Application Note No. 005

Analysis low volatility samples using high temperature PTV injection.

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Introduction

Selecting the appropriate chromatographic technique for a given separation problem is a challenging task for analytical chemists. The answer to the question whether a given problem should be tackled by gas chromatography, liquid chromatography, supercritical - fluid chromatography or one of the newer electrophoretic methods depends on numerous parameters. In general however, one could say that if capillary GC can be used, it should be preferred over any of the other techniques. Capillary GC offers a resolving power, separation speed and a user-friendliness unsurpassed by the other chromatographic methods. In this respect high temperature capillary gas chromatography is an interesting new development as it opens possibilities for the analysis of components that in the past could only be analysed using liquid chromatography or packed- or open-tubular supercritical-fluid chromatography.
The definition of high temperature GC is somewhat arbitrary. In the present paper separations that are performed at oven temperatures below 325 ºC are called 'normal' GC separations. This form of GC is restricted to the analysis of relatively volatile materials (MW up to roughly 600 Dalton). High temperature GC extends the molecular weight range amenable to GC to molecular weights as high as about 1500 Dalton. The current maximum operating temperature for high temperature GC is about 450 ºC. Of course it is evident that it is a prerequisite that the components to be analysed are thermally stable at the temperatures used in the separation. In general, however, the terminal stability of organic compounds in a fully inert system, i.e. properly deactivated fused- silica column, inert carrier gas and a highly purified stationary phase is much larger than generally accepted.

With the development of high temperature GC the practical applicability of GC for the analysis of high molecular weight materials such as hydrocarbon oils, triglycerides, polymer additives, surfactants and polymer additives, surfactants and poly aromatic hydrocarbones has significantly increased.

Unfortunately, sample introduction in high temperature GC is extremely difficult. Conventional hot split and hot splitless injection can not be used as these techniques suffer from severe discrimination of high boiling components. Until now the only injection technique suitable for high temperature GC is on-column injection. This technique is, at least from the fundamental point of view, far superior over any of the other samples introduction techniques available at this moment. In on-column injection discrimination is absent, the thermal stress applied to the sample molecules is Minimal and trace analysis is possible as the entire sample is introduced on the column. On-column injection, however, also suffers from a number of, mainly practical, disadvantages. This technique is difficult to automate, easily leads to contamination of the column inlet and is not applicable for polar solvents. To overcome the solvent polarity limitation, but also to avoid contamination of the column inlet, it is recommended to use a retention gap. Unfortunately, however, coupling of the retention gap to the analytical column is by no means trivial. Leakage is difficult to avoid and as high temperature columns are still fairly susceptible to breakage, they are easily damaged every time a new retention gap is installed.
Programmed-temperature injection has proven to be an excellent and versatile sample introduction system for normal temperature GC. Combining a cool injection step with a controlled vaporisation eliminates a number of important disadvantages associated with the use of conventional hot sample inlets. When components with molecular masses below about 600 Dalton are to be analysed, discrimination is absent. The sample is introduced into the liner of the injector in the liquid state and is than vaporized and transferred
into the column in gaseous state. To be adequate for use in high temperature GC, the PTV injector should be capable of operating up to temperatures of approximately 500 to 600 ºC. Only at these temperatures do high molecular
weight materials have a sufficiently high vapour

pressure to permit quantitative transfer on to the column in a sort time. Lower transfer temperature unavoidably result in severe input band spreading and, eventually , discrimination of high boiling sample constituents. In this contribution the applicability of high temperature PTV injection for sample introduction in high temperature GC examined. The influence of the PTV final temperature on the GC performance is evaluated. The quantitative aspects of high temperature PTV injection, i.e. repeatibility of absolute and relative peak areas, and the accuracy and precision of the technique are evaluated. On-column injection is used as a frame of reference.

Instrumentation

High temperature GC requires adapted GC instruments with a maximum oven temperature of about 450 ºC , which is the current maximum operating temperature of dimethyl silicone stationary phase. Most manufacturers offers instruments that are capable of working at these temperatures. In the present study high temperature PTV injections were made with the AI Cambridge OPTIC injector fitted on an HP 5890-A GC equipped with an FID. The on-column reference experiments were also performed using this injector. For these experiments the split liner of the injector was replaced by a special on-column insert. As the on-column experiments and high temperature PTV experiments were performed on the same instrument, a direct comparison of PTV and on-column data was possible. The column used in the experiments was a Chrompack SimDist column with a length of 8 meters and an inner diameter of 320 µm. The detector temperature was 400 ºC, which was the maximum temperature for this instrument. Nitrogen was used as the make-up gas. The GC oven temperature was programmed from 40 ºC (1 min. initial hold) to 400 ºC at a rate of 20 ºC/min. The OPTIC injector was programmed from 35 ºC to 599 ºC at rate of 8ºC/s, unless stated otherwise.

Applications of high temperature GC with PTV injection

Normal PTV injection with final temperatures of about 400 to 450 ºC is an excellent sample introduction technique for use in 'normal temperature' GC. At a final PTV temperature of 400 to 450 ºC, rapid and quantitative transfer of the components from the liner of the injector on to the GC column is obtained for components that are amenable analysis with conventional GC. In high temperature GC much higher PTV temperatures are necessary for obtaining quantitative transfer of the components of the column.

Polymer additives

The importance of using sufficiently high temperatures when using PTV injection in high temperature GC is shown in the analysis of a polymer additive mixture (figure 1). At a final injector temperature of 599ºC a sharp, symmetrical peak is observed for Irganox 1010. Figure 1B shows the same analysis but now at a final PTV temperature of only 400 ºC.

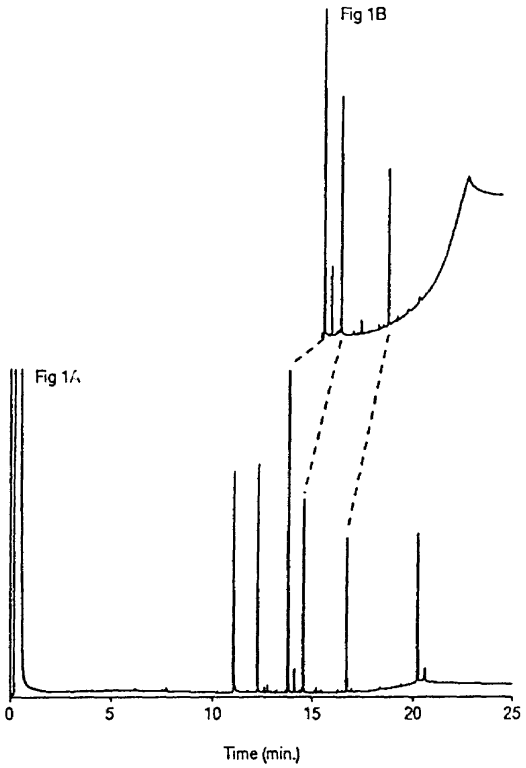

Figure 1. Analysis of polymer additive mixture. Influence of PTV final temperature A: Final PTV temperature 599 ºC. B(insert): final PTV temperature = 400 ºC Components in elution order: Cyasorb 531, Tinuvin 770, Irganox 1076, Tinuvin 144, DSTDP, Irganox 1010.

Under these conditions the Irganox 1010 peak is completely absent. Apparently the vapour pressure of this component at 400 ºC is too low to allow transfer to the column. For the components presents in this polymer additive test mixture thermal decomposition does not occure. For other additives such as for example Irgafos 168, thermal degradation can occur during PTV sample introduction or during the chromatographic analysis if poorly deactivated capillary column are used. Figure 2 shows a comparison of the analysis of polymer additives by high temperature GC with on-column injection (Fig. 2A) and with high temperature PTV injection (Fig. 2B).
From these two figures it is clear that the results of on-column injection and high temperature PTV injection are at least qualitatively comparable.

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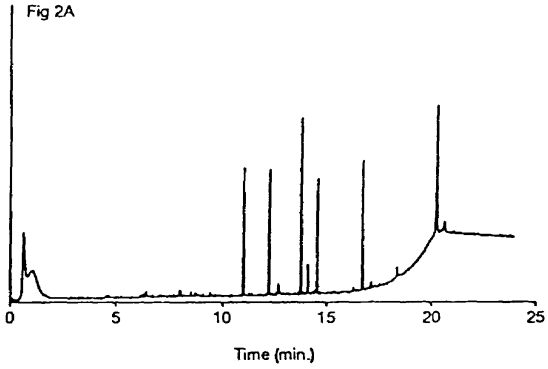

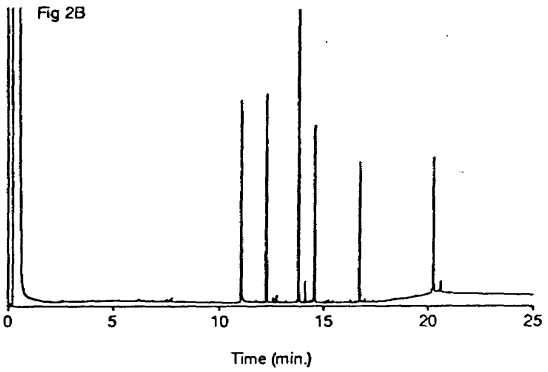

Figure 2 Analysis of polymeradditive test mixture. Comparison of (A) on-column injection and (B) high temperature PTV injection.

Table I gives an overview of retention times and relative peak areas obtained using high temperature PTV injection. Even if manual injection is used, the reproducibility of retention times in high temperature PTV (HT-PTV) injection is better than 0.2% which is an acceptable value for manual injection. The reproducibility of relative peak areas varies from 0.28% for Irganox 1076 to 4.04% for DSTDP. On-column injection yielded comparable values for the reproducibility of retention times. The reproducibility of relative peak areas in the on-column injection experiments was slightly better than in the HT-PTV mode. In the on-column injection an RSD value for relative peak areas of about 2.0% was found. Large differences between on-column and high temperature PTV injection were found when the reproducibility of absolute peak areas was compared. The RSD value for HT-PTV was approximately 24%. On-column injection gave an RSD value of about 5% for absolute peak areas. Fortunately, however, for daily practice the reproducibility of absolute peak areas is only of minor importance. More important are the relative peak areas. For this parameter high temperature PTV injection and on-column injection yielded comparable values.

A. Retention times [min.].

Cyasorb 531	Tinuvin 770	Irganox 1076	Tinuvin 144	DSTDP	Irganox 1010
10.879	12.085	13.615	14.343	16.480	19.980
10.839	12.064	13.570	14.308	16.441	19.941
10.850	12.054	13.580	14.315	16.449	19.946
10.879	12.080	13.613	14.342	16.479	19.972
RSD=	RSD=	RSD=	RSD=	RSD=	RSD=
0.188%	0.119%`	0.168%	0.127%	0.123%	0.096%

B. Relative peak areas [%]

Cyasorb 531	Tinuvin 770	Irganox 1076	Tinuvin 144	DSTDP	Irganox 1010
14.76	16.03	26.63	11.89	13.04	17.65
14.98	16.26	26.63	11.73	11.99	18.41
14.98	16.11	26.64	11.78	12.28	18.21
14.93	16.11	26.78	12.21	12.93	17.04
RSD=	RSD=	RSD=	RSD=	RSD=	RSD=
0.70%	0.70%	0.28%	1.81%	4.04%	3.54%

Table 1. Reproducibility of retention times and relative peak areas obtained with high temperature PTV injection. Test components: polymer additives.

A distinct advantage of high temperature PTV injection over on-column injection is the fact that PTV injection is relatively insusceptible to the presence of high molecular weight residues in the sample. Extracts from polymers often contain a considerable amount of co-extracted oligometers that cannot be eluted from a GC column, not even at the maximum allowable operating temperature. The presence of this material renders the use of a retention gap mandatory, especially if larger series of samples are to be analysed. If no retention gap is used, the column inlet is rapidly contaminated with involatile material resulting in band broadening and excessive retention. The incorporation of an uncoated, deactivated column upstream of the analytical columns helps to overcome these problems, unfortunately only at the expense of an increased instrument complexity. Apart from the problem with leakage at the column connector also the fact that the retention gap has to be replaced frequently hampers the use of on-column injection for samples containing high concentrations of high molecular weight impurities. If PTV injection is used, the high molecular weight impurities from the sample are retained in the liner. It is evident that cleaning or replacing the liner is much easier and faster than is installing a new retention gap.

Hydrocarbon waxes

A second interesting application of high temperature PTV injection is the analysis of hydrocarbon waxes. It has been proven in the literature that hydrocarbons up to C_{120} can be eluted quantitatively on short capillary columns coated with a thin film of dimethyl silicone. Until now all these separations have been performed using on-column injection. To investigate the applicability of high temperature PTV injection for this high type of sample the performance of PTV injection was again compared with on-column injection. Figure 3 illustrates the influence of the PTV final temperature on the separation of a Polywax 655 sample. When the maximum

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PTV temperature of 400 ºC is used, serious broadening of the later eluting peaks is observed. The explanation for this observation is straight forward. Transfer of the components from the liner of the injector to the GC column at a temperature of 'only' 400 ºC is extremely slow. Even despite the refocusing step that occurs in the GC column the peaks are still significantly broadened. Only if higher PTV temperatures are used is the transfer fast enough for obtaining narrow input bands.

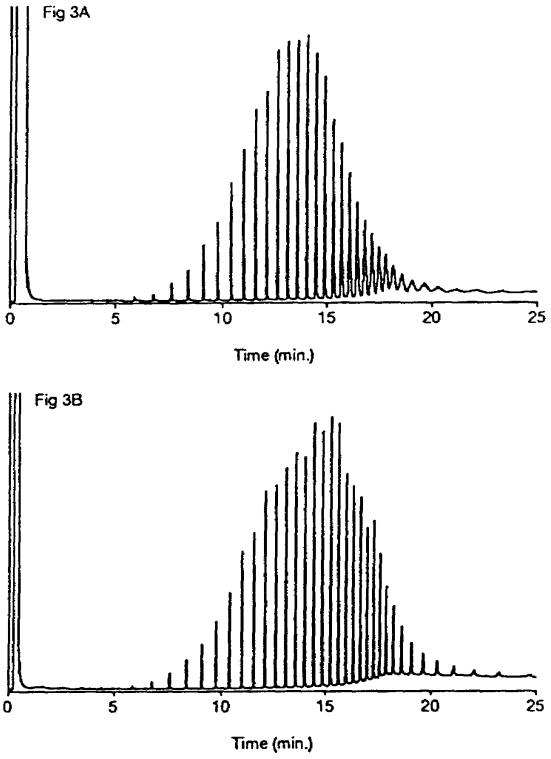

Figure 3. HT-GC separation of Polywax 655. Influence of PTV final temperature. A: final temperature = 400 ºC. B: Final temperature = 599 ºC. GC temperature programme started at 75 ºC.

A comparison of the quantitative data obtained with PTV injection and on-column injection is presented in figure 4. This figure shows the molecular weight distribution, i.e. relative peak areas as a function of the carbon number, for both PTV injection and on-column injection. The excellent agreement observed between PTV injection and on-column injection indicates that the high temperature PTV technique is free discrimination even if extremely high molecular weight components are analyzed (up to at least C_{80}). Figure 5 shows the analysis of Polywax 1000, a polyethylene standard with an average molecular weight of 1000 Dalton. This mixture shows peaks beyond C_{100}.

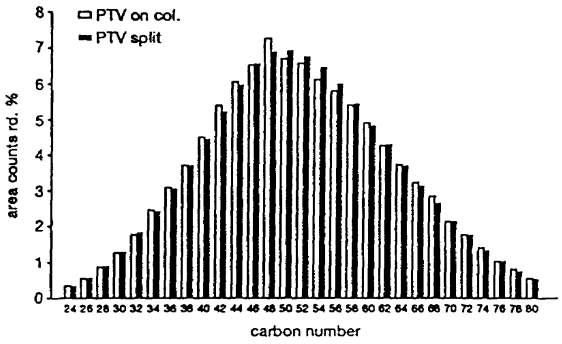

Figure 4. Molecular weight distribution of Polywax 655 determined by on-column injection and high temperature PTV injection.

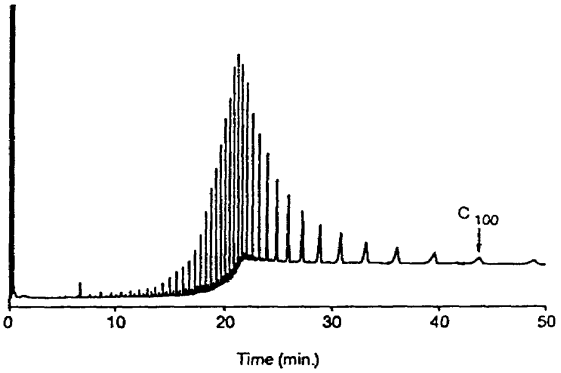

Figure 5. HT-GC separation of Polywax 1000. GC temperature programme started at 75 ºC.

Triglycerides

Both high temperature GC and capillary SFC have been put forward for the analysis of triglycerides. The analysis of this type of components is an important subject in different fields, i.e. characterisation of natural products, food products and bacterial identification. It is often claimed that high temperature GC yields erratic quantitative results because of thermal degradation or polymerisation of the triglycerides. Recent research indicates that except for the highly unsaturated triglycerides, most of the oils and fats can be analysed perfectly well by high temperature GC. The resolution offered by GC is far superior to that observed in SFC. High temperature GC in now routinely applied for the analysis of various natural- and food products. An example is quality control in the chocolate industry where the relative concentration of the POP, POS and SOS triglycerides can be used to determine whether a chocolate sample contains artificial cacao products. Figure 6 shows a chromatogram of a milk chocolate extract analysed using high temperature GC with PTV injection. The relative concentrations found for the tree components specified above were 19.3%, 47.29% and 33.37%. These concentrations were in good agreement with the data found using on-column injection and indicate that the chocolate does not contain articial cacao products. Also for this sample a retention gap is required when on-column

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injection is used because of the high concentrations of high molecular weight material co-extrected during extraction of the triglycerides. As the need for using a retention gap is eliminated when using high temperature PTV injection, a considerable reduction in the maintanance time can be obtained by using PTV injection instead of on-column sample introduction.

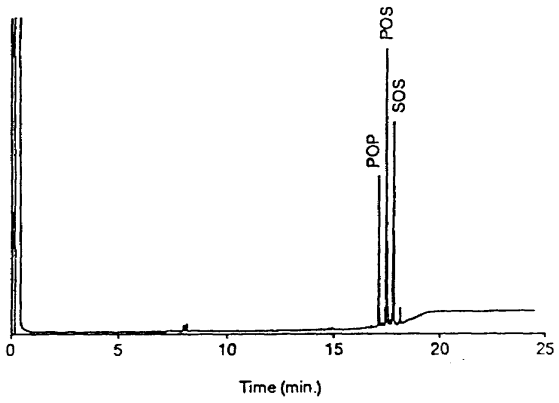

Figure 6. Analysis of triglycerides extracted from chocolate. Peak identification: P=palmitic-, O=oleic and S=stearic acid.

Surfactants

Ethoxylated alcohols represent an important class of industrial surfactants. For ethoxylated compounds with a molecular mass below about 1500 Daltons, high temperature GC can be used. An example of this class of surfactants is Triton X-100, an ethotylated alcohol which contains oligomers consisting from 2 to about 20 monomer units. Another example of this class of components is the surfactant Tergitol which is used in the manufacturing process of integrated circuits. Triton X-100 has been widely used to illustrate the potential of capillary SFC for the analysis of low volatility samples. Sandra et al. have shown that this material can also be analysed using high temperature GC. These authors also concluded that the derivatisation of this component into the TMS derivative was not necessary. Figure 7 shows the analysis of Triton X-100 using high temperature GC with PTV injection. This chromatogram shows a Gaussian distribution of the various oligometers. The top of the distribution occurs around about 10 monomers units which is in good agreement with the data obtained from SFC separations.

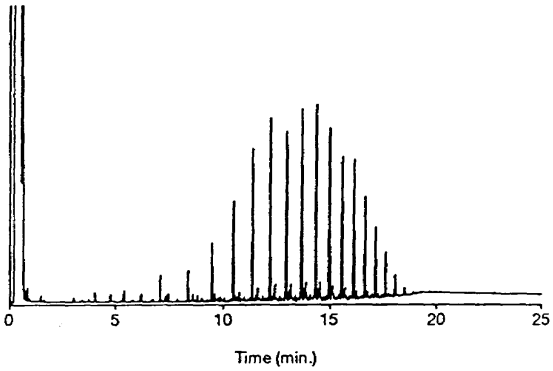

Figure 7. Analysis of Triton X-100.

Conclusions

High temperature capillary GC is an excellent analytical technique for the analysis of stable low volatility samples with molecular weight up to about 1500. Sample introduction in high temperature GC is the most difficult step of the analytical procedure. Up until now only on-column injection could be used as the sample introduction technique in HT-GC. The introduction of high temperature PTV injection where maximum PTV temperatures up to 600 ºC can be used significantly extends the applicability range of PTV injection, discrimination-free sample introduction of high molecular weights materials is possible. The reproducibility of relative peak areas and retention times obtained with on-column injection and PTV injection with high temperature PTV injection, are of comparable magnitude. For absolute peak areas ,however, on-column injection yields a better reproducibility. The main advantage of high temperature PTV injection is that this technique is easier to automate than on-column injection and, moreover, the need for coupling a retention gap to the analytical column is eliminated. Column contaminated. Column contamination with high molecular weight components can not occur as these impurities are retained in the liner of the injector. Contaminated liners can be easily replaced or cleaned. Thus reducing the maintance and down time costs.

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