226. McCormick, J.P., Sommerville, B.A., Eggert, F., Wobst, B. and Broom, D.M. 1995. Gas chromatography and pattern matching of headspace samples from human sweat. In: *Chemical Signals in Vertebrates, VII,* ed. R. Apfelback, D. Müller-Schwarze, K. Reutter and E. Weiler, *Adv. Biosci.*, 93, 539-542. Oxford: Pergamon.

Gas Chromatography and Pattern Matching of Headspace Samples from Human Sweat

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ABSTRACT

In order to obtain reproducible chromatograms of head space samples, a recirculating system powered by a pump sufficiently powerful to load large Tenax traps, was built. All parts of the system could be solvent cleaned and the sample holder and trap could be maintained at any convenient temperature. To demonstrate the versatility and reliability of this system, head space analysis of human underarm sweat was carried out and pairs of chromatograms pattern matched using a computer programme. With four different match measures, it was found that sweat from three pairs of identical twins consistently matched better than sweat samples from pairs of unrelated people.

KEYWORDS

Headspace sampling; new technique; chromatograms; pattern matching.

INTRODUCTION

Head-space sampling and the trapping and concentration of trace volatiles is commonly employed in environmental control, semiochemical and medical research and in the food, drink, flavour and perfume industries. Such samples are commonly composed of 50 to 300 volatiles covering a wide range of boiling points and small changes in the volume of headspace sampled, the ambient temperature or humidity can greatly affect the profile of the chromatograms. Any automated method of pattern matching will only give valid results if successive chromatograms can be accurately replicated and so it is essential to be able to control all the factors affecting the chromatographic profile. The new trap loading system described below, allows this to be done.

METHODS

The apparatus shown in Fig. 1 was used to load the sweat volatiles into the Tenax traps. The oven was set at 70° C and 120 ml of dry air recirculated for 2 min to load the first trap and then, immediately, a second trap was loaded for 3 min and lastly a third trap for 5 min. Full details of the design and performance of this loading system are given in Sommerville *et al.* (1994a).

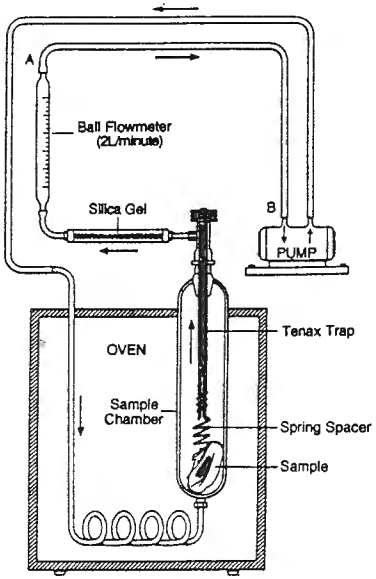

Fig. 1: A recirculating system for loading Tenax traps

After loading, a trap was introduced into the injector port of a gas chromatograph (GC) and the sample desorbed from the trap at 320°C and injected onto a 12 m capillary column (BP 10 / OV 1701; internal diameter 0.22 mm; external diameter 0.33 mm; film thickness 0.25 µm) using an S.G.E. updated head space injector system. The GC oven was programmed to run from 40°C to 190°C ramping at 6°C / min. The GC / flame ionisation detector (FID) was interfaced with an ATARI ST 1040 computer which stored the FID output on disc. Using pattern matching software modified from Marshall et al. (1987), four computerised pattern matching measures were carried out on pairs of chromatograms A and B:

1. The alignment coefficient measured the ratio of the number of peaks aligned in A and B to the total number. If A and B were identical, all peaks would be aligned and the ratio would be 1.
2. The profile correlation is a similarity measurement of the shapes of A and B for a selected length of the chromatograms. A perfect match again gave a figure of 1.
3. The Euclidean distance is a measure of dissimilarity that summated the difference in height of each aligned peak and was useful where there were a few major differences in peak height between A and B. The better the match, the lower was the figure.
4. The box car distance is also a dissimilarity measure based on peak height and was useful where there were a lot of small differences.

Full details of these match measures are given in Sommerville *et al.* (1994b).

The donors were three pairs of twins whose DNA profiles proved that they were monozygous. Samples of their sweat were collected on cotton squares pinned to the underarm region of a T-shirt for 8 hours. Chromatograms of the sweat volatiles were matched in twin pairs and also matched across the pairs to give a measure of a non-related person match.

RESULTS AND DISCUSSION

Figure 2 shows the effect of loading three successive traps from the same sample enabling the analyst to select different ranges of volatiles. Chromatograms derived from the first and third trap loads are shown.

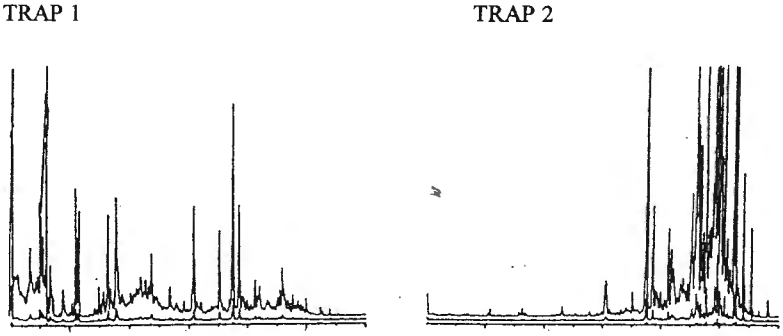

Fig. 2: Chromatograms from Tenax trap 1 (loaded 0-2 min.) and Tenax trap 3 (loaded 5-10 min.) illustrating the weighting of high volatiles to the first trap and low volatiles to the third

The pattern matching was carried out on only the second trap load which gave the best resolution of the mid volatile region with both high and low volatiles evident. One-tailed t-tests (probability) comparing the means of twin pair matches and non-related pair matches for the four match measures were:

alignment coefficient	5.18	($p>0.0002$)
profile correlation	7.33	($p>0.0001$)
Euclidean distance	4.26	($p>0.0009$)
box car distance	2.96	($p>0.007$)

The significant ($p < 0.007$-0.0001) differences between the twin matches and the non-related matches, were far higher than the $p < 0.05$ for Euclidean difference obtained by Sommerville *et al.* (1990) using an older less versatile technique to load the Tenax traps. In that report, none of the other three match measures achieved statistical significance. The approximately two-fold difference between the Euclidean and box car distances, suggest that volatile identity signals may depend upon a lot of small, rather than a few large variations in peak height.

Work is now in progress, using mass spectrometry, to identify the volatile compounds that may be involved in signalling identity.

ACKNOWLEDGMENTS

We should like to express our gratitude to the sweat donors, who have gone to a great deal of trouble on behalf of this project, to Dr. Alan Bleasby who wrote the pattern matching programme and, last but not least, to the Welcome Trust who funded this project.

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