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ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN POLYMERS BY DYNAMIC HEADSPACE–MULTI-DIMENSIONAL GAS CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

The use of dynamic headspace–multi-dimensional gas chromatography–mass spectrometry in studies of volatile organic compounds in plastics is described. The results demonstrate the utility of this technique to increase the resolution of selected compounds, to generate less overlapped mass spectra and to obtain a higher confidence of the analysis results. Some construction features of the laboratory-assembled system are discussed.

INTRODUCTION

The analysis of volatile organic compounds in solid materials, *e.g.*, plastics, by gas chromatography can be carried out by a number of methods, which include solvent extraction[1,2], solid injection[3], headspace[4-7] and pyrolytic techniques[8]. A review of static and dynamic headspace analysis in non-environmental applications has been presented by McNally and Grob[9].

In dynamic headspace analysis the sample is constantly swept by a stream of inert gas, which removes the volatile compounds from the sample matrix and the sample chamber to some kind of collection device, *e.g.*, a cold trap. The thermodynamic equilibrium between the condensed and the gaseous phases will therefore be dependent not only on the temperature and nature of the sample matrix, as in a static headspace, but also on the flow-rate of the stripping gas. However, adequate equilibrium may not be attained.

The prime advantage of dynamic headspace over static headspace analysis is that a greater range of compounds with regard to concentration and vapour pressure can be analysed. Thus, as a pre-concentration technique for the trace analysis of volatile compounds in polymeric systems, the dynamic headspace method is a very likely choice. In combination with high-resolution gas chromatography–mass spectrometry (GC–MS), the dynamic headspace method is versatile and powerful for the

analysis of volatile compounds from polymer matrices. However, although capillary column GC is a high-resolution technique, the separation problems encountered in, e.g., the dynamic headspace capillary GC analysis of polypropylene[5] are too complex to allow complete resolution of the chromatographic peaks within a single run. This is especially evident during identification studies, where this situation often leads to heavily overlapped mass spectra owing to insufficient chromatographic resolution.

In order to increase the resolution and to obtain a higher confidence in the analysis of volatile organic compounds in polymers, multi-dimensional capillary column GC has been used.

In this paper, we demonstrate the use of laboratory-constructed dynamic headspace system in combination with capillary column multi-dimensional GC–MS. We also discuss some features of the laboratory-constructed systems and present some results obtained in the analysis of a polypropylene–polyethylene copolymer.

EXPERIMENTAL

Both the dynamic headspace equipment and the multi-dimensional gas chromatograph were designed and assembled in our laboratory. The dynamic headspace equipment consisted of a dynamic headspace chamber of glass-lined steel tubing (12 cm × 6.3 mm O.D. × 4.0 mm I.D.) (SGE, Melbourne, Australia), connected to a six-port flow-switching valve (Valco C6T or C6WT; VICI, Untertannberg, Switzerland) via an intermediate splitting zone (see Fig. 1). The three different zones could be heated separately; further, the dynamic headspace chamber could also be temperature programmed. The construction features of the six-port valve–cold trap–re-injection system is similar to a system we described earlier[10]. Cryogenic trapping was performed in a deactivated fused-silica capillary (30 cm × 0.25 mm I.D.) (Chrompack, Middelburg, The Netherlands), attached to the six-port valve. The cold-trap was partly immersed in liquid nitrogen in a Dewar flask. To obtain a suitable negative temperature gradient over the cold trap, the gas phase above the liquid nitrogen was flushed with a stream of nitrogen. The dynamic headspace chamber was kept at 120°C and the six-port valve at 225°C; the flow-rate of helium was 20 ml/min.
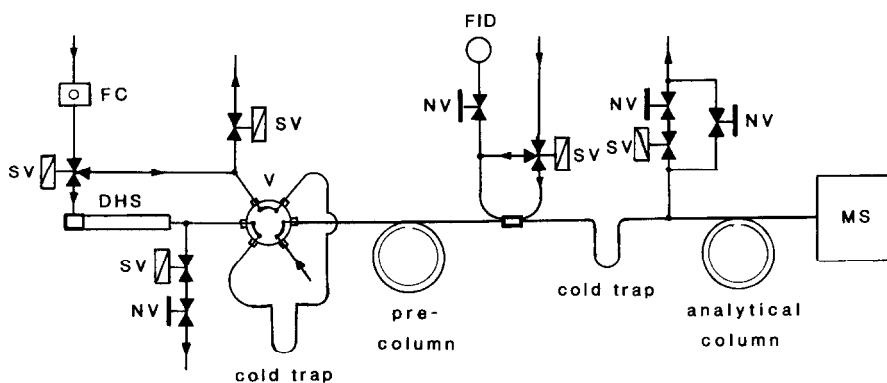

Fig. 1. Schematic diagram of the dynamic headspace–multi-dimensional gas chromatograph–mass spectrometer system. DHS = Dynamic headspace chamber; FC = flow controller; FID = flame ionization detector; MS = mass spectrometer; NV = needle valve; SV = solenoid valve; V = Valco six-port valve.

The collected headspace compounds were re-injected into a Varian 1400 gas chromatograph (Varian, Walnut Creek, CA, U.S.A.), which had been modified so as to accommodate capillary columns. The pre-column was a CP-WAX 52 B (10 m × 0.53 mm I.D.) (Chrompack). The column was temperature programmed from 40 to 220°C at 8°C/min. A flame ionization detector, kept at 280°C, was used as a pre-column detector. Fractions from the pre-column were transferred to the analytical column by intermediate cryogenic trapping. For this purpose, we used a cold trap–re-injection interface, developed especially for multi-dimensional capillary column GC; this interface has been described elsewhere[11]. Cryogenic trapping was performed in a simple cold trap, similar to the one used for enrichment of the compounds obtained in dynamic headspace sampling. Flow switching was carried out by the Deans switching technique[12]. The interface was kept at 250°C.

Fractions that condensed in the cold trap of the interface were re-injected into a Shimadzu QP-1000 gas chromatograph–mass spectrometer (Shimadzu, Kyoto, Japan). The GC–MS system was equipped with a CP-Sil 8 CB column (16.5 m × 0.22 mm I.D.) (Chrompack). The column, programmed from 40°C (5 min) to 250°C at 10°C/min, was interfaced directly with the ion source of the mass spectrometer. The mass spectrometer was scanned from m/z 35 to 350 at a cycle time of 1 s. The ion source was kept at 250°C and an ionization energy of 70 eV (electron impact) was used. Isobutane was used as the chemical ionization reagent gas. Chemical ionization was performed at an ion source temperature of 200°C.

The plastic material studied consisted of a polypropylene–polyethylene co-polymer not intended for pharmaceutical use.

RESULTS AND DISCUSSION

In the system depicted in Fig. 1, flow switching is effected both by means of rotary valves and also by flow switching according to the Deans method[12]. The use of rotary valves simplifies the construction of the flow-switching system, eliminates the need for careful pressure balancing and facilitates automation. For full utilization of the separating power of the chromatographic column, it was found advantageous to instal a flow splitting arrangement between the valve and the column. When the larger valve (C6T, 1/16-in. fittings) and the wide-bore, fused-silica capillary column were used in combination, a minor splitting of 1:3 to 1:2 was preferred. The low-volume valve (C6WT; 1/32-in. fittings) could be used without a splitting arrangement, especially in combination with the wide-bore capillary column.

The independent flow paths obtained through the use of the six-port valve in the dynamic headspace system facilitate changes of sample in the dynamic headspace chamber and dynamic headspace sampling during simultaneous chromatographic analysis of the headspace of the previous sample. The main disadvantage introduced by use of rotary valves is a less inert system. This is due to the presence of metallic surfaces, but it can be avoided if flow switching is accomplished by the Deans technique. However, in our experience, no major differences between the valve and the Deans technique have been demonstrated with regard to sample adsorption and losses. Thus, from a practical viewpoint, the utility of the low-volume six-port valve was found satisfactory. The reason why we used the larger six-port valve in this study was that the low-volume valve had been damaged in the course of the experiments.

In order to avoid too rapid a release of volatile compounds from the polymer sample on introduction into the headspace chamber, the system was constructed with linear temperature programming facilities. The sample chamber is temperature programmed, after sample introduction, from 50 to 120°C at 14°C/min and then held at 120°C for 5 min. It was considered that a more homogeneous flow through the chamber and the cold trap could be obtained with the temperature programming technique, which probably gives rise to better cryogenic trapping conditions. An indication of this was that the average relative standard deviation of the peak areas decreased from 35 to 14% by the introduction of the temperature programming technique.

Fractions from the pre-column were transferred to the analytical column by intermediate cryogenic trapping, utilizing the cold trap–re-injection interface. The cold trap–re-injection interface based on flow switching according to Deans can be characterized as an open system, i.e., switching points and the cold trap are in principle in contact with the outside atmosphere. Therefore, in order to avoid back-diffusion of air, the open capillary tubes should be constantly flushed. Despite this, an increase in air components by a factor of ca. 3 could be monitored in the mass spectrometer, compared with a more closed system, i.e., a cold trap–rotary valve–re-injection system. However, this increase in background level was considered acceptable, as it is of the same order of magnitude as if the column had been connected to a standard split–splitless injector of the Grob type.

As the analytical column in our experimental set-up is directly connected to the ion source, it is preferable to use thin, non-polar, chemicaly bonded stationary phases, such as methyl- and methylphenylpolysiloxanes in order to obtain low bleed and a high maximum operating temperature. This restricts the multi-dimensional set-up to a pre-column of higher polarity. Usually, this implies that, in order to obtain narrow band width on introduction of the headspace sample into the analytical column, solute band concentration should be achieved. As phase ratio focusing, i.e., thin to thick film and/or distribution constant focusing, from a less retentive stationary phase to a more retentive phase[13], were not possible with this set-up, cryogenic trapping was the method of choice.
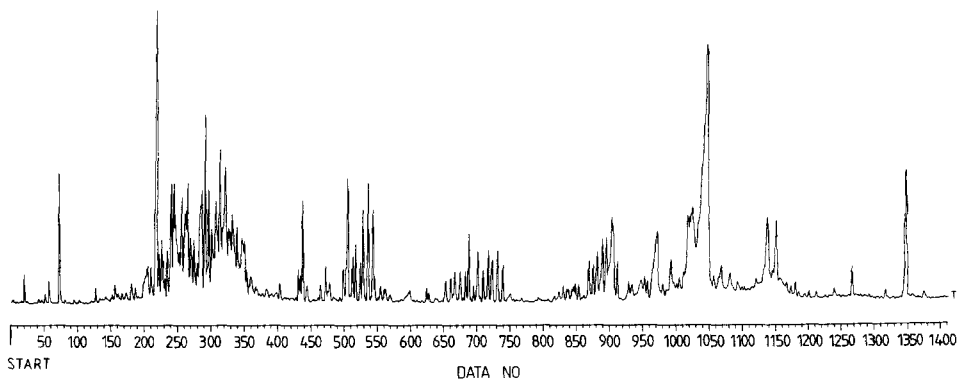

Fig. 2. Chromatogram of volatile organic compounds from a typical polypropylene–polyethylene copolymer sample. The chromatogram was generated on the CP-Sil 8 CB column.

In the single-column analysis of the polymer sample a chromatogram with over 200 countable peaks could be obtained (see Fig. 2). The chromatogram shown in Fig. 2 has a peak capacity[14] of *ca.* 200. According to Davis and Giddings' statistical theory of component overlap in multi-component chromatograms[14], it would be expected that at most 37 single-component peaks would be present in the chromatogram. Hence *ca.* 160 or more peaks would contain two or more components. Consequently, a single-column separation cannot be expected to provide the individual components for the mass spectrometer in the purities required for definitive identification. Strategies such as extracting single-ion chromatograms from the total-ion data or changing to a column with a different stationary phase could partially improve the situation. It should be stressed that the 1-s minimum resolution cycle time of the GC–MS unit decreases the obtainable peak capacity of the single column system.

Giddings[15] has theoretically examined the concepts of two-dimensional separations and pointed out that the combination of two independent selective separations increases the peak capacity power of the systems by a power of two. This is due to the increased space available in two dimensions for distributing separated zones and from the ability of independent separation mechanisms to use that space.
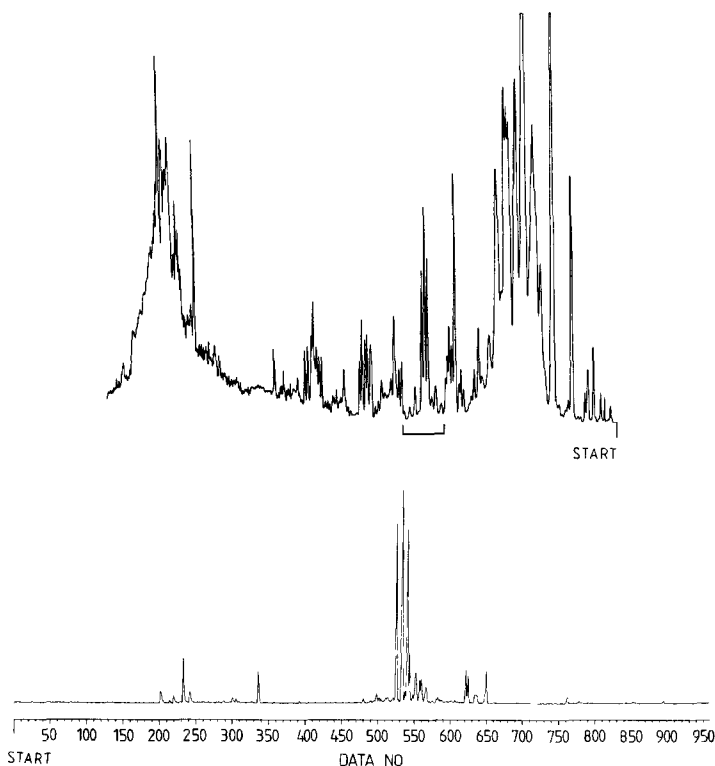

Fig. 3. Chromatograms generated by volatile compounds from the polypropylene–polyethylene sample. Top: a normal chromatogram generated on the CP-Wax 52 CB column. The indicated section was transferred to the non-polar CP-Sil 8 CB column through intermediate cryogenic trapping (bottom).

In multi-dimensional GC, the space available in two dimensions for distributing separated zones will partly be collapsed owing to varying degrees of dependence of the separation mechanisms. Nevertheless, a substantial increase in resolving power could be obtained with the multi-dimensional GC system described here (see Fig. 3). The ability to increase the peak capacity of the multi-dimensional gas chromatograph will be highly compound dependent. For non-polar compounds, such as alkanes, no or only a slightly improved peak resolution is obtained, owing to the high dependence of the separation mechanisms of the two stationary phases, whereas for more polar compounds, such as alcohols and aldehydes, a substantial increase in peak capacity could be obtained. Generally, the latter is manifested as in Fig. 3 by an increase in peak number and peak capacity.
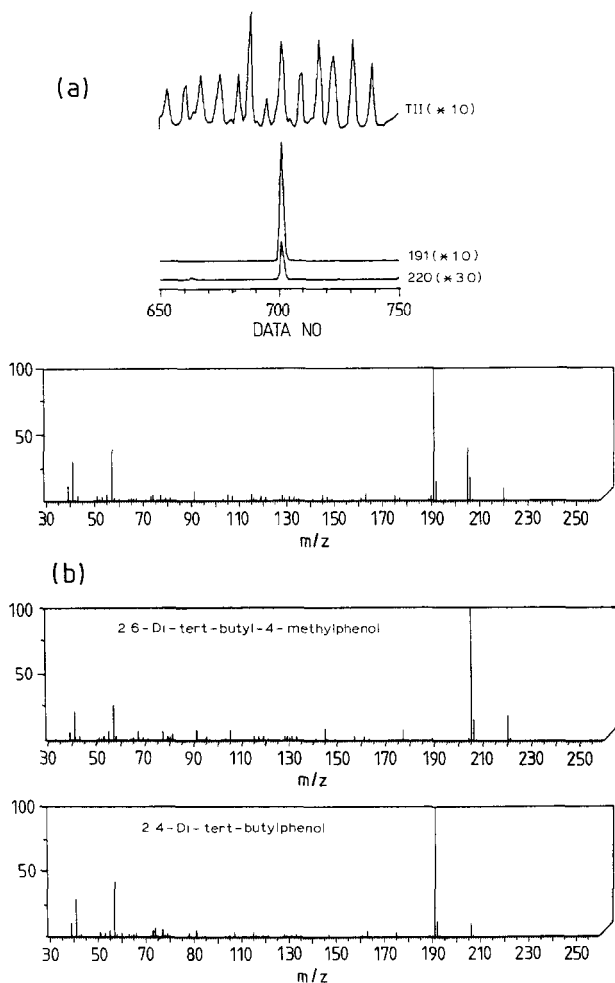

Fig. 4. (a) Part of the reconstructed ion chromatogram and selective ion monitoring single-column tracing (CP-Sil 8 CB). The corresponding mass spectrum, obtained at the indicated chromatographic peak, is also shown. (b) Mass spectra obtained by use of multi-dimensional GC–MS. The compounds coincided on the non-polar CP-Sil 8 CB column, as is indicated by the mass spectrum shown in (a).

The ability to obtain pure mass spectra is illustrated in Figs. 4 and 5. Fig. 4a shows a single-column separation (CP-Sil 8CB) and the corresponding mass spectrum. Examination of the mass spectrum suggests a multi-component mass spectrum, owing to the presence of m/z 206 and 220 and/or a compound with a molecular weight above 220. Further, owing to the 1-s time resolution of the GC–MS unit, the band width of the GC peak gives poor information concerning possible component overlap. However, by use of the multi-dimensional GC system and two different fractions from the polar pre-column, two different mass spectra could be obtained at the same retention time on the non-polar analytical column (see Fig. 4B). The compounds have been identified as 2,6-di(*tert.*-butyl)-*p*-methylphenol and 2,4-di-(*tert.*-butyl)phenol. Fig. 5 shows the mass spectra of diphenylamine obtained in the single-column and multi-dimensional mode. The mass spectral information obtained in the multi-dimensional mode is clearly superior to that from the single-column experiment and provides a more unequivocal identification of diphenylamine.

The compounds sampled from the polypropylene–polyethylene copolymer consisted predominantly of alkanes and alkenes, *e.g.*, 2-methylhexane, decane and 2-pentene. A number of aliphatic aldehydes and alcohols, *e.g.*, *n*-octanal and 3-hexanol, were also identified. These compounds give low molecular ion abundances in the 70 eV electron-impact mode. The absence of molecular weight information severely restricts the ability to assign a structure of the compound studied. The use of isobutane chemical ionization could significantly improve the ability to achieve molecular weight information (see Fig. 6). The complementary nature of electron impact and chemical ionization thus produces a more definitive identification of the compounds studied.
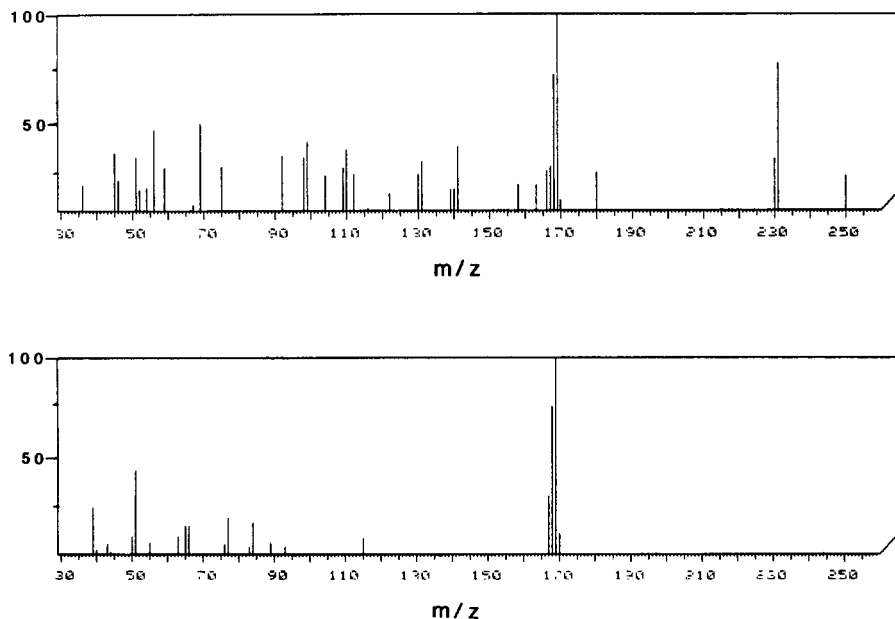

Fig. 5. Mass spectra of diphenylamine obtained in the single-column mode on CP-Sil 8 CB (top) and in the multi-dimensional mode (bottom).
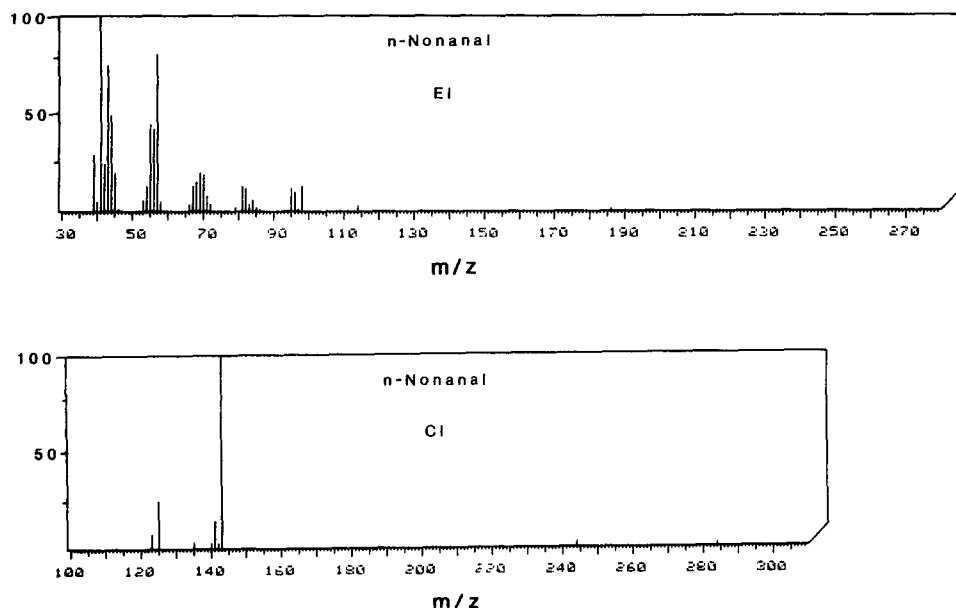
Fig. 6. Mass spectra of a compound sampled from the polymer sample. Top: electron impact at an ionization energy of 70 eV. Bottom: isobutane chemical ionization mass spectrum. The compound was identified as *n*-nonanal.

CONCLUSION

        In papers on two- or multi-dimensional GC–MS[16,17] it was stressed that the sample preparation time involved in analysing for relatively minor components in complex mixtures is greatly reduced, that the labour-saving afforded by multi-dimensional GC–MS reduces costs, increases the information content, improves target compound analysis and results in more definitive identifications. In our opinion, the present work supports such statement, especially in studies of very complex mixtures. Further, the unique combination of multi-dimensional capillary GC–MS with dynamic headspace analysis offers a powerful technique for studies of volatile organic compounds in polymers. The technique should also be applicable to the analysis of solid matrices other than polymers, *e.g.*, pharmaceutical preparations.

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