Application Note No. 039

Applications of PTV Injectors for Problem Solving in the Petrochemical Industry Part 1:- Thermal Desorption with GC and GC-MS

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Summary

Programmable Temperature Vaporising Injection (PTV) has been used extensively as a means of injecting large volumes of samples to enhance sensitivity. This paper describes the use of PTV injection in the desorption mode for the analysis of a range of solid samples, and four examples of this application as a problem solving tool are described in detail. Detection by mass spectrometry was used extensively as a means of identification of the components in the various samples characterised.

1. Introduction

Conventional gas chromatographic injection techniques include split, splitless and on column. These techniques are widely used and each offers its own advantages. The application of split injection is simple and reliable but has a number of important disadvantages including loss of sensitivity due to large sample loss, thermal degradation of thermally labile components and discrimination of less volatile components. The application of the splitless injection technique results in more sensitivity and is more suitable for trace analysis though thermal degradation can be more severe due to the dwell time in the heated injector. On-column injection is highly reproducible and is suitable for high boiling components, problems due to discrimination and thermal degradation are eliminated and detection limits similar to splitless injection can be achieved. On-column injection is therefore the method of choice for the introduction of unstable components. Despite the advantages on-column injection has not gained wide spread acceptance in routine analysis due to its less rugged nature and difficulties of automation. Additionally the risk of column contamination is significant as the entire contents of the syringe are loaded directly onto the column.

Temperature programmed sample introduction was first described by Vogt in 1979 [1,2]. The technique was originally developed as a means of introducing large sample volumes (up to 250 l) onto capillary GC columns. In his preliminary work, Vogt introduced the sample into the liner at a controlled rate and held the liner temperature slightly below the boiling point of the solvent used. The low boiling solvent was therefore continually evaporated and vented through the split line. Poy extended this principle and developed the Programmed Temperature Vaporising injector (PTV) [3]. The low liner temperature resulted in reduction of many of the problems associated with classical hot injection techniques.

Current commercial PTV injectors are versatile instruments with fully programmable temperature and pressure capability with different modes of injection easily accessible through microprocessor control. They have been used predominantly as a means of enhancing sensitivity by employing large injection volumes which often enables quantification of trace analytes without employing conventional sample pre-treatment techniques, e.g. liquid-liquid extraction or solid phase extraction [4]. This paper however, describes the use of PTV injection for the analysis of solid samples. The installation of the Optic Model 2-200 PTV injector on a GCs with both FID and mass spectrometer detection has proved an invaluable aid to industrial problem solving in a number of areas. Particular use has been made of this injector in the thermal desorption mode for polymer materials, powders and molecular sieve catalysts. It has enabled characterisation of these materials by GC mass spectrometry without any sample pre-treatment. A number of examples of the characterisation of solids are described.

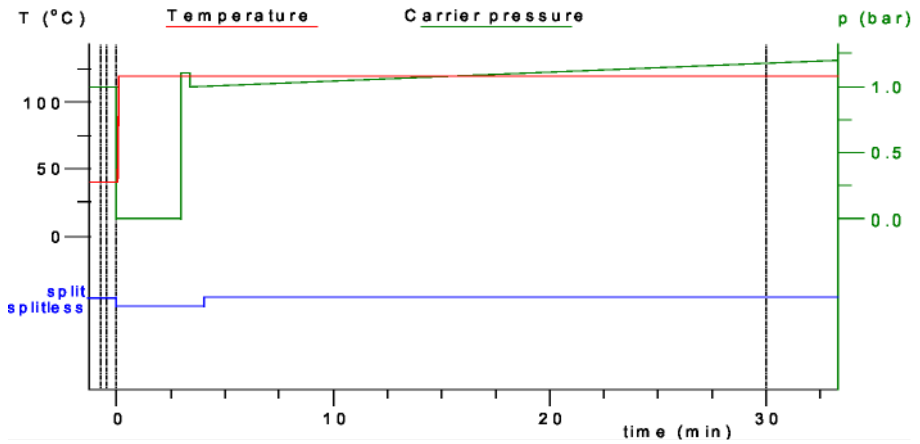
2. Experimental

2.1 Instrumental conditions

GCMS applications were carried out using Optic 2-200 injectors installed in the HP5890 GCs of a VG Trio3 and Trio 1000 GCMS systems. GC-FID work was also carried out on a Chrompack CP9000 instrument equipped with an Optic 2-200 injector. For thermal desorption applications, samples (between 1-15 mg, which have been ground to a fine powder if necessary) are placed in a fritted injection port liner. For some quantitative applications an ‘internal’ standard was added by loading a known volume of a solution containing the standard into the liner and allowing the solvent to evaporate before loading the liner with the sample. Two methods of desorption were employed for this work, the standard desorption mode programming provided with the Optic 2-200, for simple split mode desorption, or the expert mode for more varied control over splitless desorption.

A typical Expert Mode programme for thermal desorption of volatiles from polyethylene samples is shown in Figure 1, where, at time 0 min, the temperature of the injector was ramped from 40°C to 120°C (@16°C/min), the inlet pressure was dropped to 0 bar, i.e. the desorption takes place in with no flow through the injector and the split vent closed. After 3.5 min the inlet pressure was raised to 1.2 bar for 30 sec to transfer the desorbed volatiles to the head of the column, which is usually held at low temperature (e.g. -50°C). The split valve was opened at 4.0 minutes into the run, while the inlet pressure was dropped to 1 bar and the temperature programme commenced. This is represented graphically in Figure 1.

Figure 1. Expert mode programme for thermal desorption of volatiles from solid samples.



Columns used were either a 50m HP-1 (0.32mm i.d., 0.52 m film), a 30m DB-5MS (0.32mm i.d., 0.25 m film), a 30m DB-Wax (0.25mm i.d., 0.25 m film) or 50m CP-SIL 8 (0.32 mm i.d, 1.2 m film) coupled directly to the mass spectrometer source. For quantitative work the columns could also be connected to a flame ionisation detector (FID).

For MS data acquisition the VG Trios were operated (in single quadrupole mode) in either the electron impact (EI) mode at 70eV, the source temperature at 200°C, or in chemical ionisation (CI) mode, the source temperature was 230°C usually with ammonia as the reagent gas. The instrument mass range (14-650 Daltons) was calibrated in the EI mode using heptacosafluoro tributylamine.

3 Applications, Results, & Discussion

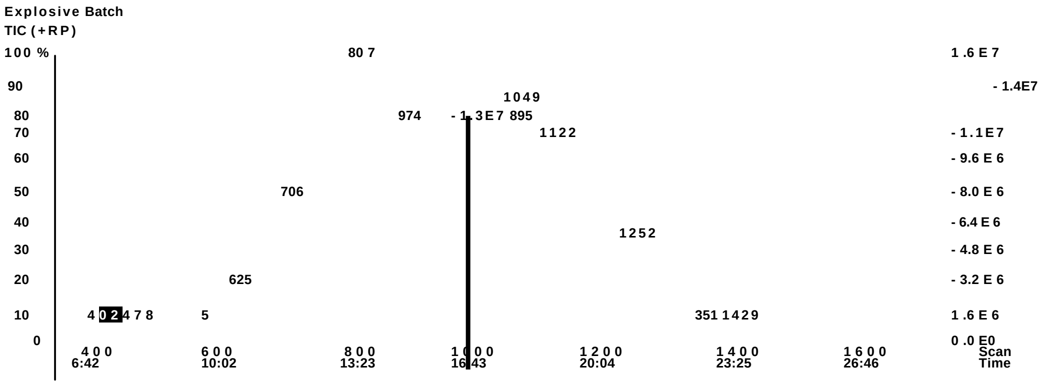
3.1 Explosive powders

Batches of a ‘powdered building material’ ‘are dried’ using the hot flue gases from the combustion of fuel oil. Under certain combustion conditions a batch of dried material caused an explosion, which was suspected to be the result of contamination with hydrocarbons from the fuel oil.

Simple split desorption at 300 ^{o}C, with the Optic 2-200, and GC-MS of the explosive material was performed on ca. 15 mg of material. The column was a DB-5MS (30 M X0.32mm i.d. 0.25 m film thickness) at 30 ^{O}C held for 3 min then ramped at 10 ^{O}C/min to 300 ^{O}C and held for 18 min. Detection was by mass spectrometry in the electron impact mode and the total ion chromatogram obtained from the explosive batch of the material is shown in Fig. 2.

The sample was found to contain a range of light hydrocarbons in the carbon number range C_8 to $_{C22}$ including saturated and aromatic compounds, which were envisaged to be derived from partial combustion of the fuel oil, and were thought to contribute to the explosive nature of this batch of material. Normal samples were also analysed, and found to contain a similar range of hydrocarbons, however. The amount of material in the different batches was estimated from the area under the total ion chromatograms compared to a known amount of a petroleum mixtures with a similar boiling range and composition, injected under the same conditions as used for the desorption. The explosive batch of material was found to contain approximately 3 times as much hydrocarbon as the ‘normal’ batches. This suggested that combustion conditions of the fuel oil produced greater quantities of entrained hydrocarbons in the flue gases contributing to high explosion risk in the dried material

Figure 2. Total ion current chromatogram of the explosive batch of building material.



3.2 Analysis of a printed polyethylene film which had an unusual odour.

A batch of printed polyethylene film used for wrapping foodstuffs was producing an unexpected odour during heat sealing. Fine slices (ca 45 mg each) were analysed using thermal desorption at 125 ^{o}C with splitless injection of the released volatiles. Column was DB-5MS (30 M x 0.32mm i.d. 0.25 m film thickness) at -50 ^{o}C held for 6 min then ramped at 5 ^{o}C/min to 50 ^{o}C, then 10 ^{o}C/min to 300 ^{o}C and held for 15 minutes. Detection was by mass spectrometry in EI and CI (ammonia) modes.

The total ion chromatogram obtained from this film is shown in Figure 3 with expanded sections of the chromatogram shown in Figures 4 and 5.

Figure 3. Total ion current chromatogram of the Film Sample

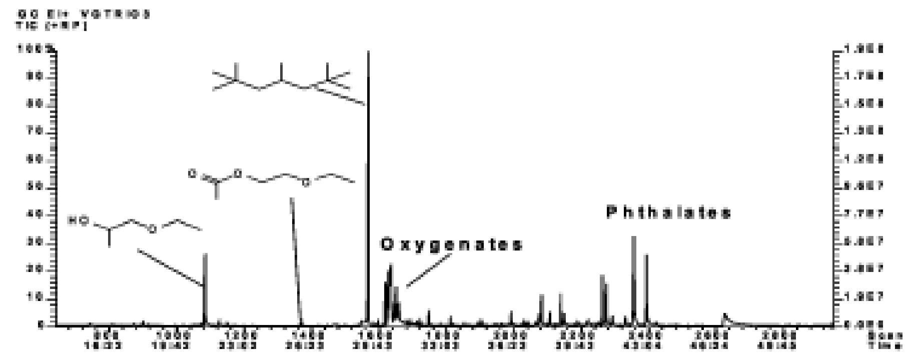


Figure 5. Expanded chromatogram

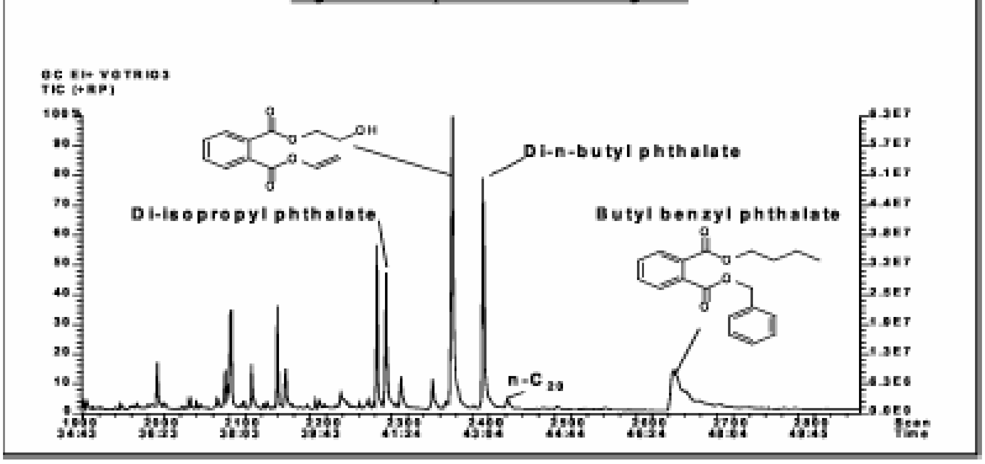
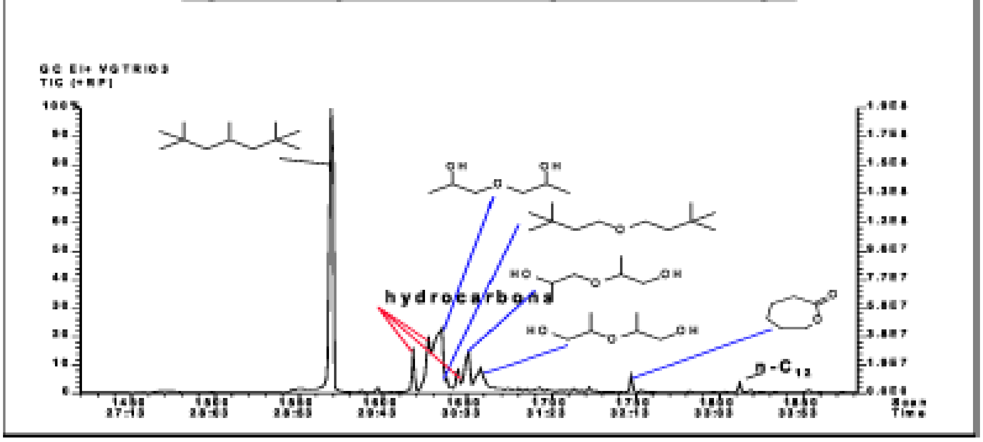


Figure 4. Expanded chromatogram of Film sample



The results show the presence of a number of oxygenated species of low and intermediate molecular weight which were not observed in the un-printed film, where only low molecular weight alkane oligomers were observed. This included the component 2,2,4,6,6-pentamethyl heptane which is used as a carrier solvent for the peroxide polymerisation initiator. The structures of the oxygenated species found in the printed film are shown on the relevant figures and the molecular weights of these components were confirmed by repeating the analysis using ammonia chemical ionisation.

These oxygenated compounds were considered to be potential candidates for the cause of the smell, and were thought to be derived from the printing process. There were no unusual hydrocarbon compounds over and above the normal polyethylene low molecular mass oligomers which could be desorbed from the film.

3.3 Determination and quantification of low molecular weight hydrocarbons in polyethylene samples taken directly from reactors and following degassing and pellet formation.

Following polymerisation of ethylene to polyethylene, the initial product contains volatile hydrocarbons (C_4 upwards) which are usually lost on degassing and during further thermal processing to form pellets. Identification and quantification of these components was required down to ppm levels. For desorption in the PTV injector, the powder sample was used directly, whereas pellet samples were freeze milled to a powder before use. The desorption GCMS analysis was carried out in the splitless mode in this case, for extra sensitivity using of the order of 8-10 mg of the powdered material and employing a desorption temperature of 120^{o}C. Chromatographic conditions were: Column HP-1 (50 M X 0.32 mm, 0.52 m film thickness), -50 ^{o}C (6 min) then at 5 ^{o}C/min to 50 ^{o}C, then 10 ^{o}C/min
to 300 ^{o}C and held for 15 minutes. Mass spectrometry (EI) and flame ionisation detection were employed. The total ion chromatograms obtained for both pellets and powder are shown in Figure 6 for comparison.

Both samples show a distribution of C_8 to $_{C24}$ even carbon numbered hydrocarbons, both n-alkanes, branched alkanes and some alkenes. The reactor sample shows a greater amount of C_8 and $_{C10}$ components and also a number of C_6 components which are shown more clearly in Figure 7, which shows an expansion of the front end of the chromatograms together with two example spectra. The “completeness” of the desorption method was assessed by repeating the same desorption experiment on the same samples which showed that all compounds up to C_{22} are desorbed in a single run, with only negligible amounts of $_{C22}$ and above being observed in a second run.

Figure 7. Expanded total ion current chromatograms.

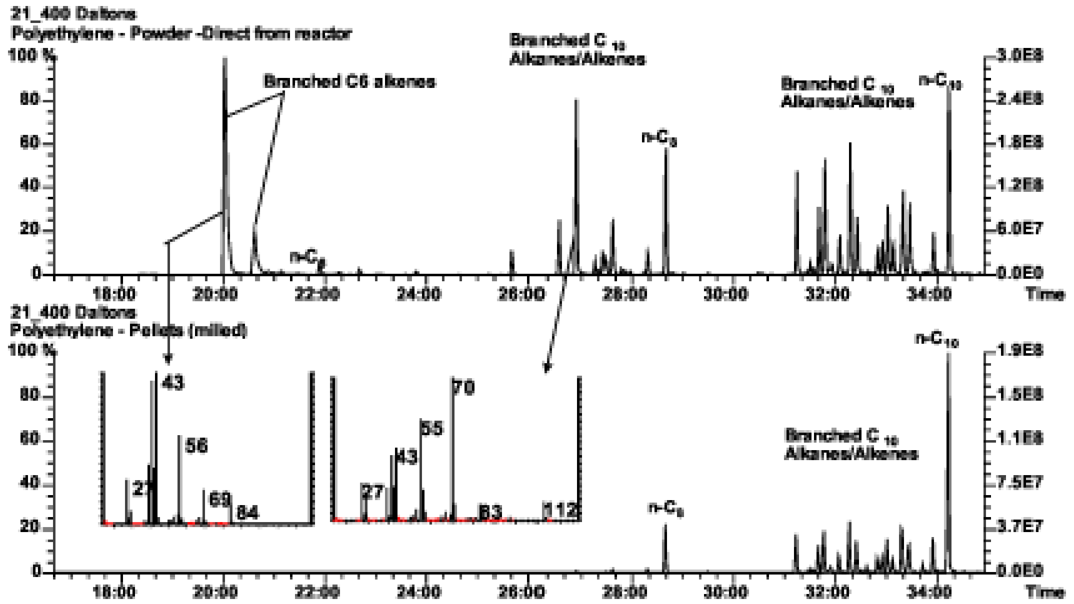
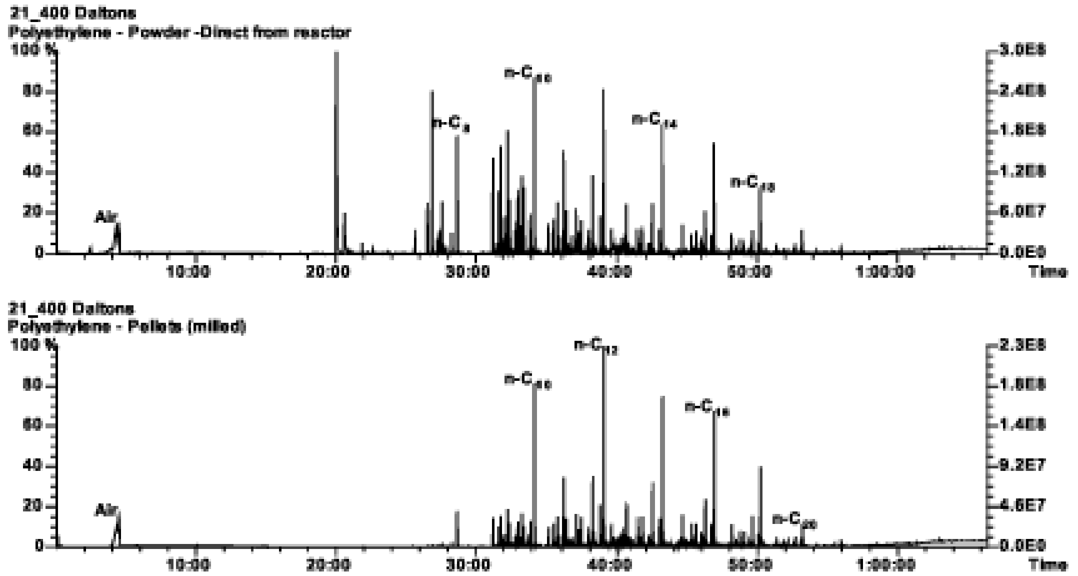


Figure 6. Total ion current chromatograms of reactor and pellet samples.



However, there was a requirement to quantify these components at the ppm level and this was achieved by using the same desorption technique with the column attached to a flame ionisation detector (FID) instead of the mass spectrometer. An ‘internal’ standard was employed by loading injector liners with a known volume of a standard solution of n-heneicosane (n-C_{21}) in pentane and allowing to evaporate before loading the liner with weighed amounts of sample. The liner was then placed in the Optic injector and the sample analysed in the same way as for MS detection. Peak areas of components were measured against the area of the internal standard and the concentration of the individual components calculated in mg/Kg. A comparison of the two samples using flame ionisation detection is shown in Figures 8 & 9. Individual components could be measured down to 1 ppm. A summary of the quantitative results for the two samples giving the n-alkanes as individuals and the branched alkanes/alkenes as a summed figure is shown in Table 1.

Figure 8. FID chromatogram of the polyethylene powder.

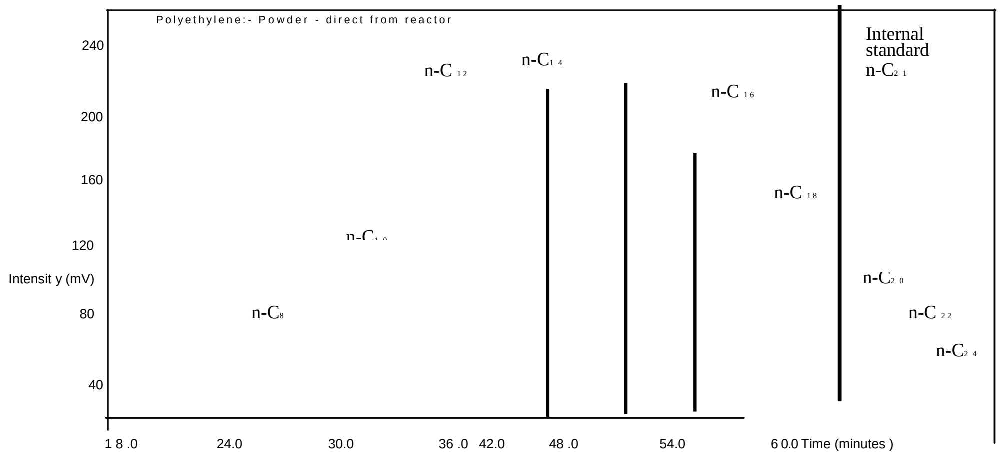


Figure 9. FID chromatogram of the pellet samples.

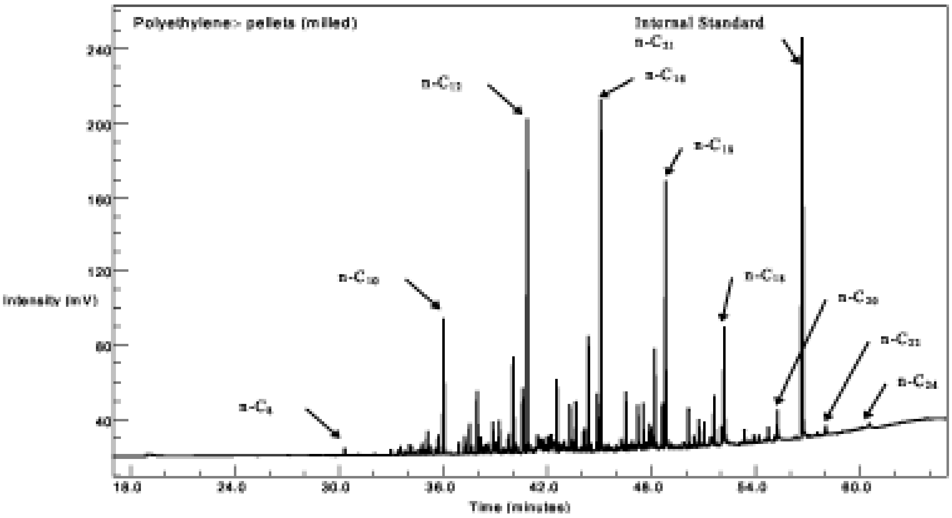


Table 1. Summary of the quantitative results for the two polyethylene samples by thermal desorption with GC-FID.

Carbon No Range	REACTOR POWDER mg/Kg	PELLETS mg/Kg
C_6	7.5	0.0
n-C_6	0.7	0.0
C_8	11.6	0.4
n-C_8	5.3	0.8
C_{10}	56.2	19.7
n-C_{10}	21.6	16.3
C_{12}	83.4	69.0
n-C_{12}	41.7	40.5
C_{14}	87.9	91.5
n-C_{14}	43.9	43.2
C_{16}	64.3	70.8
n-C_{16}	36.7	36.5
C_{18}	41.2	40.6
n-C_{18}	21.4	20.7
C_{20}	19.3	16.3
n-C_{20}	8.0	7.2
C_{22}	10.2	5.9
n-C_{22}	3.2	2.2
C_{24}	5.2	6.1
n-C_{24}	2.9	4.0
Total (mg/Kg)	572.1	491.6

These results show that trace quantitative analysis can be performed directly on solid samples using the PTV injector in the thermal desorption mode. Future work using trapping of head-space volatiles is anticipated.

3.4 Characterisation of phthalate ester PVC plasticisers

Phthalate and trimellitate esters are common plasticisers added to PVC to alter its physical properties such as robustness and maximum/minimum working temperatures and it is important to be able to identify the type of plasticiser used in a particular PVC product. Traditionally gas chromatographic analysis is employed which involves preparation of solid samples prior to analysis by extracting/dissolving the polymer in an appropriate solvent such as THF in order that a liquid sample may be inj ected into the gas chromatograph. This sample preparation is both time consuming and wasteful of organic solvent. The application of the thermal desorption mode on a PTV injector allows the characterisation of phthalate ester plasticisers in their solid PVC host matrix with no sample preparation.

In the GC-FID mode chromatograms of standard phthalate esters were obtained, together with those for PVC samples, in order to characterise the PVC plasticisers by matching retention times to those of the standards. The conditions employed for thermal desorption on the PTV injector, and analysis by GC-FID were as follows:-
A Chrompack CP9000 GC fitted with an Optic 2-200 PTV Injector was employed with a 10m x 0.53mm i.d. CPSil 5 column and flame ionisation detection.
Solid samples (1 to 2 mg) were placed in a fritted injector liner at an initial temperature of 50 $_0$C and the injector purged to remove air. PVC samples analysed typically contain circa 30% phthalate ester plasticiser and standard plasticiser solutions were prepared as 30% w/w solutions in acetone. The liquid standards were injected (1 L) through the septum as solutions and then treated as per solid samples. The carrier gas flow was then stopped and the injector ramped at 16 ^{0}C/Sec to 250 ^{0}C and held there for 2 minutes. The column temperature programme was then started and the desorbed products were transferred onto the analytical column using a transfer pressure of 0.55 bar for 30 seconds. The column head pressure was reduced to 0.48 bar and then programmed linearly to 0.55 Bar over 36 minutes. The column temperature programme was 50 ^{0}C held for 2 minutes then ramped at 10 ^{0}C/min to 300 ^{0}C and held for 10minutes.

The application of the method is demonstrated by the analysis of a PVC sample of unknown origin. Conventional tests had indicated that the polymer did not contain simple phthalates such as dibutyl or dioctyl phthalate but contained a either a multi-isomer phthalate or a mixture.

The chromatogram obtained for the analysis of the sample is shown in Figure 10 and the standard chromatograms obtained forDi-Undecyl Phthalate ester (DUP), Di-Iso-Undecyl Phthalate ester (DIUP) which contains a range of isomers, and the Linear C9 to C11 phthalate ester (L9-11) which also contains a range of isomers are shown in Figure 11, 12, and 13 respectively.

Figure 10. FID chromatogram obtained the unknown PVC samples.

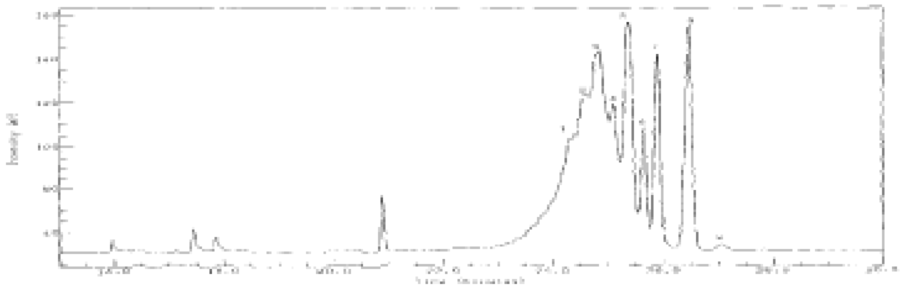


Figure 11. FID chromatogram obtained from DIUP standard solution.

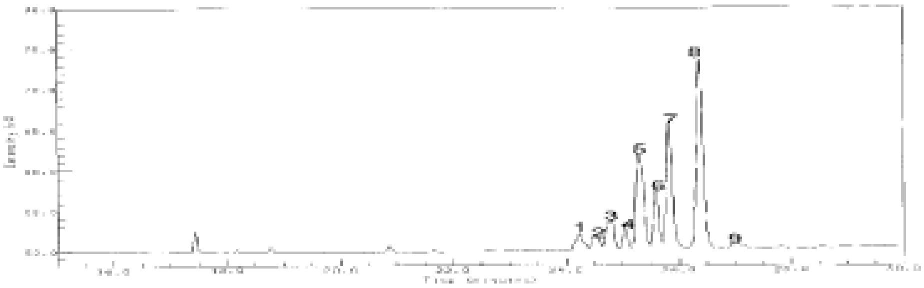


Figure 12. FID chromatogram obtained from DUP standard solution.

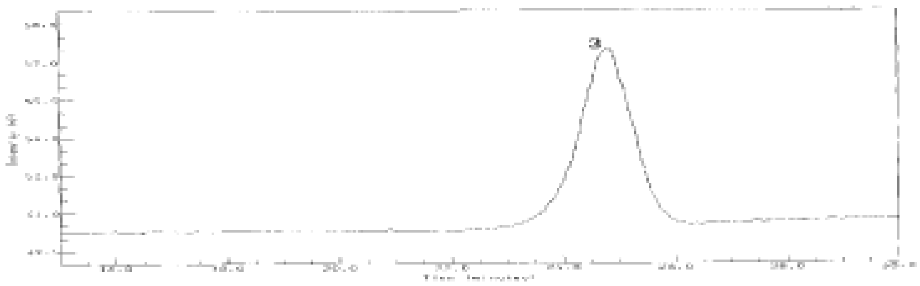
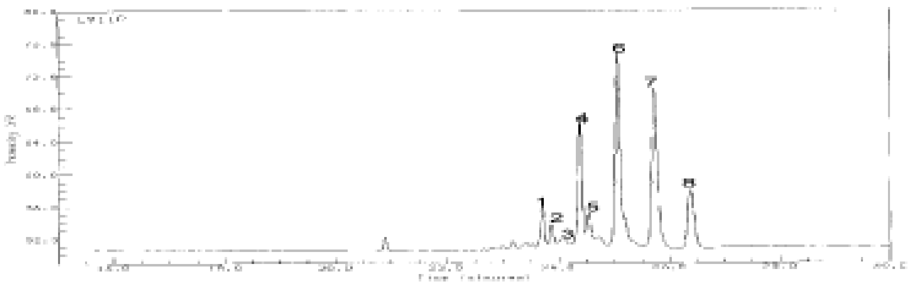


Figure 13. FID chromatogram obtained from L9-11 standard solution.



Retention times for the nine largest peaks from the standards and sample are listed in Table 2.

Carbon No Range	REACTOR POWDER mg/Kg	PELLETS mg/Kg
C_6	7.5	0.0
n-C_6	0.7	0.0
C_8	11.6	0.4
n-C_8	5.3	0.8
C_{10}	56.2	19.7
n-C_{10}	21.6	16.3

The results clearly show that the unknown PVC sample contains a mixture of DUP and DIUP and this example demonstrates that thermal desorption with a PTV injector and GC offers a rapid method for the characterisation of phthalate ester plasticisers in PVC compounds.

In many cases however standards are not always available and therefore a GC-MS method was also developed to allow positive identification of the desorbed compounds. The Optic 2-200 /VG Trio 1000 system was employed with a simple split desoprtion injector mode programme from 50 ^{o}C to 400 ^{o}C at 16 ^{o}/second to identify the plasticisers present. The same short column (10m CP-SIL 5, 0.53mm i.d) used for the GC-FID work was employed to allow result comparison and also to acilitatae rapid elution of the higher boiling phthalates. A column effluent splitter was employed, diverting 10 % to the mass spectrometer and 90 % to waste or to a FID. The GC oven temperature programme was 50 ^{o}C held for 6 min then ramped at 10 ^{o}C/min to 300 ^{o}C and held for 15 minutes. A range of phthalate and trimellitate esters commonly used as plasticisers have been analysed under identical conditions and their retention times and mass spectra documented. This has enabled rapid and reliable positive identification of all these plasticisers in unknown samples.

References

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