Application Note No. 003

Use of a temperature programmable injector in the static and dynamic headspace analysis of aroma volatiles.

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Introduction

The equipment available for the static or dynamic headspace analysis of volatiles such as those found in aromas is expensive and often lacks the versatility required for research purposes. The objective of this investigation was to evaluate the use of the temperature programmable injector to both trap and desorb *in situ*, typical aroma components, such that subsequent GC analysis resulted in good chromatographic performance without intermediate cryofocusing.

Experimental

Instrumentation : An OPTIC temperature programmable injector (ATAS GL) fitted to an HP 5890 with FID.

Columns : A: 30 m x 0.25 mm i.d., 0.5 µm methyl silicone.
B: 30 m x 0.25 mm i.d., 5.0 µm diphenyl 5%) dimethyl silicone.

Carrier : Hydrogen at 26 cm/sec. Split ratio: 1:5-1:10

Adsorption traps.

Traps were constructed using the glass injector inserts supplied with the injector. The trap material (Tenax GC, 60/80 mesh) was held between silanized glass wool plugs. Traps were conditioned at 300°C in the injector for 8 hrs.

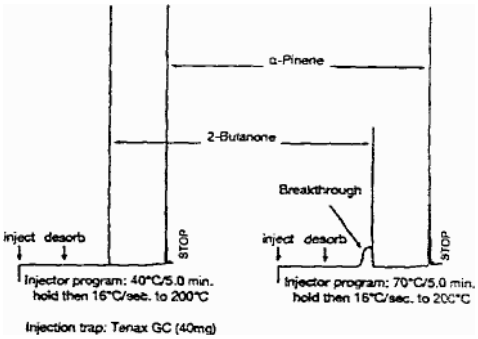
Test mixtures.

Test mixtures consisting of combinations of ethyl acetate, 2-butanone, butyl acetate and a-pinene were sealed in vials fitted with a septum. Samples of the headspace were injected using a range of syringes.

Results and discussion.

Trap characteristics. and breakthrough volumes.

A knowledge of the trap retention characteristics especially the breakthrough volumes of the analyses of interest is important in correctly interpreting subsequent analyses. The breakthrough volumes depend on the physical attributes of the trap, the type and amount of adsorbent, the temperature and the sample load. The breakthrough characteristics of the test mixture components were determent by injecting samples into the packed injector insert, held at known temperature and flow rate, in the injector body. Trap breakthrough if it occurred could be detected in the resulting chromatogram. An example is shown in Figure 1.



Column: B Temperature program: 40°C/5.5 min. hold then 15°C/min. to 180°C.

Figure 1.

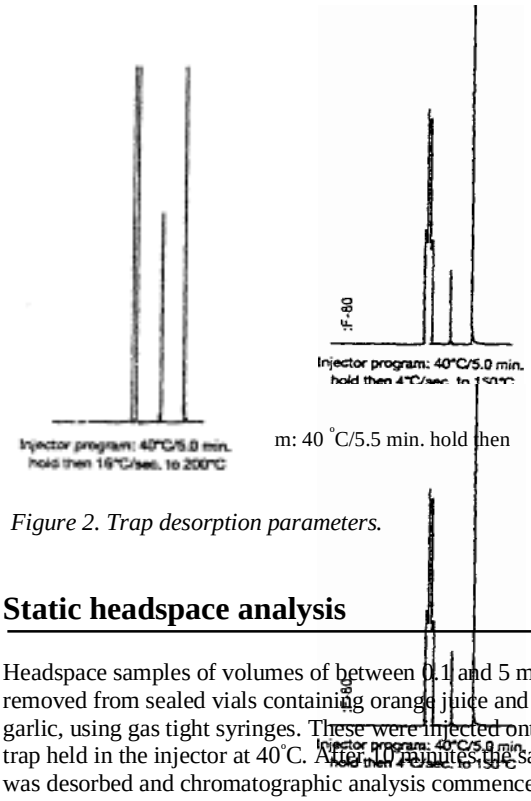
Traps containing 5, 10, 20 and 40 mg of Texan GC were tested. The 40 mg trap proved to have superior handling and breakthrough characteristics. When samples were desorbed

by heating from 40°C to 200°C at 16°C per second all four traps produced injection bands which resulted in identical and satisfactory, subsequent chromatographic performance. Trap temperature of 40°C were found to allow the complete retention of the low boiling compounds i.e.2- butanone and ethyl acetate for 10 minutes at flow rates of 7-12 ml per minute. Dimethyl sulfide could not be completely retained

under these conditions but was so at trap temperature of 30°C.

Trap desorption conditions.

The production bands sufficiently narrow to provide good chromatographic performance, for a given adsorbent, on the heating rate and final temperature of the injector and on the properties of the adsorbed components. For the compounds of the test mixtures a heating rate of 16°C/second and a final temperature of 200°C gave chromatograms with peaks having peak with values almost identical with those obtained by ordinary isothermal split injections. Lower heating rates (4 or 8°C/second) and/or upper temperatures (150°C) resulted in a notable decrease of resolution and overall chromatographic performance. See Figure 2.

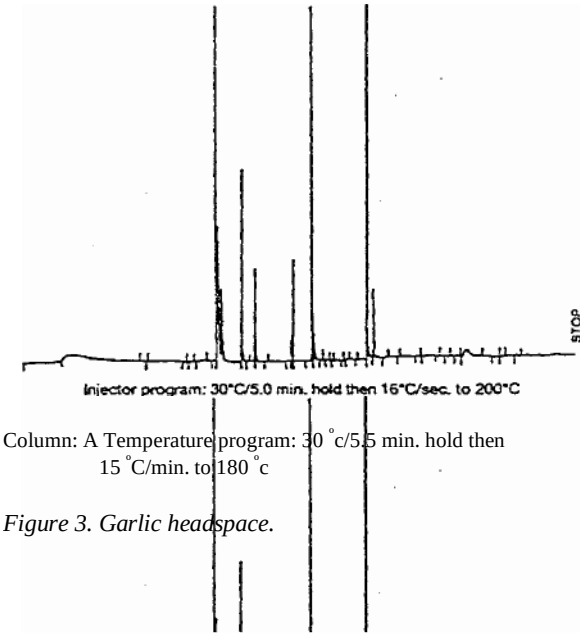


m: 40 °C/5.5 min. hold then

Figure 2. Trap desorption parameters.

Static headspace analysis

Headspace samples of volumes of between 0.1 and 5 ml were removed from sealed vials containing orange juice and crushed garlic, using gas tight syringes. These were injected onto the trap held in the injector at 40°C. After 10 minutes the sample was desorbed and chromatographic analysis commenced. Figure 3 shows an example of a chromatogram obtained from crushed garlic headspace.
Sample preconcentration by trapping multiple injections before analysis was also investigated. Figure 4 shows the chromatogram resulting from the injection of five successive 0.1 ml headspace injections of the headspace over orange peel made over two minute period. No loss of chromatographic performance was observed.



Column: A Temperature program: 30 °c/5.5 min. hold then 15 °C/min. to 180 °c

Figure 3. Garlic headspace.

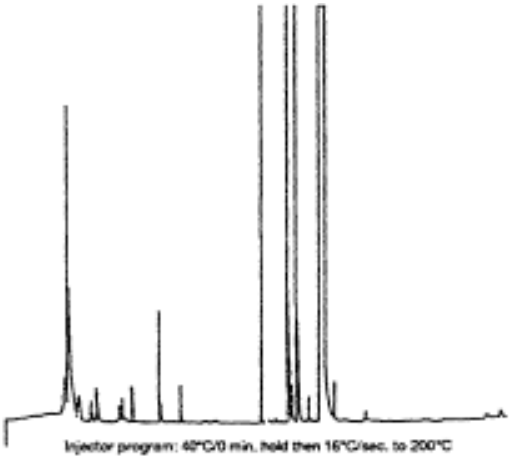
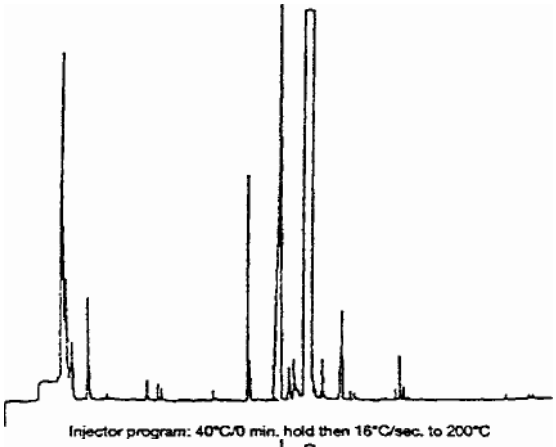


figure 4. Orange peel headspace (five successive 0.1 ml injections)

Dynamic headspace analysis

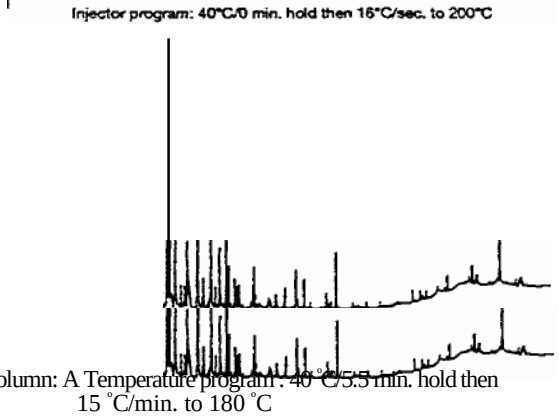
Two modes of collection, “offline” and “online” were evaluated. In the offline mode the packed injector insert was connected to the outlet of a suitable purge system. The sample for times ranging from 5 to 180 min. The trap was then transferred to the injector held at 40 °C and desorbed in the usual manner. An example of the chromatogram obtained from the headspace of commercial orange juice in this manner is shown in Figure 5.



Column: A Temperature program: 40 °C/0.5 min. hold then 8 °C/min. to 220 °C

Figure 5. Orange juice headspace.

In the 'online' system the exit from the purge system was lead directly into the injector held at 40 °C using a fused silica capillary. After passage of the appropriate. volume of headspace (measured at the splitter outlet) the capillary was disconnected and analysis commenced.
Figure 6 is an example of the chromatogram obtained from 50 ml of headspace from brewed coffee collected in this manner.



Column: A Temperature program: 40 °C/5.5 min. hold then 15 °C/min. to 180 °C

Figure 6. On-line collection of cofee headspace.

Chromatographic performance

One of the aims of this work was to see if a temperature programmable injector could both trap and adsorb a volatile sample such that subsequent GC analysis could take place without loss of resolution and without cryofocusing. Columns of both low (β = 16) and medium phase ratio (β = 125) were used since such columns are often the most suitable for volatiles analysis. Neither column showed any loss of resolution as evaluated by peak widths when used in combination with the correct sample desorption parameters.

Conclusion

The strengths and weakness of the various headspace methods are well documented[1] and variety of sophisticated equipment has been developed to meet particular applications. However the food chemist often needs a less complex and more flexible system such as that suggested by Kaipainen [2] for example. A programmable temperature injector with appropriate packed injector inserts enables many headspace analysis in both static and dynamic modes to be readily carried out without the necessity for cryofocusing. Correct choice of trapping and desorption conditions allows the maintenance of chromatograrphic integrity and provides opportunities for a range of samples introduction techniques. A variety of suitable adsorbents of different proporties are available and have the potential to enable selective trapping and analysis of components of complex mixtures. A PTV type injector is of course able to operate in all the usual injection modes as well and therefore constitutes 2 very flexible gas chromatographic accessory.

References.

1. B. Kolb, "Porc. 13th Int. Symp. Capillary Chromatography, "Riva del Garda, Italy, May 13 - 16 1991. Huthig, Heidelberg, Germany, Ed. P. Sandra and references therein.
2. A. Kaipainen, *J. High Resolut. Chromatogr.* 15 (1992) 751-755.

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