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COMPARATIVE ASSESSMENT OF THE ARTEFACT BACKGROUND ON THERMAL DESORPTION OF TENAX GC AND TENAX TA

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SUMMARY

The artefact background on thermal desorption of pre-conditioned Tenax GC and Tenax TA is compared. Superior blank gas chromatograms were obtained from Tenax TA, and an efficient pre-conditioning procedure to minimise background on heat desorption is proposed. The pooling technique described is suitable for the analysis of trace components of food aromas, especially relatively high-boiling components. The majority of the volatiles identified by combined gas chromatography–mass spectrometry analysis of pooled blank tubes were aliphatic, alicyclic and aromatic hydrocarbons. Many are common food aroma components, and their existence in blank experiments must be monitored carefully.

INTRODUCTION

Over recent years, the adsorption of volatile components onto synthetic porous polymers has been used widely as a means of investigating food aromas, and Tenax GC has been reported frequently as the adsorbent[1–6]. The aroma compounds are retrieved for subsequent analysis by thermal desorption or by solvent elution. Heat desorption has the advantage of rapidity and also that the aroma isolated has no solvent odour to interfere with any sensory analysis[7,8].

Tenax GC is a polymer based on 2,6-diphenyl-*p*-phenylene oxide[9]. It has a high affinity for organic compounds[10] and is regarded as the best porous polymer adsorbent when relatively high-boiling aroma components are of interest[11,12]. Unlike other polymers, *e.g.* the Chromosorbs and Porapaks, it has a very high temperature stability of 380–400°C[13,14] and is, therefore, particularly suited to heat desorption. It is fairly hydrophobic, and high recoveries of volatiles are obtained quickly on thermal elution[10,15]. Its thermal stability accounts for relatively low background levels, which can be decreased further by pre-conditioning at an elevated temperature, *e.g.* 200–360°C for 0.5–48 h under a stream of purified inert gas[10,16,17]. Nevertheless, the presence of certain artefacts on blank gas chromatograms has been established[18]. In order to characterise these potential contaminants, Lewis and Williams heated unconditioned Tenax GC at 250°C for 6 h under a purified nitrogen flow of 30 ml

min^{-1}, and identified several aliphatic and aromatic hydrocarbons in the effluent together with 27 unknown components[19]. Even after careful clean-up of the polymer, some artefacts remain[20] and in an attempt to overcome this problem, Tenax TA has become available recently[20].

In this paper we compare the background produced on heat-desorbing pre-conditioned Tenax GC and Tenax TA adsorption tubes treated identically, and describe a method for preparing Tenax TA adsorption tubes showing a minimal background on thermal elution.

EXPERIMENTAL

Preparation and conditioning of Tenax tubes

Tenax GC. Single tubes were prepared as follows. Acid (conc. hydrochloric acid)-washed glass tubes (20 cm × 4 mm I.D., 6 mm O.D.) were silanised by injecting 1 μl Silyl 8 (Pierce) under a nitrogen flow of 50 ml min^{-1} at 200°C for 30 min. The deactivated tubes were then packed with 200 mg Tenax GC (60–80 mesh, Chrompack) pre-conditioned under a nitrogen flow of 50 ml min^{-1} at 275°C for 24 h. The packed tubes were plugged with silanised glass wool (Phase Separations) and capped. Immediately before use, the tubes were conditioned under a nitrogen flow of 50 ml min^{-1} at 250°C for 2 min, cooled to room temperature, and this procedure repeated.

Pooled tubes were obtained by heat-desorbing thirteen single tubes, prepared as described above, onto another (collector) tube equilibrated at −76°C. Heat desorption occurred at 250°C for 1 min under a nitrogen flow of 30 ml min^{-1}, maintained for 2 min after heating.

All nitrogen supplies (BOC, CP grade) were dried and purified using 200 g molecular sieves 5A and 13X (BDH).

Tenax TA (tubes I). Single and pooled Tenax TA (60–80 mesh, Chrompack) tubes were prepared as described above for Tenax GC.

Tenax TA (tubes II). Single and pooled Tenax TA tubes were prepared as described above except that the Tenax TA was pre-conditioned at 340°C for 2 h under nitrogen. The packed tubes were then re-conditioned at 340°C for 2 h under nitrogen. Immediately before use, the tubes were further conditioned under nitrogen at 300°C for 15 min, cooled to room temperature, and this procedure repeated.

Gas chromatography

Single and pooled tubes were analysed by capillary gas chromatography (GC) using a Perkin Elmer Sigma 2B instrument. The normal capillary injector system was not used. Instead, the Tenax tube was attached to the helium carrier gas line and flushed with helium at 250 ml min^{-1} (1 p.s.i.) for 5 s to remove air. The remote end of the tube was then immediately attached to a fused-silica bonded phase DB5 open tubular GC column (60 m × 0.32 mm I.D. × 1 μm film; J & W Scientific), the first 0.3 m of which formed a U-trap cooled in liquid nitrogen. The helium pressure was increased to 20 p.s.i. (3 ml min^{-1} flow through the column). All connections were made using appropriate zero dead volume unions with graphite ferrules or Viton O-rings.

The Tenax was heated to 250°C over a period of 1 min and maintained at 250°C for an additional minute. During this time, helium carrier gas transferred any heat-desorbed volatiles into the cold trap, and the helium flow was maintained for

10 min after heating. The cold trap was then removed from the liquid nitrogen and fed into the GC oven, the temperature program being simultaneously started.

Other relevant GC conditions of analysis were: injector setting, 30°C; flame ionisation detector, 250°C; the oven temperature was increased from 30 to 55°C at 1°C min^{-1}, and from 55 to 200°C at 2°C min^{-1}, and held at 200°C until the end of the run; nitrogen make-up gas, hydrogen and air flows of 30, 30 and 500 ml min^{-1}, respectively; attenuation, ×64 (32 · 10^{-11} A f.s.). This attenuation setting is typical of that used in this laboratory for the analysis of trace volatile components of food aromas.

Gas chromatography–mass spectrometry

Components were identified as far as possible by gas chromatography–mass spectrometry (GC–MS) analysis of pooled tubes using a Perkin-Elmer Sigma 3 gas chromatograph interfaced via a single-stage all glass jet separator at 250°C to a Kratos MS 25 mass spectrometer linked on-line to a Kratos DS 50S data processing system and equipped with a computer-controlled multipeak monitoring (MPM) unit. The GC conditions described above were used. Significant operating parameters of the mass spectrometer were: ionisation voltage, 70 eV; ionisation current, 100 μA; source temperature, 200°C; accelerating voltage, 4 kV; resolution, 600; scan speed, 1 s per decade, repetitive throughout the run.

RESULTS AND DISCUSSION

After evaluating a range of conditioning parameters, including different temperatures and different flow-rates for varying time periods, best results were obtained
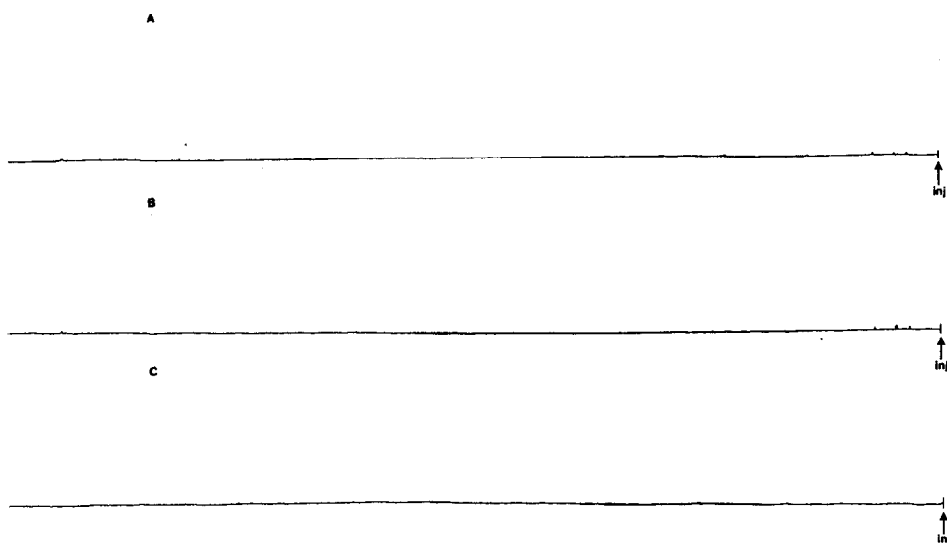

Fig. 1. Gas chromatograms obtained on heat-desorption of single Tenax tubes. (A) Tenax GC pre-conditioned under nitrogen at 275°C for 24 h and 250°C for 2 min (twice); (B) Tenax TA (tubes I) preconditioned under nitrogen at 275°C for 24 h and 250°C for 2 min (twice); (C) Tenax TA (tubes II) preconditioned under nitrogen at 340°C for 4 h and 300°C for 15 min (twice).

as described in the Experimental section. Experience also showed that the additional brief conditioning treatment immediately before use was particularly beneficial for minimising background on blank gas chromatograms. This technique was therefore implemented in all the comparisons made in this study.

Gas chromatograms obtained from single Tenax GC and Tenax TA (tubes I) tubes conditioned identically are shown in Fig. 1A and B. The baselines obtained are good and there is no significant difference between the two. This small amount of background was reduced further to negligible proportions (as shown in Fig. 1C) by subjecting Tenax TA to a more rigorous heat-conditioning treatment (tubes II). For some food aromas, where the main sensory contributors are present in fairly large concentrations, single tube analyses are adequate, and the excellent baseline from Tenax TA shown in Fig. 1C is certainly acceptable.

However, in many instances nowadays, flavour research has advanced to the point where the main requirement is to analyse trace components, and the pooling technique described in the Experimental section is useful. Clearly, the number of tubes pooled depends on the composition of the aroma being analysed, and in this laboratory, up to fourteen pooled tubes have been used on different occasions.
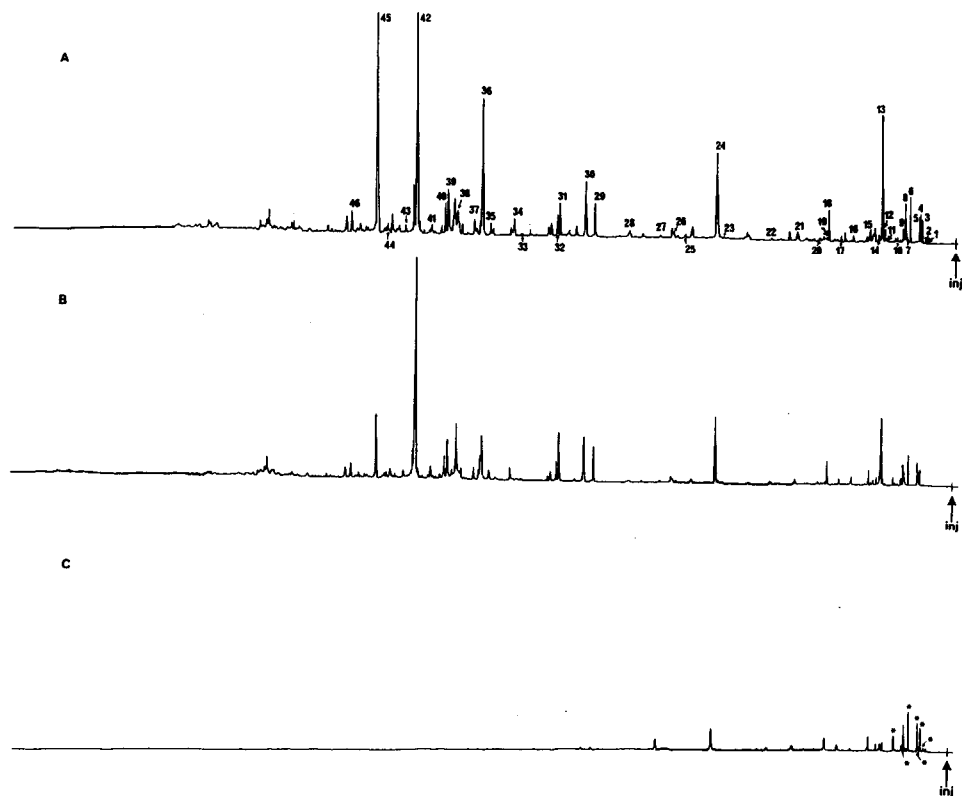

Fig. 2. Gas chromatograms obtained on heat-desorption of pooled Tenax tubes. (A) Tenax GC pre-conditioned under nitrogen at 275°C for 24 h and 250°C for 2 min (twice); (B) Tenax TA (tubes I) pre-conditioned under nitrogen at 275°C for 24 h and 250°C for 2 min (twice); (C) Tenax TA (tubes II) pre-conditioned under nitrogen at 340°C for 4 h and 300°C for 15 min (twice). (For peak identification see Table I.)

TABLE I

COMPONENTS IDENTIFIED BY GC–MS ANALYSIS OF POOLED TUBES

Peak numbers correlate with Fig. 2.

Component and class	Peak number	Component and class	Peak number
Aliphatic hydrocarbons		*Benzenoids*	
Butane*	5	Benzene	18
Pentane	9	Toluene	24
Hexane	15	Ethylbenzene	29
Heptane	21	Propylbenzene	35
Octane	26	Butylbenzene	44
Nonane	32	Xylenes	30, 31
Decane	39	A trimethylbenzene	40
Undecane	46	C_3 alkylbenzenes	33, 37, 38, 42
Methylpropane*	3	A methylstyrene or indan	43
2-Methylbutane*	6	Benzaldehyde	36
2-Methylpentane	13	Acetophenone	45
3-Methylpentane	14	*Halogenated compounds*	
3-Methylhexane	20	Dichloromethane*	11
2-Methylheptane	23	Trichlorofluoromethane*	7
A branched-chain hydrocarbon	19	1,1,1-Trichloroethane	17
Methylpropene*	4	1,1,2-Trichloro-1,2,2-trifluoroethane	10
? 2,2-Dimethylhex-3-ene	25	Tetrachloroethene	27
Alicyclic hydrocarbons		A dichlorobenzene	41
Cyclohexane	18	*Miscellaneous compounds*	
Methylcyclopentane	16	Carbon dioxide**	1
Methylcyclohexane	22	Carbonyl sulphide*	2
Ethylcyclohexane	28	Acetone	8
Propyl or isopropylcyclohexane	34	Trimethylsilanol***	12

    * Component contributed by the pooling gas.
    ** Component contributed by the pooling coolant (carbon dioxide).
    *** Component contributed by silanisation of glass tubes.

    Gas chromatograms obtained from fourteen pooled Tenax GC and Tenax TA (tubes I) tubes conditioned identically are shown in Fig. 2A and B. Neither is acceptable as a blank chromatogram. The more rigorous heat-conditioning of Tenax TA (tubes II) before pooling produced the chromatogram shown in Fig. 2C, which represents the best baseline obtained from fourteen pooled tubes. Experiments involving the use of different temperatures for different times for conditioning the Tenax TA, and also the use of purified helium instead of nitrogen as purge gas, whether purified as described in the Experimental section or using a rare gas purifier (British Oxygen, RGP MK 3), resulted in inferior blank chromatograms. Pellizzari *et al.*[21] have reported that extracting Tenax GC with acetone for 18 h reduced background levels, but this procedure did not improve blank chromatograms when applied to Tenax TA in this study. The peaks asterisked in Fig. 2C are, in fact, contributed by the pooling gas and could not be minimised further. For the analysis of relatively high-boiling components, Fig. 2C is an acceptable blank, but generally speaking, the technique is being pushed to its limits under the conditions described, as far as very low boiling components are concerned.

Components identified by combined GC–MS analysis of pooled tubes are listed in Table I, in which the peak numbers correlate with Fig. 2. In all cases, mass spectra agreed with those in the *Eight-Peak Index of Mass Spectra*[22]. The majority of the components identified were aliphatic, alicyclic or aromatic hydrocarbons. Many are commonly-occurring food aroma components[23], and therefore their existence in blank experiments needs to be monitored with care.

CONCLUSION

Superior blank chromatograms were obtained from Tenax TA than from Tenax GC. The most efficient pre-conditioning procedure for Tenax TA, in order to minimise artefact background on thermal desorption, consisted of heating the adsorbent under purified nitrogen for 4 h at 340°C and then at 300°C for two separate periods of 15 min immediately before use [see Experimental section, *Tenax TA (tubes II)*]. The pooling technique described is suitable for the analysis of trace components of food aromas, and especially so for relatively high-boiling components.

ACKNOWLEDGEMENTS

REFERENCES

1 P. E. Palkert and I. S. Fagerson, *J. Food Sci.*, 45 (1980) 526.
2 P. Simon, R. Lindsay and C. Peterson, *J. Agric. Food Chem.*, 28 (1980) 549.
3 R. G. Buttery, R. M. Seifert, L. C. King, E. L. Soderstrom, J. M. Ogawa and J. G. Turnbaugh, *J. Agric. Food Chem.*, 32 (1982) 1208.
4 D. S. Mottram, R. A. Edwards and J. J. H. MacFie, *J. Sci. Food Agric.*, 33 (1982) 934.
5 D. S. Mottram and R. A. Edwards, *J. Sci. Food Agric.*, 34 (1983) 517.
6 D. S. Mottram, S. E. Croft and R. L. S. Patterson, *J. Sci. Food Agric.*, 35 (1984) 233.
7 C. G. Tassan and G. F. Russell, *J. Food Sci.*, 39 (1974) 64.
8 A. M. Galt and G. MacLeod, *Chem. Ind.*, (1984) 445.
9 R. van Wijk, *J. Chromatogr. Sci.*, 8 (1970) 418.
10 W. Bertsch, R. C. Chang and A. Zlatkis, *J. Chromatogr. Sci.*, 12 (1974) 175.
11 A. L. Boyko, M. E. Morgan and L. M. Libbey, in G. Charalambous (Editor), *Analysis of Foods and Beverages: Headspace Techniques*, Academic Press, London, 1978, p. 57.
12 R. A. Cole, *J. Sci. Food Agric.*, 31 (1980) 1242.
13 K. Sakodynskii, L. Panina and N. Klinskaya, *Chromatographia*, 7 (1974) 339.
14 W. Bertsch, E. Anderson and G. Holzer, *J. Chromatogr.*, 112 (1975) 701.
15 R. D. Barnes, L. M. Law and A. J. MacLeod, *Analyst (London)*, 106 (1981) 412.
16 S. S. Lin, *J. Agric. Food Chem.*, 24 (1976) 1252.
17 C.-C. Chen, M.-C. Kuo, L. S. Hwang and J. S.-B. Wu, *J. Agric. Food Chem.*, 30 (1982) 1211.
18 G. Holzer, H. Shanfield, A. Zlatkis, W. Bertsch, P. Juarez, H. Mayfield and H. M. Liebich, *J. Chromatogr.*, 142 (1977) 755.
19 M. J. Lewis and A. A. Williams, *J. Sci. Food Agric.*, 31 (1980) 1017.
20 *Chrompack News Special*, Tenax, Chrompack, Middelburg, 1982, p. 1.
21 E. D. Pellizzari, B. H. Carpenter and J. E. Bunch, *Environ. Sci. Tech.*, 9 (1975) 556.
22 *Eight Peak Index of Mass Spectra*, Mass Spectrometry Data Centre, Aldermaston, 3rd ed., 1983.
23 S. van Straten, F. L. de Vrijer and J. C. de Beauveser (Editors), *Volatile Compounds in Foods*, Central Institute for Nutrition and Food Research, TNO, Zeist, 4th ed., 1977, Supplements 1983, 1984.