 30% hydrogen peroxide. In the former, at a power input of 450 W, the temperature and pressure rose to 180 °C and 0.7 MPa. At that point, microwave power was reduced to maintain the temperature and pressure at those values for an additional 50 minutes. In the

Table 11.8 Solid sample - microwave digested in 1:1 HNO_3:H_2O			
(a) in 1:1 HNO_3:H_2O		**(b) in 5:3 HNO_3:H_2O_2**	
Element	Amount recovered (%)	Amount recovered (%)	Certified value (%)
			0.0066
As	0.0060, 0.0060	0.0075, 0.0070	0.0012 ± 0.00015
Cd	0.0012, 0.0012	0.0011, 0.0012	2.96 ± 0.28
Cr	3.00, 2.98	3.04, 2.96	0.0109 ± 0.0019
Cu	0.0122, 0.0113	0.0118, 0.0119	0.74 ± 0.02
Mg	0.72, 0.72	0.70, 0.70	0.0785 ± 0.0097
Mn	0.0790, 0.0780	0.0720, 0.0725	0.00458 ± 0.00029
Ni	0.0050, 0.0050	0.0044, 0.0044	0.0714 ± 0.0028
Pb	0.0736, 0.0737	0.0736, 0.0733	(0.00015)
Se	0.0001, 0.0001	0.0001, 0.0001	0.172 ± 0.017
Zn	0.170, 0.168	0.160,0.160	
Reproduced with permission from T.R. Crompton, The Polymer Reference Book*, Rapra Technology, Shrewsbury, UK, 2006 [26]*			

latter case, 1 g samples were open-vessel digested in 1:1 nitric acid:water for 10 minutes at 180 W. After cooling to room temperature, 5 ml of concentrated nitric acid and 3 ml of 30% hydrogen peroxide were added to each. The vessels were then sealed and power was applied for 15 minutes at 180 W followed by 15 minutes at 300 W.

As can be seen, the temperature rose to 115 °C after the first 15 minutes and to 152 °C at 0.3 MPa after the final 15 minutes of heating. With both reagent systems, element recoveries are in good agreement with the values obtained using a hot plate total sample digestion technique, which typically requires 4-6 hours.

Flame and GFAAS techniques have adequate sensitivity for the determination of metals in polymer samples. In this technique up to 1 g of dry sample is digested in a microwave oven for a few minutes with 5 ml of *aqua regia* in a small polytetrafluoroethylene-lined bomb, and then the bomb washings are transferred to a 50 ml volumetric flask prior to analysis by flame AAS. Detection limits (mg/kg) achieved by this technique were: 0.25 (cadmium, zinc); 0.5 (chromium, manganese); 1 (copper, nickel, iron); and 2.5 (lead). Application of this technique gave recoveries ranging between 85% (cadmium) and 101% (lead, nickel, iron) with an overall recovery of 95%.

11.1.13 Visible and UV Spectroscopy

The theory of visible and UV Spectroscopy is discussed in an HMSO publication [41]. The reader is also referred to Appendix 1.

Visible spectrophotometers are commonly used for the estimation of colour in a sample or for the estimation of coloured products produced by reacting a colourless component of the sample with a reagent.

Visible spectrophotometry still finds extensive use in the determination of some anions such as chloride, phosphate and sulfate formed by the decomposition of chlorine, phosphorus and sulfur in polymers. An extensive modern application of visible spectrophotometry is in the determination of organic substances, including non-ionic detergents, in polymer extracts.

Some commercially available instruments, in addition to visible spectrophotometry, can also perform measurements in the UV and near-infrared regions of the spectrum.

11.1.14 Polarography and Voltammetry

A large proportion of trace metal analysis carried out in polymer laboratories is based on the techniques of AAS and ICP-AES. Both of these methods give estimates of the total

concentration of metal present and do not distinguish between different valency states of the same metal. For example, they would not distinguish between arsenic and antimony in the tri- or pentavalent states present in aqueous extracts of polymers. Polarographic techniques can make such distinctions and can be used to determine electroreducible organic materials such as antioxidants and monomers in polymers.

11.1.14.1 Instrumentation

Three basic techniques of polarography are of interest. The basic principles of these are outlined next.

- *Universal: differential pulse (DPN, DPI, DPR)*. In this technique a voltage pulse is superimposed on the voltage ramp during the last 40 ms of controlled drop growth with a standard dropping mercury electrode - the drop surface is then constant. The pulse amplitude can be pre-selected. The current is measured by integration over a 20 ms period immediately before the start of the pulse and again for 20 ms as the pulse nears completion. The difference between the two current integrals (l_2-l_1) is recorded and this gives a peak-shaped curve. If the pulse amplitude is increased, but the peak current value is raised then the peak is broadened at the same time.

- *Classic: direct current (DCT)*. In this direct current method integration is performed over the last 20 ms of controlled drop growth (Tast procedure). During this time, the drop surface is constant in the case of a dropping mercury electrode. The resulting polarogram is step-shaped. Compared with classic DC polarography according to Heyrovsky, i.e., with a free-dropping mercury electrode, the DCT method offers great advantages: considerately shorter analysis times, no disturbance due to current oscillations, simpler evaluation, and larger diffusion-controlled limiting current.

- *Rapid: square-wave (SQW)*. Five square-wave oscillations with a frequency of around 125 Hz are superimposed on the voltage ramp during the last 40 ms of controlled drop growth - with a dropping mercury electrode the drop surface is then constant. The oscillation amplitude can be pre-selected. Measurements are performed in the second, third, and fourth square-wave oscillation; the current is integrated over 2 ms at the end of the first and the end of the second half of each oscillation. The three differences of the six integrals ($l_1 - l_2$, $l_3 - l_4$, $l_5 - l_6$) are averaged arithmetically and recorded as one current value. The resulting polarogram is peak-shaped. Various suppliers of polarography equipment are summarised in Appendix 1.

11.1.14.2 Applications

Polarography is an excellent method for trace and ultra-trace analysis of inorganic and organic substances and compounds. The basic process of electron transfer at an electrode is a fundamental electrochemical principle, and for this very reason polarography can be used over a wide range of applications. After previous enrichment at a ranging mercury drop electrode, metals can be determined using differential pulse-stripping voltammetry. Detection limits are of the order of 0.05 µg/l.

Mal'kova and co-workers [42] described an AC polarographic method for the determination of cadmium, zinc, and barium stearates or laurates in PVC. The samples are prepared for analysis by being ashed in a muffle furnace at 500 °C, a solution of the ash in hydrochloric acid being made molar in lithium chloride and adjusted to a pH of 4.0 ± 0.2. The solution obtained is de-aerated by the passage of argon and the polarogram is recorded. Cadmium, zinc, and barium give sharp peaks at -0.65, -1.01, and -1.90 V, respectively, against the mercury-pool anode.

Tin has been determined in PVC digests by polarography at $E_{1/2}$ -0.52 V in 4 M ammonium chloride [43].

11.1.15 Ion Chromatography

When it is necessary to determine several metals in a polymer then application of ion chromatography has several advantages over AAS, ICP-AES, and polarography. These include specificity, freedom from interference, speed of analysis, and sensitivity. It is, of course, necessary to digest the polymer using suitable reagent systems to produce an aqueous solution of the ions to be determined. Ion chromatography can complement AAS and plasma methods as a back-up technique.

At the heart of the ion chromatography system is an analytical column containing an ion exchange column on which various anions and/or cations are separated before being detected and quantified by various detection techniques such as spectrophotometry, AAS (metals), or conductivity (anions).

Ion chromatography is not restricted to the separate analysis of only anions or only cations. With the proper selection of the eluant and separator columns the technique can be used for the simultaneous analysis of both anions and cations.

The principles of ion chromatography are discussed in an HMSO publication [44].

11.1.15.1 Instrumentation

The reader is referred to Appendix 1 for further details.

Numerous manufacturers now supply instrumentation for ion chromatography. However, Dionex are still the leaders in the field; they have been responsible for many of the innovations introduced into this technique and are continuing to make such developments. Some of the features of the Dionex series 4000i ion chromatograph instruments are discussed next.

• *Chromatography Module*

The following features are found in the Dionex series 40002 ion chromatograph:

- Up to six automated valves made of chemically inert, metal-free material eliminate corrosion and metal contamination.

- Liquid flow path is completely compatible with all HPLC solvents.

- Electronic valve switching, multi-dimensional, coupled chromatography, or multi-mode operation.

- Automated sample clean-up or pre-concentration.

- Environmentally isolates up to four separator columns and two suppressers for optimal results.

- Manual or remote control with Dionex Autoion 300 or Autoion 100 automation accessories.

- Individual column temperature control from ambient to 100 °C (optional).

• *Dionex lon-Pac Columns*

The properties of the Dionex Ion Pac column are:

- Polymer ion exchange columns are packed with pellicular resins for anion or cation exchange applications.

- New 4 µm, polymer ion exchange columns have maximum efficiency and minimum operating pressure for HPLC ion and liquid chromatography applications.

- New ion exclusion columns with bifunctional cation exchange sites offer more selectivity for organic acid separations.

- Neutral polymer resins have high surface area for reversed phase ion pair and ion suppression applications without pH restriction.

- Five and 10 µm silica columns are optimised for ion pair, ion suppression and reversed phase applications.

• *Micromembrane Suppressor*

The micromembrane suppressor makes it possible to detect non-UV-absorbing compounds such as inorganic anions and cations, surfactants, fatty acids, and amines in ion exchange and ion pair chromatography.

Two variants of this exist: the anionic micromembrane suppression (AMMS) and the cationic micromembrane (CMMS) suppressor. The micromembrane suppressor consists of a low dead volume eluent flow path through alternating layers of high-capacity ion exchange screens and ultra-thin ion exchange membranes. Ion exchange sites in each screen provide a site-to-site pathway for eluent ions to transfer to the membrane for maximum chemical suppression.

Dionex anion and cation micromembrane suppressors transform eluent ions into less conducting species without affecting sample ions under analysis. This improves conductivity detection, sensitivity, specificity, and baseline stability. It also dramatically increases the dynamic range of the system for inorganic and organic ion chromatography. The high ion exchange capacity of the micromembrane suppressor permits changes in eluant composition by orders of magnitude making gradient ion chromatography possible.

In addition, because of the increased detection specificity, preparation is dramatically reduced, making it possible to analyse most samples after simple filtering and dilution.

• *Conductivity Detector*

The properties of the conductivity detector are:

- High-sensitivity detection of inorganic anions, amines, surfactants, organic acids, group I and II metals, oxy-metal ions, and metal cyanide complexes (used in combination with micromembrane suppressor).

- Bipolar-pulsed excitation eliminates the non-linear response with concentration found in analogue detectors.

- Microcomputer-controlled temperature compensation minimises the baseline drift with changes in room temperature.

• *UV/Visible Detector*

The properties of the UV/visible detector are:

- High-sensitivity detection of metals, silica, and other UV-absorbing compounds using either post-column reagent addition or direct detection.

- Non-metallic cell design eliminates corrosion problems.

- Filter-based detection with selectable filters from 214 to 800 nm.

- Proprietary dual wavelength detection for ninhydrin-detectable amino acids and 2-pyridyl resorcinol-detectable transition metals.

• *Optional Detectors*

Dionex also offers visible, fluorescence, and pulsed amperometric detectors for use with the series 4000i. Dionex also supply a wide range of alternative instruments, e.g., single channel (2010i) and dual channel (2020i). The latter can be upgraded to an automated system by adding Autoion 100 or Autoion 300 controllers to control two independent ion chromatograph systems. Dionex also supply 2000i series equipped with conductivity pulsed amperometric, UV/visible, visible, and fluorescence detectors.

11.1.15.2 Applications

A typical system for the determination of metals is shown in **Figure 11.6**. A liquid sample is introduced at the top of the ion exchange analytical column (the separator column, **Figure 11.6**). An eluant (containing a complexing agent in the case of metal determination) is pumped through the system. This causes the ionic species (metal ions) to move through the column at rates determined by their affinity for the column resin. The differential migration of the ions allows them to separate into discrete bands.

As these bands move through the column they are delivered, one at a time, into the detection system. For metals, this comprises a post-column reactor that combines a colouring reagent - pyridyl azoresorcinol (PAR) - with the metal bands. The coloured bands can then be detected by the appropriate detection mode. In the case of metal-PAR complex detection, visible wavelength absorbance is used.

The detector is set to measure the complexed metal band at a pre-selected wavelength. The results appear in the form of a chromatogram, essentially a plot of the time the band was retained on the column versus the signal it produces in the detector. Each metal in the sample can be identified and quantified by comparing the chromatogram against that of a standard solution.
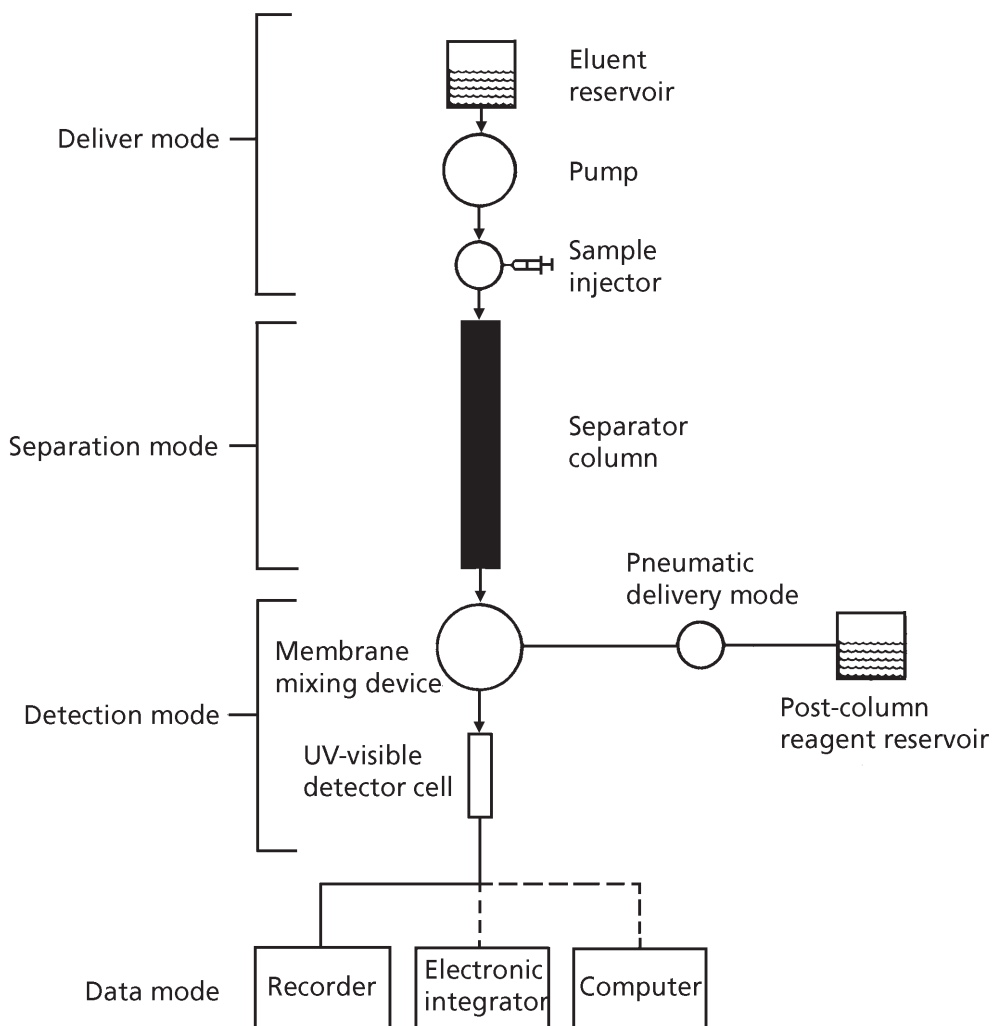
Figure 11.6 Ion chromatography with post-column reaction configuration for metals
Source: Author's own files

Because only the metal ions of interest are detected, ion chromatography is less subject to interferences compared with other methods. Since individual metals and metal compounds form distinct ions with differing retention times, it is possible to analyse several of them in a single run - typically less than 20 minutes.

By selecting the appropriate column for separating the ions of interest in a sample, it is possible to separate and analyse the oxidation state of many metals, and determine group I and II metals, metal complexes, and a complete range of inorganic and organic ions in a sample with excellent speed sensitivity.

Table 11.9 shows a comparison of the detection limits of ion chromatography *versus* flame AAS for ideal, single components in deionised water. On small-volume injections (50 µl), results obtained with ion chromatography compare well with those obtained by AAS. With sample pre-concentration techniques, the detection limits for ion chromatography can surpass those of GFAAS. While a high concentration of acids or bases can limit the applicability of AAS, ion chromatography allows direct injection of up to 10% concentrated acids or bases. This is extremely convenient in the direct analysis of acid-digested samples such as digests of polymers (**Figure 11.7**). Utilising ion exchange pre-

Metal	Conc. (mg/l)	Metal	Conc. (µg/l)
Lead (Pb^{2+})	10	Iron III (Fe^{3+})	1.0
Iron III (Fe^{3+})	1	Copper (Cu^{2+})	0.5
Copper (Cu^{2+})	1	Nickel (Ni^{2+})	2.0
Nickel (Ni^{2+})	1	Zinc (Zn^{2+})	2.0
Zinc (Zn^{2+})	1	Cobalt (CO^{2+})	2.0
Cobalt (CO^{2+})	1		
Cadmium (Cd^{2+})	3		
Manganese (Mn^{2+})	1		
Iron II (Fe^{2+})	1		
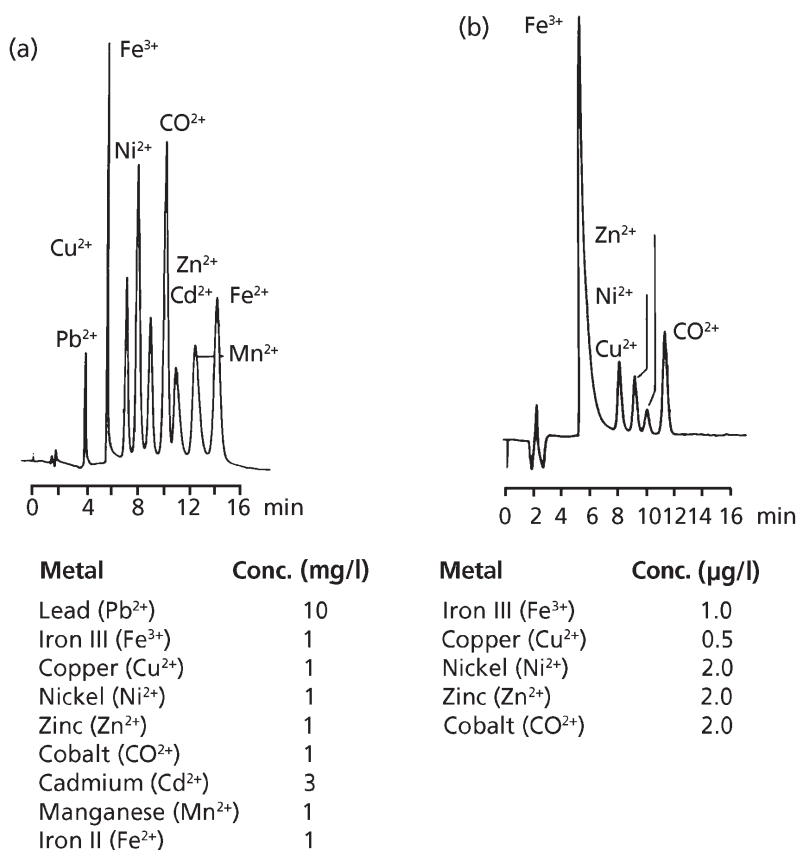
Figure 11.7 Ion chromatography: (a) determination of nine transition metal ions; (b) trace metals in 0.1 M sulfuric acid (8 ml pre-concentrated)
Source: Author's own files

Table 11.9 Metal detection limits by ion chromatography				
Metal species detected by ion chromatography		Detection limit (mg/l)		
		Direct	Preconcentrated	Flame AA
Aluminium	Al^{3+}	56	0.5	20
Barium	Ba^{2+}	100	0.1	20
Cadmium	Cd^{2+}	10	0.1	1
Calcium	Ca^{2+}	50	0.5	3
Caesium	Cs^+	100	0.1	20
Chromium	Cr(III) as CrEDTA	1000	10	3
Chromium	Cr(VI) as CrO_4	50	1	3
Cobalt	Co^{2+}	3	0.03	5
Copper	Cu^{2+}	5	0.05	2
Dysprosium	Dy^{3+}	10	1	60
Erbium	Er^{3+}	100	1	60
Europium	Eu^{3+}	10	1	-
Gadolinium	Gd^{3+}	100	1	2000
Gold	Au(I) as $Au(CN)^-$	100	10	10
Gold	Au(III) as $Au(CN)_4^-$	100	10	10
Holmium	Ho^{3+}	100	1	60
Iron	Fe(II)	10	0.1	5
Iron	Fe(III)	3	0.03	5
Lead	Pb^{2+}	100	1	1
Lithium	Li^+	50	0.5	2
Lutetium	Lu^{3+}	100	1	-
Magnesium	Mg^{2+}	50	0.5	0.2
Molybdenum	as MoO_4	50	1	10
Nickel	Ni^{2+}	25	0.3	8
Palladium	as $PdCl_4^{2-}$	10	1	20
Platinum	as $PtCl_6^{2-}$	10	1	50
Potassium	K^+	50	0.5	1
Rubidium	Rb^+	100	1	2
Samarium	Sm^{3+}	100	1	700
Silver	as $Ag(CN)_2^-$	100	10	2
Sodium	Na^+	50	0.5	0.4

Table 11.9 Continued...				
Metal species detected by ion chromatography		Detection limit (mg/l)		
		Direct	Preconcentrated	Flame AA
Strontium	Sr^{2+}	100	1	6
Terbium	Tb^{3+}	100	1	2000
Thulium	Tm^{3+}	100	1	-
Tin	Sn(II)	100	1	80
Tin	Sn(IV)	100	1	80
Tungsten	as WO_4^{2-}	50	1	100
Uranium	as UO_2^{2+}	5	0.05	7000
Ytterbium	Yb^{3+}	100	1	-
Zinc	Zn^{2+}	10	0.1	0.6
Reproduced with permission from T.R. Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, UK, 2006 [26]*				

concentration methods, extremely low concentrations of metals in polymer digests can be measured with ion chromatography. These detection limits are typically in the sub-picogram range.

11.2 Non-destructive Methods

11.2.1 X-ray Fluorescence Spectrometry

11.2.1.1 Theory

The XRF technique has a true multi-element analysis capability and requires no previous knowledge of the elements present in the sample. As such it is very useful for the examination of many of the types of samples encountered in the plastics laboratory.

This technique is very useful for solid samples especially if the main constituents (matrix) are made of low atomic weight elements and the impurities or constituents sought are of relatively high atomic weight.

Samples are irradiated with high-energy radiation, usually X-rays, to produce secondary X-rays which are characteristic of the individual elements present. The X-ray intensity due to a particular element is proportional to the concentration of that element in the sample. There are two types of instrument in production: those in which the emitted radiation is separated by wavelength using crystals as gratings, i.e., total reflection XRF [wavelength dispersive XRF (WDXRF) or total reflection XRF (TRXRF)], and those in which the radiation is not separated but identified by energy dispersive electronic techniques using solid-state detectors and multi-channel analysers, i.e., energy dispersive XRF (EDXRF).

EDXRF instruments rely on solid-state energy detectors coupled to energy discriminating circuitry to distinguish the radiation by its energy level and measure the amount at each level. Most X-ray detectors now in use are solid-state devices which emit electrons when X-rays are absorbed, the energy of the electrons being proportional to that of the incident X-rays and the quantity proportional to the intensity.

Typically, instruments will determine from a few percent down to parts per million in a solid sample.

WDXRF tend to be most accurate and precise for trace element determinations. EDXRF instruments tend to lose precision for traces of light elements in heavy element matrixes unless longer counting times are used. With short counting times, for example, the coefficient of variation for a minor constituent element determination by an EDXRF instrument should be better than 10%, but for a light trace element it may only be 50%. The advantage of the EDXRF instrument is that it can be made so that almost all the radiation emitted hits the detector. Qualitative analysis is made by comparison with standard samples of known composition using total line energy. This is given by the total detector output of the line, or line peak area depending on the method of read-out used.

Due to the simple spectra and the extensive element range (sodium upwards in the periodic table) that can be covered using an Si(Li) detector and a 50 kV X-ray tube, EDXRF spectrometry is perhaps unparalleled for its qualitative element analysis power.

Qualitative analysis is greatly simplified by the presence of a few peaks that occur in predictable positions and by the use of tabulated element/line markers, which are routinely available from computer-based analysers.

To date, the most successful method of combined background correction and peak deconvolution has been the method of digital filtering and least squares fitting of reference peaks to the unknown spectrum [45]. This method is robust, simple to automate, and is applicable to any sample type.

The major disadvantage of conventional EDXRF has been poor elemental sensitivity, a consequence of high background noise levels resulting mainly from instrumental geometries

and sample matrix effects. TRXRF is a relatively new multi-element technique with the potential to be an impressive analytical tool for trace element determinations for a variety of sample types. The fundamental advantage of TRXRF is its ability to detect elements in the picogram range in comparison to the nanogram levels typically achieved by traditional EDXRF spectrometry.

The principles of TRXRF were first reported by Yoneda and Horiuchi [46] and further developed by Aiginger and Wobrauschek [47] and others [48-51]. In TRXRF the exciting primary X-ray beam impinges upon the specimen prepared as a thin film on an optically flat support of synthetic quartz or Perspex at angles of incidence in the region of 2 to 5 minutes of arc below the critical angle. In practice the primary radiation does not (effectively) enter the surface of the support but skims the surface, irradiating any sample placed on the support surface. The scattered radiation from the sample support is virtually eliminated, thereby drastically reducing the background noise. A further advantage of the TRXRF system, resulting from the geometry used, is that the solid-state energy dispersive detector can be accommodated very close to the sample (0.3 mm), which allows a large solid angle of fluorescent X-ray collection, thus enhancing a signal sensitivity and enabling the analysis to be carried out in air at atmospheric pressure.

11.2.1.2 Instruments

Various suppliers of instruments are listed in Appendix 1.

Instruments include the Philips PW 1404 spectrometer which is a powerful, versatile sequential X-ray spectrometer system developed from the PW 1400 series and incorporating many additional hardware and software features that further extend its performance. All system functions are controlled by powerful microprocessor electronics, which make routine analysis a simple, push-button exercise and provide extensive safeguards against operator error. The microprocessor also contains sufficient analytical software to permit stand-alone emergency operation, plus a range of self-diagnostic service-testing routines. The layout of the Philips PW 1404 instrument is shown in **Figure 11.8**.

An example is quoted of the detection limits achieved by the Seifert EXTRA III (3σ above background, counting time 1000 s) using a molybdenum anode X-ray tube and for excitation with the filtered Bremsstrahlung spectrum from a tungsten X-ray tube. The data shown were obtained from diluted aqueous solutions which can be considered to be virtually free from any matrix effects. A detection limit of 10 pg for a 10 µl sample corresponds to a concentration of 1 µg/l. A linear dynamic range of four orders of magnitude is obtained for most elements. For example, lead at concentrations of 2-20,000 µg/l using cobalt as an internal standard at 2000 µg/l.
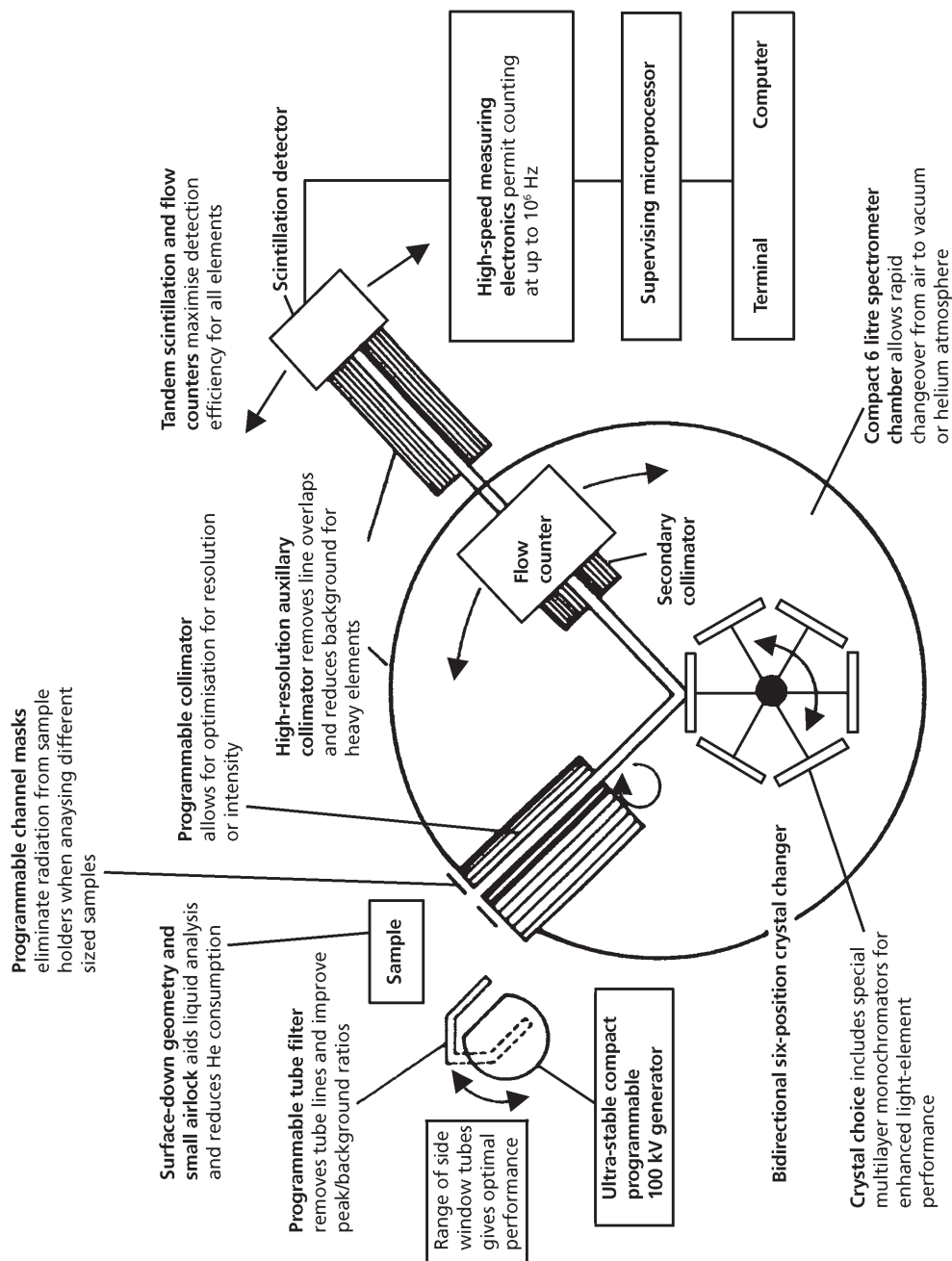
Figure 11.8 Layout of Philips PW 1404 energy-dispersive X-ray fluorescence spectrometer
Source: Author's own files

Table 11.10 Detection limits obtained using a Seifert Extra II x-ray spectrometer	
	Detection limit (pg)
Atomic numbers 18-38 (argon to strontium) and 53-57 (iodine - lanthanum) and 78-83 (osmium to bismuth)	< 5
Chlorine atomic numbers 39-43 (yttrium to technetium), 47-52 (silver to tellurium), 65-71 (terbium to lutetium) and 90-92 (thorium to uranium)	5-10
Phosphorus (15)	10-30
Sulfur (16)	
Ruthenium (44)	
Rhodium (45)	
Palladium (46)	
Neptunium (93)	
Plutonium (94)	
Aluminium (13)	30 - 100
Silicon (14)	
Sodium (11)	> 100
Magnesium (12)	
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Seifert manufactures a TRXRF spectrometer [48-51]. Detection limits obtained for 60 elements by this technique are listed in **Table 11.10**.

11.2.1.3 Applications

This technique can be used to conduct destructive or non-destructive analysis of polymers. XRF spectrometry has been used extensively for the determination of traces of metals and non-metals in polyolefins and other polymers. The technique has also been used in the determination of major metallic constituents in polymers, such as cadmium selenide pigment in polyolefins.

Specimen preparation is simple, involving compressing a disc of the polymer sample for insertion in the instrument, and measurement time is usually less than for other methods, and X-rays interact with elements, i.e., the intensity measurement of a constituent element

is independent of its state of chemical combination. However, the technique does have some drawbacks, and these are evident in the measurement of cadmium and selenium. For example, absorption effects of other elements present, e.g., the carbon and hydrogen of a PE matrix, and excitation of one element by X-rays from another, e.g., cadmium and selenium affect one another. The technique has been applied to the determination of metals in polybutadiene, polyisoprene, and polyester resins [52]. The metals determined were cobalt, copper, iron, nickel and zinc. The samples were ashed and the ash dissolved in nitric acid prior to X-ray analysis. Concentrations as low as 10 ppm can be determined without inter-element interference.

Many investigators have obtained much higher recoveries using various ashing aids such as sulfuric acid [53], elemental sulfur [54, 55], magnesium nitrate [32, 56], and benzene and xylene sulfonic acids [57].

Leyden and co-workers [58] used XRF spectrometry to determine metals in acid digests of polymers. The aqueous solutions were applied to filter paper discs. They found that recoveries of metals by the X-ray technique were 101-110% compared to 89-94% by chemical methods of analysis.

XRF spectrometry has been applied very successfully, industrially, to the routine determination in hot-pressed discs of PE and PP down to a few parts per million of the following elements: aluminium, bromine, calcium, chlorine, magnesium, potassium, sodium, titanium and vanadium.

Ellis and Leyden (private communication) used dithiocarbamate precipitation methods to determine between 2 mg/l and 2 µg/l of five elements. **Table 11.11** shows the excellent agreement generally found between XRF results obtained using a Link XR 200/300 instrument and AAS techniques in the analysis of pre-concentrates. Agreement does not extend over the whole concentration range examined for manganese. Some disparity also occurs in zinc determinations and it is believed that the error is in the graphite furnace results.

Wolska [59] reviewed recent advances in the application of XRF spectroscopy to the determination of antimony, bromine, copper, iron, phosphorus, titanium, and zinc, in various plastics. The ED2000 high-performance EDXRF spectrometer manufactured by Oxford Instruments can determine up to 80 elements qualitatively and up to 50 elements quantitatively between sodium and uranium in various materials, including polymers [60]. X-ray fluorescence methods are available for the determination of tin stabilisers in PVC [61, 62].

Germany's SPECTRO Analytical Instruments GmbH [63] has developed a solution for heavy metal analysis (cadmium, chromium, lead, mercury) in plastics and polymers in

Sample	Mn		Fe		Ni		Cu		Zn	
	XRF	**AA**	**XRF**	**AA**	**XRF**	**AA**	**XRF**	**AA**	**XRF**	**AA**
1	96	104	22	22	4	37	10	4	76	17
2	195	158	75	38	18	23	5	6	44	30
3	114	182	59	56	0.9	2.3	nd	nd	7	nd
4	450	450	46	42	0.9	2.2	1.8	5	61	51
5	2400	2700	15	22	20	25	5	14	1059	342
6	360	335	76	62	12	2.4	6	6	104	92

Table 11.11 The analysis of polymer digests by dibenzyldithiocarbamate precipitation - energy-dispersive x-ray spectrometry and electrothermal atomisation atomic absorption spectrometry

nd: not determined
Reproduced with permission from T.R. Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, UK, 2006 [26]*

response to the new directives restricting the levels of certain additives in end-of-life vehicles (ELV) and waste electrical and electronic equipment.

This EDXRF system SPECTRO XEPOS utilises proprietary polarisation technology to improve the limits of detection for individual elements by a factor of 4-7 compared to conventional EDXRF spectrometers. With XEPOS the average detection limit achieved for cadmium, for example, for measurements on ground polymer samples is 8 ppm, comfortably below the 100 ppm limit set by the ELV directive.

11.2.2 Neutron Activation Analysis

This is a very sensitive technique. Due to the complexity and cost of the technique most laboratories do not have facilities for carrying out NAA. Instead, samples are sent to one of the organisations that possess the facilities.

An advantage of the technique is that knowledge of the elements present is not essential. It can be used to indicate the presence and concentration of entirely unexpected elements, even when present at very low concentrations.

In NAA, the sample in a suitable container, often a pure PE tube, is bombarded with slow neutrons for a fixed time and standards are bombarded in parallel with the samples. Transmutations convert analyte elements into radioactive elements, which are either different elements or isotopes of the original analyte. After removal from the reactor the product is subjected to various counting techniques and various forms of spectrometry to identify the elements present and their concentrations.

11.2.2.1 Applications

This technique is capable of determining a wide range of elements, e.g., chlorine in polyolefins, metals in polymethylmethacrylate [64], total oxygen in polyethylene-ethylacrylate and polyethylene-vinylacetate copolymers [65], and total oxygen in polyolefins.

In many cases the results obtained by NAA can be considered as reference values and these data are of great value when these samples are analysed by alternative methods in the originating laboratory.

To illustrate this, some work is discussed on the determination of parts per million of sodium in polyolefins. It was found that replicate sodium contents determined on the same sample by a flame photometric procedure were frequently widely divergent. NAA offers an independent non-destructive method of checking the sodium contents which does not involve ashing.

In the flame photometric procedure the sample is dry ashed at 650-800 °C in a nickel crucible and the residue dissolved in hot water before determining sodium by evaluating the intensity of the line emission occurring at 589 nm.

NAA (flux of 10^{12} neutrons/cm/s) for sodium was carried out on PE and PP moulded discs containing up to about 550 ppm sodium which had been previously analysed by the flame photometric method. The results obtained in these experiments (**Table 11.12**) show that significantly higher sodium contents are usually obtained by NAA, and this suggests that sodium is being lost during the ashing stage of the flame photometric method. Sodium can also be determined by a further independent method, namely emission spectrographic analysis, which involves ashing the sample at 500 °C in the presence of an ashing aid consisting of sulfur and the magnesium salt of a long-chain fatty acid [55, 57, 66, 67]. **Table 11.13** shows that the results obtained by NAA and emission spectrography agree well with each other. The losses of sodium in the flame photometric ashing procedure were probably caused by the maximum ashing temperature used, exceeding that used in the emission spectrographic method by some 150-300 °C. The results in **Table 11.13** show clearly that flame photometry following dope ashing at 500 °C gives a quantitative recovery of sodium. Direct ashing without an ashing aid at 500 °C causes losses of 10% or more of sodium, while direct ashing at 800 °C causes even greater losses.

Table 11.12 Interlaboratory variation of flame photometric sodium determinations in polyolefins (sodium content, ppm)		
Neutron activation analysis		Flame photometry (moulded discs)
Powder	Moulded discs	
Polyethylene		
207	211, 204	35, 165, 140
177	175, 172	100, 140, 148
266	267, 263	85, 210, 221
203	187, 191	70, 160, 150
Polypropylene		
165	151, 161	50, 130, 133
198	186, 191	95, 173
322	333, 350	95, 138
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Table 11.13 The effects of modification of ashing procedure on the flame photometric determination of sodium (sodium ppm)				
By neutron activation	By emission spectrography	By flame photometry		
		Original (ashed between 650 and 800 °C)	Dope ash at 500 °C	Direct ash at 500 °C
99, 96, 99	95	60, 75, 55	200	75
256, 247, 259	258, 259	160, 178, 271	225	208
343, 321, 339	339, 287	250, 312	282	265
213, 210, 212	218, 212	140, 196	210	191
194, 189, 192	209, 198	80, 158, 229	196	169
186, 191, 198	191, 191	95, 95, 173	193	173
Reproduced with permission from T.R. Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, UK, 2006 [26]*				

Commonly, nowadays, the active catalyst (based on chromium, titanium, or vanadium) used in HDPE manufacture is adsorbed onto a highly porous silica support. Determination of the silica catalyst support content of the final polymer gives an assessment of the economic productivity of the reactor, i.e., its output of PE per gram of catalyst, and also enables the very low concentration of active catalyst metal in the polymer to be calculated.

Battiste and co-workers [68] have described three methods based on NAA, infrared spectroscopy (IR), and ashing for the determination of silica catalyst supports in PE. In the NAA method approximately 2 g of PE powder is irradiated with neutrons obtained with a 500 keV neutron activator according to the following reaction:

$^3H(D,n)\ ^4He$

Silicon is activated by the reaction:

$^{28}Si(n,p)\ ^{28}Al$

and the concentration of silicon is then measured by the 1.78 MeV γ-ray emission from the decay of ^{28}Al. A Conostan 5000 ppm Si standard is used for the instrument calibration. Two 7.5 cm sodium iodide detectors are used to measure the 1.78 MeV γ-rays. Silica can be estimated by direct measurement of the silica absorbance at the 21.27 μm absorbance band of silica. This is the region of the IR spectrum that is relatively free from PE absorbance bands. The absorbance of the 21.27 μm band is calculated for each standard by use of the peak height determined by means of the baseline technique between minima near 28.57 and 17.24 μm.

Results of analysis of PE samples containing residual silica supports of three different catalysts are shown in **Table 11.14**. IR results differ from NAA results by 0-5% while results from ashing and weighing techniques differ from results from NAA by 5-21% and 5-28%, respectively.

Table 11.14 Catalyst productivity (g polymer/g silica) for some test samples				
Sample	IR at 21.27 μm	NAA	Ashing at 650 °C	Weight
1[a]	1893 (3.3)	1923 (4.9)	1923 (4.9)	1923 (4.9)
2[a]	4165 (0)	4165	4545 (9.1)	3571 (14.3)
3[b]	1759 (2.9)	1709	2222 (30.0)	2007 (17.4)
4[c]	1727 (5.4)	1825	2000 (9.6)	2000 (9.6)
5[c]	2207 (3.5)	1288	2778 (21.4)	2941 (28.5)
[a]: Catalyst A - a Davidson Grade 952 silica supported catalyst [b]: Catalyst B - a modified, silica supported catalyst [c]: Cabosil 5-17 Values in brackets are % deviation from NAA Source: Battiste and co-workers, Analytical Chemistry [68]				

11.2.3 Metal Stearate Stabilisers

Various methods for the determination of stearate stabilisers are listed in **Table 11.15**.

Table 11.15 Metal stearate stabilisers in PVC		
		Reference
Metal stearates	Solvent extraction, TLC	[60, 69]
Cd, Pb, Zn stearates	Solvent extraction, paper chromatography	[70]
Cd, Pb, Zn stearates	Solvent extraction or ashing, polarography	[71]
Cd, Pb, Zn stearates	Solvent extraction, IR spectroscopy	[72]
Na, K, Ba stearates	Solvent extraction, chemiluminescence techniques	[73, 74]
Cd, Zn, Ba stearates	Ashing and elemental analysis by polarography	[75]
Na, K, Ba, Cd, Pb stearates	Ashing, flame photometry	[76]
TLC: thin-layer chromatography *Source: Author's own files*		

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12 Non-metallic Elements

Non-metallic elements such as boron, halogens, nitrogen, oxygen, phosphorus and sulfur, can occur in polymers either as major constituents present as impurities or as components of low percentage additions of additives containing the element, e.g., the addition of 0.5% dilauryl thiodipropionate antioxidant to a polymer during processing will introduce parts per million concentrations of sulfur into the final polymer. Another source of non-metallic elements in polymers is catalyst residues and processing chemicals.

It is advisable when commencing the analysis of a polymer to determine the content of various non-metallic and metallic elements first. Initially, these tests could be qualitative, simply to indicate the presence or absence of the element. All that is required here is that the test is of sufficient sensitivity so that elements of importance are not missed. If in these tests an element is found it may then be necessary to determine it quantitatively as discussed next. The analytical methods used to determine elements should be sufficiently sensitive to determine about 10 ppm of an element in the polymer, e.g., should be able to detect in a polymer a substance present at 0.01% and containing down to 10% of the element in question.

This requirement is met for almost all the important elements by the use of optical emission spectroscopy and X-ray fluorescence spectrometry (XRFS). XRFS is applicable to all elements with an atomic number greater than 12. Using these two techniques, all metals and non-metals down to an atomic number of 15 (phosphorus) can be determined in polymers at the required concentrations [1-4].

Nitrogen is determined by micro Kjeldahl digestion techniques. A cautionary note is that, in addition to the polymer itself, the polymer additive system may contain elements other than carbon, hydrogen, and oxygen. The detection of an element such as boron, halogens, nitrogen, phosphorus, silicon, or sulfur, in a polymer is indicative that the element originates in the polymer and not the additive system, if the element is present at relatively high concentrations such as several percent. This is highlighted by the example of a high-density polyethylene (HDPE) which might contain 0.2-1% chlorine originating from polymerisation residues and polyvinyl chloride (PVC) homopolymer which contains more than 50% chlorine.

Commercial instrumentation available for the determination of halogens; sulfur; halogens and sulfur; nitrogen; nitrogen, carbon, and sulfur; carbon, hydrogen, and nitrogen; and total organic carbon (TOC) is the subject of this chapter.

12.1 Instrumentation

12.1.1 Furnace Combustion Methods

The reader is also referred to Appendix 1.

12.1.1.1 Halogens

The Dohrmann DX 20B system is based on combustion of a sample to produce a hydrogen halide, which is then swept into a microcoulometric cell and estimated. It is applicable at total halide concentrations up to 1000 µg/l with a precision of ±2% at the 10 µg/l level. The detection limit is about 0.5 µg/l. Analysis can be performed in five minutes. A sample boat is available for carrying out analysis of solid samples.

Mitsubishi also supplies an automatic total halogen analyser (model TOX-10) which is very similar in operating principles to the Dohrmann system discussed previously, i.e., combustion at 800-900 °C, followed by coulometric estimation of the hydrogen halide produced.

Manatt [5] determined chlorine in polystyrene (PS) by ^{13}C nuclear magnetic resonance spectroscopy.

12.1.1.2 Sulfur

The Mitsubishi trace sulfur analyser models TS-02 and TN-02(S) again involve a microcombustion procedure in which sulfur is oxidised to sulfur dioxide, which is then titrated coulometrically with triiodide ions generated from iodide ions:

$$SO_2 + I_3^- + H_2O \rightarrow SO_3 + 3I + 2H^+$$
$$3I^- \rightarrow I_3 + 3e^-$$
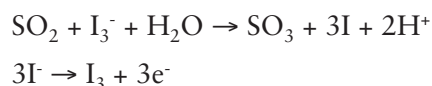
12.1.1.3 Total Sulfur/Total Halogens

The Mitsubishi TSX-10 halogen-sulfur analyser expands the technology of the TOX-10 to include total chlorine and total sulfur measurement. The model TSX-10, which consists of the TOX-10 analyser module and a sulfur detection cell, measures total sulfur and total chlorine in liquid and solid samples over a sensitivity range of milligrams per litre to a percentage. Dohrmann also produces automated sulfur and chlorine analyser (models MCTS 130/120). This instrument is based on combustion microcoulometric technology.

Inductively coupled plasma atomic emission spectrometry has been used to determine sulfur in various polymers [6, 7].

12.1.1.4 Total Bound Nitrogen

Mitsubishi supply two total nitrogen analysers: the model TN-10 and the model TN-05 microprocessor-controlled chemiluminescence total nitrogen analysers. These measure down to micrograms per litre amounts of nitrogen in solid and liquid samples.

The sample is introduced into the combustion tube packing containing oxidative catalyst under oxygen carrier gas. High temperature (800-900 °C) oxidation occurs and all chemically bound nitrogen is converted to nitric oxide (NO): R-N $\rightarrow$ CO_2 + NO. Nitric oxide then passes through a drier to remove water formed during combustion and moves to the chemiluminescence detector, where it is mixed with ozone to form excited nitrogen dioxide (NO_2^*):

$$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow + O_2 + h\nu$$
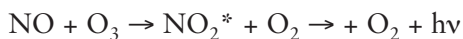
Rapid decay of the NO_2^* produces radiation in the 590-2900 nm range. It is detected and amplified by a photomultiplier tube. The result is calculated from the signal produced and is given in milligrams per litre or as a percentage.

Dohrmann also supplies an automated nitrogen analyser with video display and data processing (model DN-1000) based on similar principles which is applicable to the determination of nitrogen in solid and liquid samples down to 0.1 mg/l.

The Dohrmann DN-1000 can be converted to the determination of sulfur and chlorine by adding the MCTS 130/120 microcoulometer detector modules. The control module, furnace module, and all the automated sample inlet modules are common to both detectors. The system automatically recognises what detector and sample inlet is present and sets the correct operating parameters for fast, simple conversion between nitrogen, sulfur, and chlorine detection.

Equipment for automated Kjeldahl determinations of organic nitrogen in water and solid samples is supplied by Tecator Ltd. Its Kjeltec system 1 streamlines the Kjeldahl procedure resulting in higher speed and accuracy compared to classic Kjeldahl measurements.

12.1.1.5 Nitrogen, Carbon and Sulfur

The NA 1500 analyser supplied by Carlo Erba is capable of determining these elements in amounts down to 10 mg/l in 3-9 minutes with a reproducibility of ±0.1%. A 196-position autosampler is available.

'Flash combustion' of the sample in the reactor is a key feature of the NA 1500. This results when the sample is dropped into the combustion reactor which has been enriched with pure oxygen. The normal temperature in the combustion tube is 1020 °C and reaches 1700-1800 °C during the flash combustion.

In the chromatographic column the combustion gases are separated so that they can be detected in sequence by the thermal conductivity detector. The output signal is proportional to the concentration of the elements. A data processor plots the chromatogram, automatically integrates the peak areas, and gives retention times, percentage areas, baseline drift, and attenuation for each run. It also computes blank values, constant factors, and relative average elemental contents.

12.1.1.6 Carbon, Hydrogen and Nitrogen

Perkin Elmer supplies an analyser (model 2400 CHN or PE 2400 series II CHNS/O analysers) suitable for determining these elements in polymers. In this instrument the sample is first oxidised in a pure oxygen environment. The resulting combustion gases are then controlled to exact conditions of pressure, temperature and volume. Finally the product gases are separated under steady-state conditions and swept by helium or argon into a gas chromatograph for analysis of the components. The equipment is supplied with a 60-position autosampler and microprocessor controller covering all system functions, calculation of results, and on-board diagnostics. Analysis time is 6 minutes for the CHN mode, 8 minutes for the CHNS mode, and 4 minutes for the oxygen mode [8-13].

Table 12.1 gives theoretical *versus* determined carbon, nitrogen and hydrogen values obtained by this instrument for three polymers.

Table 12.1 Automated determination of carbon, hydrogen and nitrogen in polymers						
Compound	Theory			Found, %		
	C	H	N	C	H	N
Nylon 6	63.68	9.80	12.38	63.58	9.85	12.35
				63.55	9.91	12.32
Styrene/25% acrylonitrile	86.10	7.24	6.60	86.00	7.28	6.62
				86.05	7.20	6.65
Teflon	24.00	-	-	23.97	-	-
				24.10	-	-
Reproduced with kind permission of Perkin Elmer Ltd, Beaconsfield, UK						

12.1.1.7 Total Organic Carbon

Dohrmann supplies a TOC analyser. Persulfate reagent is continuously pumped at a low flow rate through the injection port (and the valve of the autosampler) and then into the ultraviolet reactor.

A sample is acidified, sparged, and injected directly into the reagent stream. The mixture flows through the reactor where organics are oxidised by the photon-activated reagent. The light source envelope is in direct contact with the flowing liquid. Oxidation proceeds rapidly, the resultant carbon dioxide is stripped from the reactor liquid and carried to the carbon dioxide-specific non-dispersive infrared (IR) detector.

The Shimadzu TOC-500 TOC analyser is a fully automated system capable of determining between 1 and 3000 µg/l TOC.

OIC Analytical Instruments produce the model 700 TOC analyser. This is applicable to solids. Persulfate oxidation at 90-100 °C followed by non-dispersive IR spectroscopy is the principle of this instrument.

Total oxygen in polyolefin-acrylate copolymers have been determined by neutron activation analysis (NAA) [14].

12.1.1.8 Silicon

Commonly, nowadays, the active catalyst (based on chromium, titanium or vanadium) used in HDPE manufacture is adsorbed on to a highly porous silica support. Determination

of the silica catalyst support content of the final polymer gives an assessment of the economic productivity of the reactor, i.e., its output of polyethylene (PE) per g of catalyst and also enables the very low concentration of active catalyst metal in the polymer to be calculated.

Battiste and co-workers [15] have described three methods based on NAA, IR spectroscopy and ashing for the determination of silica catalyst supports in PE.

In the NAA technique approximately 2 grams of PE powder are irradiated with neutrons obtained with a 500 keV neutron activator according to the following reaction: ^{3}H(D,n)^{4}He. Silicon is activated by the reaction ^{28}Si(N,p) ^{28}Al, and the concentration of silicon is then measured by counting the 1.78 MeV gamma ray emission from the decay of ^{38}Al. A Conostan 5000 ppm Si standard is used for instrument calibration. Two 7.5 cm sodium iodide detectors are used to measure the 1.78 MeV gamma rays.

Silica can be estimated by direct measurement of the silica absorbance i.e., at the 21.27 µm absorbance band of silica. This is in the region of the IR spectrum which is relatively free of PE absorbance bands. The absorbance value of the 21.27 µm band is calculated for each standard by use of the peak height determined by means of the base line technique between minima near 28.57 and 17.24 µm.

Results for analysis of PE samples containing residual silica support of three different catalysts, by IR, NAA, ashing and weight are shown in **Table 11.14**. IR results differ from NAA results by 0-5% while ashing and weighing technique results differ from NAA results by 5-21% and 5-28%, respectively.

12.1.2 Oxygen Flask Combustion Methods

12.1.2.1 Total Halogens

Oxygen flask combustion methods have been used to determine traces of chlorine in PVC [15] and in polyolefins and chlorobutyl rubber [16].

Traces of chlorine have been determined in polyolefins [17] at levels between 0 and 500 ppm. The Schoniger oxygen flask combustion technique requires a 0.1 g sample and the use of a 1 litre conical flask. Chlorine-free PE foil is used to wrap the sample, which is then supported on a platinum wire attached to the flask stopper. Water is used as the absorbent. Combustion takes place at atmospheric pressure in oxygen. The chloride formed is potentiometrically titrated in nitric acid/acetone medium with 0.01 M silver nitrate solution.

In the method of determining chlorine in chlorobutyl and other chlorine-containing polymers [16] the sample is combusted in a 1-2 litre oxygen-filled combustion flask containing 0.01 M nitric acid. After the combustion the flask is allowed to cool and 0.01 M silver nitrate added. The combustion solution containing silver chloride is evaluated turbidometrically at 420 mm using a grating spectrophotometer. Alternatively, to determine bromine, chlorine, iodine, or mixtures thereof, the combustion solution can be titrated with dilute standard silver nitrate solution or can be evaluated by ion chromatography.

A method for the determination of fluorine in fluorinated polymers such as polytetrafluoroethylene (PTFE) is based on decomposition of the sample by oxygen flask combustion followed by spectrophotometric determination of the fluoride produced by a procedure involving the reaction of the cerium(III) complex of alizarin complexan (1,2-dihydroxy-anthraquinone-3-ylmethylamine *N,N*-diacetic acid). The blue colour of the fluoride-containing complex (maximum absorption, 565 nm) is completely distinguishable from either the yellow of the free dye (maximum absorption, 423 nm) or the red of its cerium(III) chelate (maximum absorption, 495 nm).

A method has been described [17] for the determination of chlorine in polymers containing chlorine, fluorine, phosphorus and sulfur, which involves oxygen flask combustion over water, addition of ethanol, and titration to the diphenylcarbazide indicator end point with 0.005 M mercuric nitrate:

$$2HCl + Hg(NO_3)_2 = HgCl_2 + 2HNO_3$$
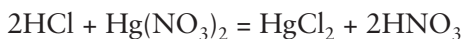
Using this method Johnson and Leonard [18] obtained from PTFE, 75.8% of fluorine using a silica or boron-free glass combustion flask against a theoretical value of 76%. Using a borosilicate glass combustion flask they obtained a low fluorine recovery of 72.1%.

12.1.2.2 Sulfur

To determine sulfur in amounts down to 500 ppm in polyolefins the sample is wrapped in filter paper and burnt in a closed conical flask filled with oxygen at atmospheric pressure. The sulfur dioxide produced in the reaction reacts with dilute hydrogen peroxide solution contained in the reaction flask to produce an equivalent amount of sulfuric acid:

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O$$
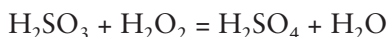
The sulfuric acid is estimated by visual titration with M/500 or M/50 barium perchlorate using Thorin indicator. The repeatability of this method is ±40% of the sulfur content determined at the 500 ppm sulfur level, improving to ±2% at the 1% level. Chlorine and nitrogen concentrations in the sample may exceed the sulfur concentration several times over without causing interference. Fluorine does not interfere unless present in

concentrations exceeding 30% of the sulfur content. Phosphorus and metallic constituents interfere when present in moderate amounts.

12.1.2.3 Oxygen Flask Combustion: Ion Chromatography

Combustion of polymers in an oxygen-filled flask over aqueous solutions of appropriate reagents converts elements such as halogens, phosphorus and sulfur into inorganic anions. For example:

- chlorine, bromine, iodine → chloride, bromide, iodide

- sulfur → sulfate

- phosphorus → phosphate

Subsequent analysis of these solutions by ion chromatography [19] enables the concentrations of mixtures of these anions (i.e., the original elements) to be determined rapidly, accurately, and with great sensitivity.

Instrumentation for ion chromatography is discussed in Section 11.1.15. See also Appendix 1.

• Applications

Figure 12.1(a) shows a separation of halides, nitrate, phosphate and sulfate, obtained in six minutes by ion chromatography using a Dionex A54A anion exchange separator.

A further development is the Dionex HPLC AS5A-SU analytical anion exchange column.

Quantitation of all the anions in **Figure 12.1(b)** would require at least three sample injections under different eluant conditions.

12.2 Acid Digestions of Polymers

12.2.1 Chlorine

Fusion with sodium carbonate is a very useful method for the fusion of polymers that, upon ignition, release acidic vapours, e.g., PE containing traces of chlorine or PVC, both
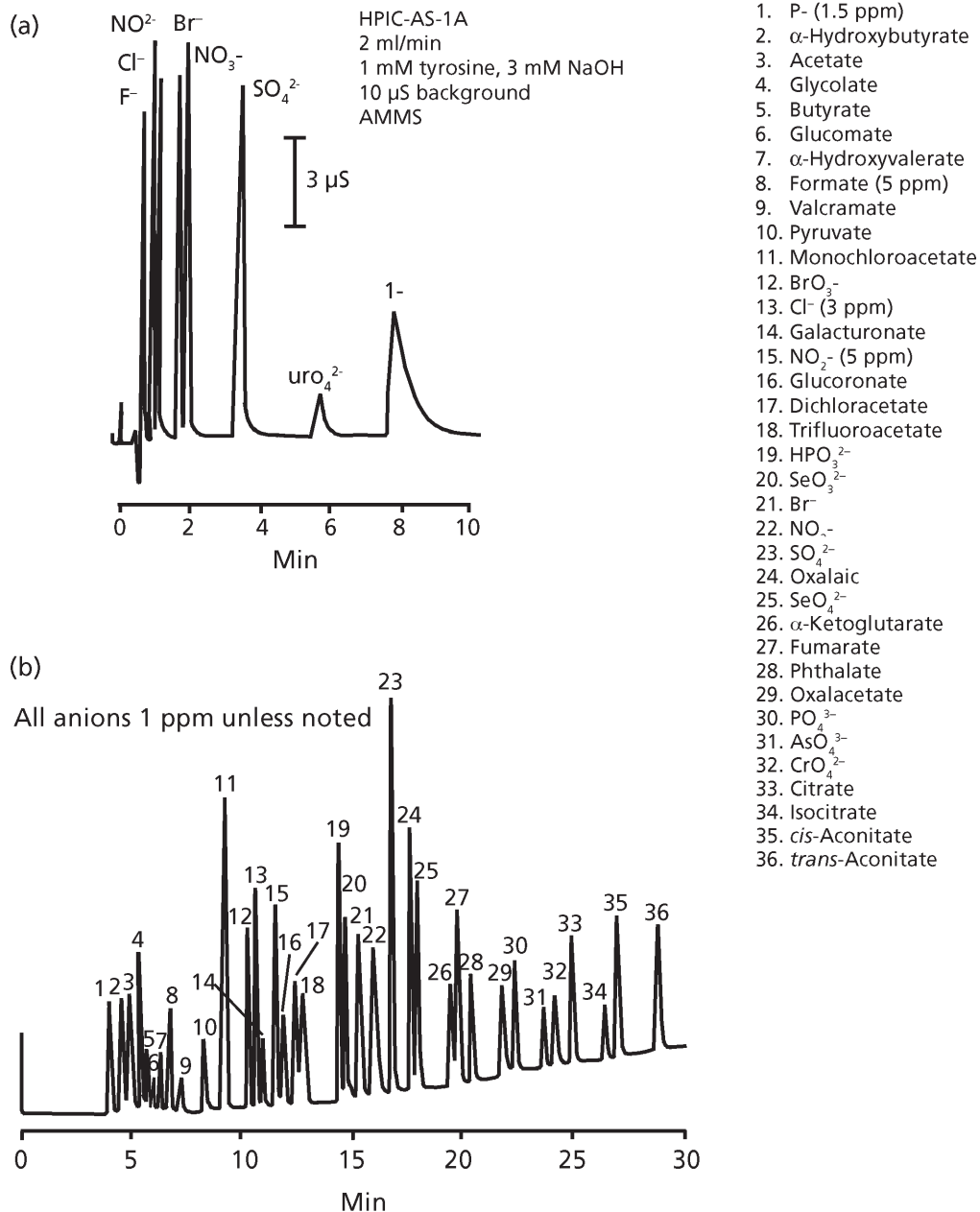
Figure 12.1 Ion exchange chromatography (a) Dionex A54A anion cartridge, (b) Dionex HPLC ASSA5U anion exchange
Source: Author's own files

of which, upon ignition, release anhydrous hydrogen chloride. To determine chlorine accurately in the polymer in amounts down to 5 ppm, the hydrogen chloride must be trapped in a solid alkaline reagent such as sodium carbonate. In this method PE is mixed with pure sodium carbonate and ashed in a muffle furnace at 500 °C. The residual ash is dissolved in aqueous nitric acid, and then diluted with acetone. This solution is titrated potentiometrically with standard silver nitrate. **Table 12.2** compares results for chlorine determinations in PE obtained by this method with those obtained by XRFS. The averages of results obtained by the two methods agree satisfactorily to within ±15% of each other.

Sodium peroxide is another useful reagent for the fusion of polymer samples preparatory to analysis for metals such as zinc and non-metals such as chlorine [20, 21] and bromine. In this method the polymer is intimately mixed with either sodium peroxide in an open crucible or with a mixture of sodium peroxide and sucrose in a micro-Parr bomb. After acidification with nitric acid, chlorine can be determined [21]. In a method for the determination of traces of bromine in PS in amounts down to 100 ppm bromine, a known weight of polymer is mixed intimately with pure sodium peroxide and sucrose in a micro-Parr bomb which is then ignited.

The sodium bromate produced is converted to sodium bromide by the addition of hydrazine sulfate:

$$2NaBrO_3 + 3NH_2NH_2 = 2NaBr + 6H_2O + 3N_2$$
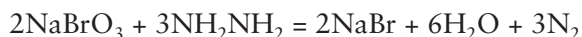
Table 12.2 Comparison of chlorine contents by X-ray method and chemical method (averages in parentheses)		
X-ray on discs	Chemical methods on same discs as used for X-ray analysis	Chemical method on powder*
865, 841 (840)	700	786, 761 (733)
535, 570 (522)	606	636, 651
785, 675 (730)	598	650, 654 (652)
625, 675 (650)	600	637, 684 (660)
895, 870 (882)	733	828, 816 (822)
*Analysis carried out on samples which had been treated with alcoholic potash to avoid losses of chlorine when preparing discs Reproduced with permission from T.R. Crompton, The Polymer Reference Book, *Rapra Technology, Shrewsbury, Shropshire, UK, 2005*		

The combustion mixture is dissolved in water and acidified with nitric acid. The bromine content of this solution is determined by potentiometric titration with standard silver nitrate solution.

12.2.2 Nitrogen

Apart from the chemical Kjeldahl digestion procedure for the determination of organic nitrogen, acid digestion of polymers has found little use. One of the problems is connected with the form in which the polymer sample occurs. If it is in the form of a fine powder, or a very thin film, then digestion with acid might be adequate to enable the relevant substance to be quantitatively extracted from the polymer. However, low nitrogen results would be expected for polymers in larger granular form, and for the analysis of such samples classic microcombustion techniques are recommended.

Hernandez [22] has described an alternative procedure based on pyro-chemiluminescence which he applied to the determination of 250-1500 ppm nitrogen in PE. In this technique the nitrogen in the sample is subjected to oxidative pyrolysis to produce nitric oxide. This when contacted with ozone produces a metastable nitrogen dioxide molecule, which as it relaxes to a stable state emits a photon of light. This emission is measured quantitatively at 700-900 nm.

12.2.3 Phosphorus

Phosphorus has been determined [23, 24] in thermally stable polymers by mineralisation with a nitric - perchloric acid mixture and subsequent titration with lanthanum nitrate or by photometric determination of the phosphomolybdic blue complex.

12.2.4 Silica

Silica has been determined in PE films by a method based on near-infrared spectroscopy. For peak height measurements a single baseline point at the minimum near 525 cm^{-1} was found to be best. An additional baseline point below 430 cm^{-1} gave poorer results because of the increased noise at longer wavelengths due to atmospheric absorption. For the same reason peak area measurements were confined to the range 525-469 cm^{-1} [25]. Both height and area measurements gave an error index close to 1%, but derivative methods were considerably poorer. Derivative spectra generally show increased noise levels so that they are unlikely to be useful except when they are overlapping bands. The results obtained with the ratio program also showed a higher error index. The band index ratio method

avoids uncertainty associated with measuring the film thickness, but in this case the error resulting from using a rather weak reference band appears greater.

12.3 X-ray Fluorescence Spectroscopy

The XRFS technique, already discussed in Chapter 1, has been applied extensively to the determination of macro- and micro-amounts of non-metallic elements in polymers.

An interesting phenomenon has been observed in applying the XRFS method to the determination of parts per million of chlorine in hot-pressed discs of low-pressure polyolefins. In these polymers the chlorine is present in two forms, organically bound and inorganic, with titanium chloride compounds resulting as residues from the polymerisation catalyst. The organic part of the chlorine is determined by XRFS without complications. However, during hot processing of the discs there is a danger that some inorganic chlorine will be lost. This can be completely avoided by intimately mixing the powder with alcoholic potassium hydroxide, then drying at 105 °C before hot pressing into discs. Considerably higher total chlorine contents are obtained for the alkali-treated polymers.

A further example of the application of XRFS is the determination of tris(2,3-dibromopropyl) phosphate on the surface of retardant polyester fabrics [26]. The technique used, involved extraction of the fabric with an organic solvent followed by analysis of the solvent by XRFS for surface bromine and by high-pressure liquid chromatography for molecular tris(2,3-dibromopropyl) phosphate. The technique has been applied to the determination of hydroxy groups in polyesters [27, 28]:
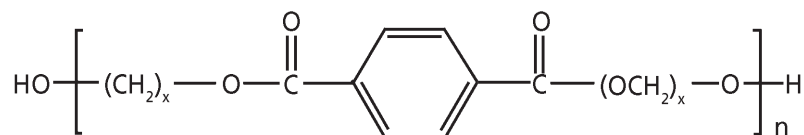
with n = 1-100 and x = 2 (polyethylene terephthalate) or χ = 4 (polybutylene terephthalate) and ester-interchange elastomers of 4-polybutylene terephthalate and polypropylene glycol. The hydroxyl groups in these products are determined by acetylation with an excess of dichloroacetic anhydride in dichloroacetic acid and measurement of the amount of acetylation by a chloride determination carried out on the derivative.

The XRFS method of Wolska [29] discussed in Section 11.1.2.1 has been applied to the determination of bromine and phosphorus in polymers. Various other workers have applied to this technique to the determination of chlorine and sulfur [30] and various other elements [31, 32].

12.4 Antec 9000 Nitrogen/Sulfur Analyser

This instrument [33] can provide analysis of nitrogen- and sulfur-containing additives in polyolefins.

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13 Appendix – Instrument Suppliers

Visible, ultraviolet and infrared spectrometers	Cecil Instruments Ltd. Foss Tecator Gilson International Kontron Instruments Perkin Elmer Corporation Philips Analytical Varian Instruments
Fourier Transform Infrared Spectroscopy, Near Infrared Fourier and Transform Raman Spectroscopy	Applied Photophysics Ltd. EDT Research Ltd. Foss Tecator JEOL Ltd. Perkin Elmer Corporation Philips Analytical Varian Instruments
Chemiluminescence analysis	Amersham Biosciences New Brunswick Scientific Ltd.
Inductively coupled plasma mass spectroscopy	GV Instruments Perkin Elmer Corporation
Inductively coupled plasma optical emission spectrometers	Philips Analytical
Zeeman atomic absorption spectrometry	Perkin Elmer Corporation Varian Instruments
Flame and graphite furnace atomic absorption spectrometry	GBC Scientific Pty Ltd. Perkin Elmer Corporation PS Analytical Ltd. Shimadzu Fisher Scientific Varian Instruments

Total elements	Emerson Process Management
Halogen, sulfur, nitrogen	Sartec Ltd.
Sulfur	Mitsubishi Chemical Industries Ltd.
Sulfur, chlorine	EDT Analytical Ltd.
Nitrogen	Foss Tecator
Carbon, hydrogen, nitrogen	Perkin Elmer Corporation
Nitrogen, carbon and sulfur	Thermo Electron
Nitrogen	Buchi Labortechnik AG Mitsubishi Chemical Industries Ltd. Thermo Electron
Spectrofluorimetry	Shimadzu
Polarography, voltammetry	EDT Research Metrohm AG
Luminescence and spectrofluorimetry	Hamilton Bonadzu AG Hamilton Co. Perkin Elmer Corporation
Headspace samplers	Hewlett Packard Perkin Elmer Corporation Shimadzu Siemens AG
NMR spectroscopy	Perkin Elmer Corporation Varian Instruments
Energy dispersive and total reflection X-ray fluorescence spectroscopy	Philips Analytical Tracor Europe BV
Gas chromatography	Dyson Instruments Ltd. Hnu-Nordion Ltd. Perkin Elmer Corporation Shimadzu Siemens AG Thermo Electron Varian Instruments
Pyrolysis – gas chromatography	CDS Analytical Inc. Perkin Elmer Corporation Philips Analytical Varian Instruments

Gas chromatography – mass spectrometry and mass spectrometry	Dyson Instruments Ltd. Perkin Elmer Corporation Shimadzu Thermo Electron Varian Instruments
Mass spectrometry	GV Instruments Hewlett Packard JEOL Oxford Analytical Ltd. Perkin Elmer Corporation Shimadzu Thermo Electron Varian Instruments
Gas chromatography – Fourier transform infrared spectroscopy	Perkin Elmer Corporation Philips Analytical Shimadzu Europa GmbH Varian Instruments
High performance liquid chromatography	Amersham Biosciences Cecil Instruments Dionex Corporation Dyson Instruments Ltd. Hewlett Packard Kontron Instruments Kratos Analytical Inc. Perkin Elmer Corporation Shimadzu Varian AG Varian Instruments
High performance liquid chromatography – mass spectrometry	Hewlett Packard
Supercritical fluid chromatography	Dionex Instruments Ltd.
Gel permeation chromatography, size exclusion chromatography	Perkin Elmer Corporation Polymer Laboratories
Thin layer chromatography	Camag JT Baker Shimadzu Europa GmbH Whatman International Ltd.
Electrophoresis	Beckman Coulter, Inc. Cole-Parmer Instrument Co.

Thermogravimetric analysis	EI DuPont de Nemours Inc. Perkin Elmer Corporation PL Thermal Sciences Inc. TA Instruments
Thermogravimetric analysis – Fourier transform infrared spectroscopy	Perkin Elmer Corporation PL Thermal Sciences Inc.
Thermogravimetric analysis – mass spectrometry	PL Thermal Sciences Inc.
Differential scanning calorimetry	EI DuPont de Nemours Inc. Perkin Elmer Corporation PL Thermal Sciences TA Instruments
Differential thermal analysis	EI DuPont de Nemours Inc. Perkin Elmer Corporation PL Thermal Sciences TA Instruments
Other suppliers of thermal analysis equipment	Mettler Corporation Polymer Laboratories Inc. Varian Instruments
Differential photocalorimetry	EI DuPont de Nemours Inc. TA Instruments
Thermomechanical analysis	PL Thermal Sciences
Dynamic mechanical analysis	EI DuPont de Nemours Inc. Perkin Elmer Corporation PL Thermal Sciences Inc. TA Instruments
Dielectric thermal analysis	EI DuPont de Nemours Inc. PL Thermal Sciences TA Instruments
Viscometry, molecular weight	Brinckmann Instruments Inc. Brookfield Engineering Laboratories Inc. Contraves Space AG
Electron spin resonance spectrometer	Varian Instruments
Auger spectrometer	Shimadzu Scientific Instruments
Electron spectrometer	GV Instruments Perkin Elmer Corporation Shimadzu Scientific Instruments

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Electron microprobe microscopy	GV Instruments JEOL Philips Analytical
Reflectance equipment	Shimadzu Scientific Instruments Varian Instruments
Secondary ion mass spectrometer	Perkin Elmer Corporation Shimadzu Scientific Instruments
X-ray photoelectron spectrometer	GV Instruments Perkin Elmer Corporation Shimadzu Scientific Instruments Tracor Europe BV
X-ray analysers and diffusion equipment	Philips Analytical Spectratech Inc. Tracor Europe BV
EDAX	EDAX International Inc.
Infrared microscopes	Leica Microsystems Carl Zeiss Inc. Gallenkamp Ltd. Perkin Elmer Corporation Southern Micro Instruments Varian Instruments
NMR microimaging spectrometer	Varian Instruments
Electron microprobe microscope	GV Instruments JEOL Philips Analytical
Electron scanning microscope	International Equipment Trading Ltd. Philips Analytical
Electron transmission microscope	International Equipment Trading Ltd.
X-ray microprobe	Hilgenberg GmbH Perkin Elmer Corporation Whatman International
Laser spectrometer	GV Instruments Shimadzu
Photoacoustic spectrometry	Perkin Elmer Corporation

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Beckman Coulter, Inc www.beckmancoulter.com	Bioresearch Information 4300 N Habor Boulevard PO Box 3100 Fullerton CA 92834-3100 USA
Brinkmann Instruments Inc. www.brinkmann.com	1 Cantiague Road PO Box 1019 Westbury NY 11590 USA
Brookfield Engineering Laboratories Inc. www.brookfieldengineering.com	11 Commerce Boulevard Middleboro MA 02346 USA
Buchi Labortechnik AG www.buchi.com	Meierseggstr 40 CH-9230 Flawil 1 Switzerland

Camag www.camag.ch	Sonnenmattstrasse 11 CH-4132 Muttenz Switzerland
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CDS Analytical, Inc www.cdsanalytical.com	PO Box 277 465 Limestone Road Oxford PA 19363-0277 USA
Cecil Instruments Ltd www.cecilinstruments.com	Milton Technical Centre Cambridge CB4 4AZ UK
Cole Parmer Instrument Co www.coleparmer.com	625 East Bunker Court Vernon Hills Illinois 60061-1844 USA
Contraves Space AG www.contraves.com	Schaffhauser Strass 580 CH-8052 Zurich Switzerland
Dionex Corp. www.dionex.com	4 Albany Court Camberley Surrey GU16 7QL UK PO Box 3063 1228 Titan Way Sunnyvale CA 94088-3603 USA
Dyson Instruments Ltd.	Hetton Lyons Industrial Estate Hetton Houghton le Spring Tyne and Wear DH5 0RH UK

EDAX International Inc. www.edax.com	915 McKee Drive Mahwah NJ 07430 USA
EDT Research Ltd. www.edt.bham.ac.uk	Department of, Electronic, Electrical and Computing Engineering University Birmingham Edgbaston Birmingham B15 2TT UK
EI DuPont de Nemours Inc. www.dupont.com	Concord Plaza Wilmington Delaware 19898 USA
Emerson Process Management www.emersonprocess.com	Rosemount Analytical Division 1201 North Main Street Orville OH 44667 USA
Foss Tecator www.foss.tecator.se	PO Box 70 S263-21 Honagas Sweden
Gallenkamp Ltd. www.gallenkamp.co.uk	Units 37-38 The Technology Centre Epinel Way Loughborough LE11 3GE UK
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Hnu-Nordion Ltd. Oy www.hnunordion.fi	Atomitie 5A3 PO Box 1 SF 00370 Helsinki Finland
GV Instruments www.gvinstruments.co.uk	Crew Road Wythenshawe Manchester M23 9BE

International Equipment Trading Ltd. www.ietild.com	960 Woodlands Parkway Vernon Hills IL 60061 USA
Japanese Electron Optics Ltd. (JEOL) www.jeol.com	1-2 Musashino 3-chome Aikshima Tokyo 196-8558 Japan
JT Baker Inc. *Division of Mallinckrodt Baker* www.imaging.mallinckrodt.com	222 Red School Lane Philipsburg New Jersey 08865 USA
Kontron Instruments	Milan Italy
Kratos Analytical Inc., part of Shimadzu group www.Kratos.com	Wharfside Trafford Wharf Manchester Road M17 1GP 100 Red Schoolhouse Road Building A Chesnut Ridge NY 10977 USA
Leica Microsystems www.hbu.de	Postfach 1120 Heidebergerstrasse, 17-19 D-6907 Nussloch Germany
Metrohm AG www.metrohm.com	68 Obersdorf Strasse CH-9101 Herisau AR Switzerland
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Oxford Analytical Ltd www.oxford-analytical.co.uk	Unit 3a Telford Road Bicester OX26 4LD
Perkin Elmer Corporation www.perkinelmer.com www.de.instruments.perkinelmer.com www.las.perkinelmer.co.uk	Chalfont Road Seer Green Beaconsfield Buckinghamshire HP9 2FX UK Life and Analytical Sciences 549 Albany Street Boston MA 02118-2512 USA Perkin Elmer (LAS) GmbH Ferdinand Porsche Ring 17 D-63110 Rodgau Germany

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Shimadzu Europa GmbH www.eu.schmadzu.de	Albert-Hahn Strasse, 6-10 D-47269 Duisburg Germany
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Abbreviations

[concs]	Concentrations
AAS	Atomic absorption spectrometry
ABS	Acrylonitrile-butadiene-styrene
AC	Alternating current
AC	Atomic composition
AED	Atomic emission detector
AFS	Atomic fluorescence spectroscopy
AMMS	Anionic micromembrane suppressor
ATR	Attenuated total reflection
ATR-FTIR	Attenuated total reflection Fourier transform infrared spectroscopy
ATR-IR	Attenuated total reflection infrared spectroscopy
AZO	Azodicarbonamide
BHT	2,6-Di-*tert*-butyl-*p*-cresol also known as butylated hydroxy toluene
bp	Boiling point
CHCl$_3$	Chloroform
CID	Collision induced dissociation
CI-MS	Chemical ionisation – mass spectrometry
CMMS	Cationic micromembrane suppressor
CVAAS	Cold vapour atomic absorption spectrometry
DC	Direct current
DIOP	Di-isooctyl phthalate
DLTDP	Dilaurylthiodipropionate

DMF	Dimethylformamide
DNPH	2,4-Dinitrodiphenylhydrazine
DOBP	4-(Dodecyloxy)-2-hydroxybenzophenone
DOP	Di(2-ethylhexyl)phthalate
DP	Degree of polymerisation
DPG	Dipropylene glycol
DSC	Differential scanning calorimeter
DTA	Dynamic thermal analysis
EDXRF	Energy dispersive
EGA	Evolved gas analysis
EI-MS	Electron impact mass spectra
ELV	End-of-life vehicle(s)
EPDM	Ethylene-propylene diene terpolymer
ESI	Electrospray ionisation
ESI-MS	Electrospray ionisation – MS
ESI-MS-MS	Electrospray ionisation MS – MS
FAB	Fast atom bombardment
FD	Field desorption
FID	Flame ionisation detector/detection
FI-MS	Field ionisation
FTIR	Fourier transform – infrared spectrometry
FT-MS	Fourier transform – mass spectrometry
GC	Gas chromatography
GFAAS	Graphite furnace atomic absorption spectrometry
GLC	Gas-liquid chromatography
GPC	Gel permeation chromatography
HALS	Hindered amine light stabiliser(s)
HDPE	High-density polyethylene
HETP	Heights of equivalent theoretical plates

HIPS	High-impact polystyrene
HMDS	Hexamethyl disilazane
HPLC	High-performance chromatography
ICP	Inductively coupled plasma
ICP-AES	Inductively coupled plasma – atomic emission spectrometry
ICP-MS	Inductively coupled plasma – mass spectrometry/spectrometer
ICP-OES	Inductively coupled plasma – optical emission spectrometer
id	Internal diameter
IGC	Inverse gas chromatography
IP	Ionisation potentials
iPP	Isotactic polypropylene
IR	Infrared
IRE	Internal reflection element
K^+IDS	Potassium ionisation of desorbed species
KOH	Potassium hydroxide
L2MS	Two-step laser desorption/laser photoionisation time-of-flight MS
LC	Liquid chromatography
LC-MS	Liquid chromatography – mass spectrometry
LD	Limit of detection
LD/EI/FT/ICR/MS	Laser desorption/electron ionisation/Fourier transform ion cyclotron resonance MS
LDPE	Low-density polyethylene
LPToFMS	Laser desorption/laser photoionisation time of flight MS
LSCC	Liquid-solid column chromatography
m/m	By mass
MALDI	Matrix-assisted laser desorption/ionisation
MALDI-MS	Matrix-assisted laser desorption/ionisation mass spectrometry
MMA	Methylmethacrylate
MN	Number average molecular weight

mp	Melting point
MS	Mass spectrometry
MSC	Multiplicative signal correction
MSR	Microspecular reflectance
MW	Molecular weight
NAA	Neutron activation analysis
NiO2	Nickel oxide
NMR	Nuclear magnetic resonance
NR	Natural rubber
NTP	Normal temperature and pressure
OD	Outer diameter
OIT	Oxidation induction time
OMT	Oxidation maximum time
PAR	Pyridyl azoresorcinol
PC	Polycarbonate
PCA	Principal component analysis
PE	Polyethylene(s)
PEG	Polyethylene glycol(s)
PET	Polyethylene terephthalate
PEUU	Polyetherurethane urea(s)
PLS	Partial least-squares regression
PMMA	Polymethylmethacrylate
POE	Polyoxyethylene(s)
PP	Polypropylene
ppm	Parts per milllion
ppt	Parts per trillion
PS	Polystyrene(s)
PSFC	Packed column supercritical fluid chromatography
PTFE	Polytetrafluroethylene

PVC	Polyvinylchloride
Py-FI-MS	Pyrolysis field ionisation
Py-GC	Pyrolysis gas chromatography
REMPI	Resonance-enhanced multiphoton ionisation
Rf	Retention factor
RSD	Relative standard deviation
RTD-GC	Reactive thermal desorption-gas chromatography
SCE	Saturated calomel electrode
SEC	Size-exclusion chromatography
SFC	Supercritical fluid chromatography
SFC-MS	Supercritical fluid chromatography – mass spectrometry
SFE	Supercritical fluid extraction
SIMS	Secondary ion MS
TBAI	Tetrabutylammonium iodide
TCE	1,1,1-Trichlorethane(s)
TG	Thermogravimetry
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TIC	Total ion current
TLC	Thin-layer chromatography
TOC	Total organic carbon
TOF-MS	Time-of-flight mass spectrometry
TRXRF	Total reflection XRF
UV	Ultraviolet
WDXRF	Wavelength dispersive XRF
XPS	X-ray photoelectron spectroscopy
XRF	X-ray fluorescence
XRFS	X-ray fluorescence spectroscopy
ZAAS	Zeeman atomic absorption spectrometry

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SMITHERS
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