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Short Communication

Thermal desorption– and sniffing–mass spectrometric monitoring of enriched trace compounds by means of a "live total transfer system"

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ABSTRACT

A system for thermal desorption of samples obtained by enrichment of airborne chemicals or column effluents is described. The enriched components from the adsorption traps are transferred to the capillary column by a valveless switching system originally developed for multi-dimensional gas chromatography. When applied to flavour analysis (*e.g.* passion fruit), the additional sniffing–mass spectrometry monitoring facility proved to be useful for the detection of sensorially active trace compounds (*e.g.* 7,8-dihydro-β-ionone, β-damascenone). The ease of changing between multi-dimensional gas chromatography operation and thermal desorption allows a maximum of flexibility with regard to different analytical tasks.

INTRODUCTION

The identification of sensorially active trace compounds in complex mixtures such as fruit flavours requires appropriate gas chromatographic (GC) systems and procedures suitable for solving different analytical problems [1]. Multi-dimensional GC (MDGC) in combination with simultaneous sniffing–mass spectrometric (MS) monitoring [2] and different sampling techniques (*e.g.*, liquid injection, dynamic headspace, thermal desorption of samples obtained by enrichment of substances on adsorption traps) have proved to be suitable tools for structure elucidation of sensorially active compounds [1,3,4].

Frequently, when dealing with flavour extracts which, apart from the main constituents, contain numerous compounds at trace levels, enrichment steps are necessary to obtain sufficient amounts for the determination of spectroscopic data (*e.g.*, MS, IR and NMR). Therefore, GC systems for micropreparative enrichment of the effluents from GC capillary columns have been developed in recent years [5–9]. Maxi-

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mum analytical information is obtained if these enriched substances can be analysed in undiluted form, which, in the case of combined GC–spectroscopic systems such as GC–sniffing–MS or GC–Fourier transform IR, is achieved by direct thermal desorption [3] of the sample. When direct sampling of sorption traps is used with capillary columns, special desorption devices are required [3].

This paper describes a thermal desorption facility obtained after minor modifications of a multi-dimensional double-oven system for coupled packed capillary columns. Apart from a flow regulator, no additional equipment is required and, owing to the modular type of construction, multi-dimensional analysis with packed or capillary columns and also direct splitless sampling of sorption traps, containing trapped airborne chemicals or enriched column effluents, into a capillary column can be performed.

SYSTEM DESCRIPTION AND OPERATION

Micropreparative enrichment of sensorially active components

This was performed on a Siemens SiChromat 2 double-oven gas chromatograph equipped with an automatic injection device, sniffing facilities for both column effluents and a micropreparative module for enrichment of capillary GC effluents as described [5].

Preseparation was achieved by splitless injection of 4 μl of passion fruit extract on an SE-54 fused-silica capillary column (20 m × 0.53 mm I.D., film thickness 1.5 μm) programmed from 120 to 200°C at 4°C/min, at a helium flow-rate of 2 ml/min (column I). By means of a valveless Live-T column-switching device, only the peak group of interest (retention range 20–35 min) was entirely transferred into an FFAP fused-silica capillary column (20 m × 0.53 mm I.D., film thickness 1.5 μm) programmed from 100°C (maintained for 20 min) to 190°C at 2°C/min, at a helium flow-rate of 3 ml/min (column II). Cuts into two different precooled sorption traps (packed with 3% OV-101 on Chromosorb W-AW) at retention ranges corresponding to the elution of two compounds of sensorial interest (cut A, 39.8–40.2 min; cut B 41.4–41.7 min) were performed as described (trapping efficiency > 90%) [5]. After 34 injection cycles (total analysis time 42.5 h), both traps were analysed by thermal desorption (see below).

Thermal desorption

Thermal desorption was carried out on a Siemens SiChromat 2 double-oven gas chromatograph by replacement of the precolumn in the first oven with a sorption trap (Fig. 1). A constant desorption flow-rate of 20 ml/min through the sorption trap is achieved by means of an orifice-type flow regulator adjusted to a specific helium pressure with pressure regulator PR1. Thermal desorption of enriched volatiles in the sorption trap is achieved by heating the first oven from 30 to 205°C (10 min). The direction of substance flow eluting from the sorption trap depends on the direction of flow in the transfer tube, which is controlled by solenoid valve SV_2 (Fig. 1). The direction of flow in the transfer tube is determined by the differential pressure set on the total transfer system by adjustment of NV1+, NV1− and NV-Dos as described [10,11]. A positive differential pressure (trapping) diverts the substance flow from the sorption tube into the precooled transfer tube (−150°C), whereas a negative differ-

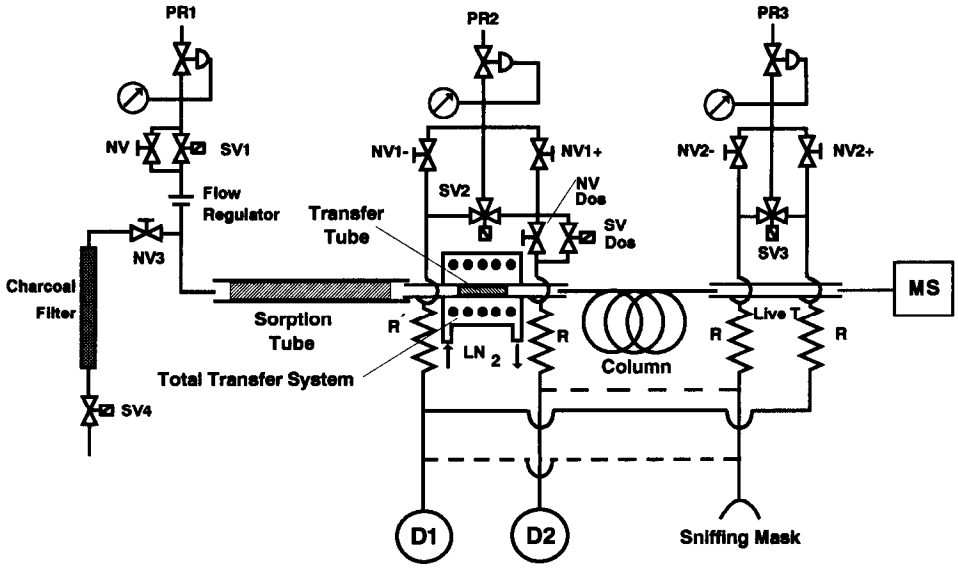

Fig. 1. Schematic diagram of the "live total transfer" system adapted for thermal desorption and GC–sniffing–MS monitoring of sorption tubes containing enriched airborne chemicals or column effluents. PR = Pressure regulator; SV = solenoid valve; NV = needle valve; R = restriction; D = flame ionization detector; LN2 = liquid nitrogen; MS = mass spectrometer.

ential pressure diverts the substance flow to flame ionization detector D1 and the "sniffing mask" via restriction R′ (Fig 1).

After cryofocusing of the volatiles, the transfer tube is heated to 200°C (2 min) in order to "inject" the sample quantitatively into the analytical capillary column. The differential pressure necessary for quantitative transfer (ejection) into the capillary is obtained by opening solenoid valve "Dos". After "injection", the gas flow in the transfer tube is reversed by actuating SV_2 and the sorption tube is backflushed by closing SV1 and opening SV4 (see Fig. 1). During GC separation, the volatiles can be sniffed and simultaneously monitored by the directly coupled mass spectrometer using a Live-T switching device as described [2].

Total transfer system

The transfer tube (1/8-in. glass-lined stainless steel) was packed with 5% SE-30 on Chromosorb G (10 mm packing length). The trapping flow-rate was 20 ml/min, ejection flow-rate 1 ml/min and backflush flow-rate 30 ml/min. Differential pressures were set to +10 mbar for trapping, +1,5 mbar for ejection and −35 mbar for monitoring the substance flow on the flame ionization detector (D1) or backflushing of the sorption tube.

Analytical column

A Carbowax 20M glass capillary column (25 m × 0.3 mm I.D., film thickness 0.3 μm) was used, programmed from 100 to 200°C at 4°C/min. The carrier gas was helium at 1.3 ml/min.

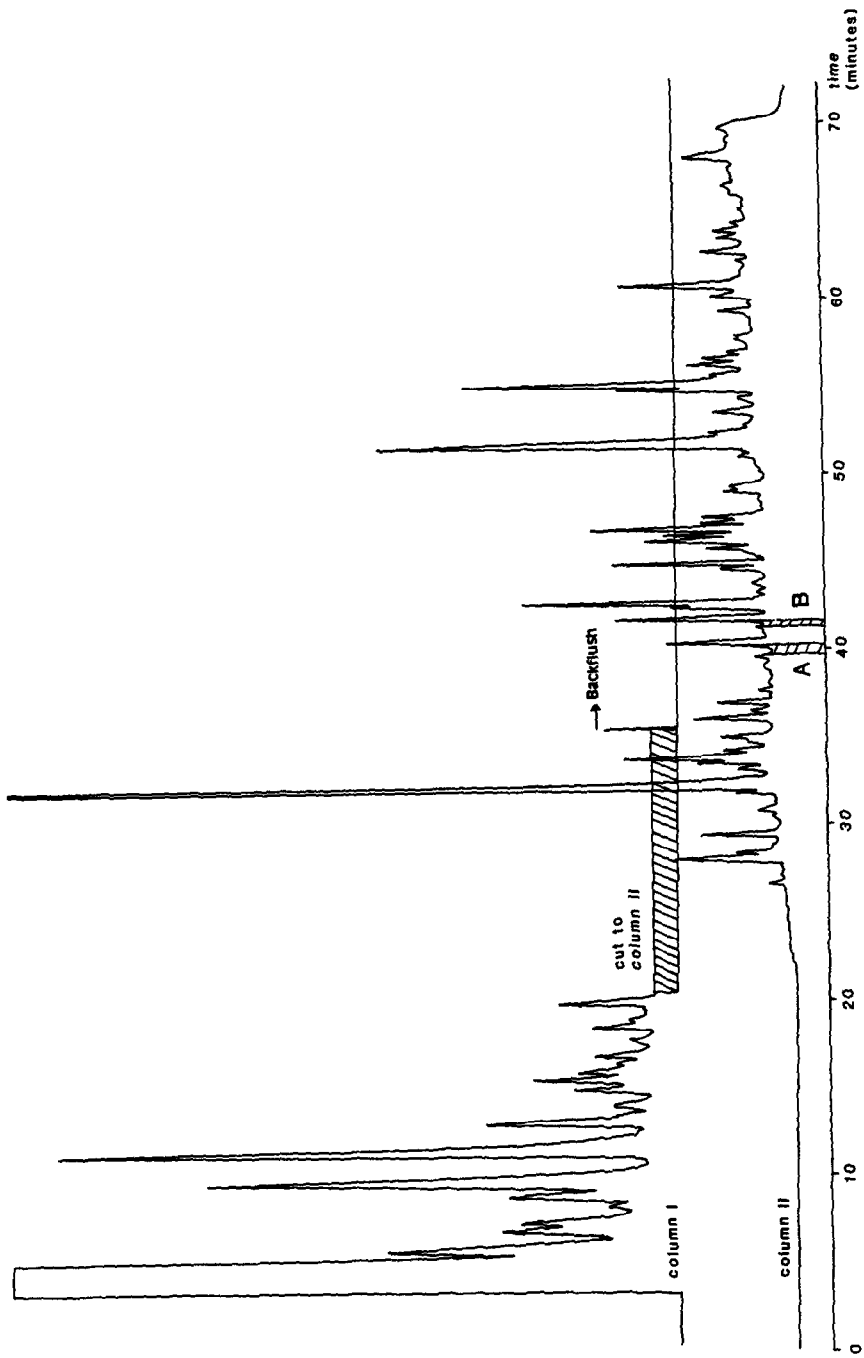

Fig. 2. Gas chromatograms of a passion fruit extract on column I and of the selected cut on column II. Marked areas A and B correspond to the elution ranges of compounds with typical fruity odour impressions (see text).

Mass spectrometer

A Finnigan Model 4021 C quadrupole mass spectrometer operated at 70 eV ionization energy and an ionization chamber temperature of 250°C was used. A mass range from 33 to 400 a.m.u. with a scan cycle time of 0.55 s was recorded.

APPLICATION

An application in the flavour field is given as an example.

GC sniffing analysis of a pentane–diethylether extract from fresh yellow passion fruits, carried out on a Carbowax 20M column, showed "fruity-tropical passion fruit-like" flavour impressions eluting after phenylethyl acetate (retention index *I* 1795–1815), but no positive identification of compounds responsible for these odours could be achieved by GC–MS analysis of the extract. On an SE-54 column (column I), the

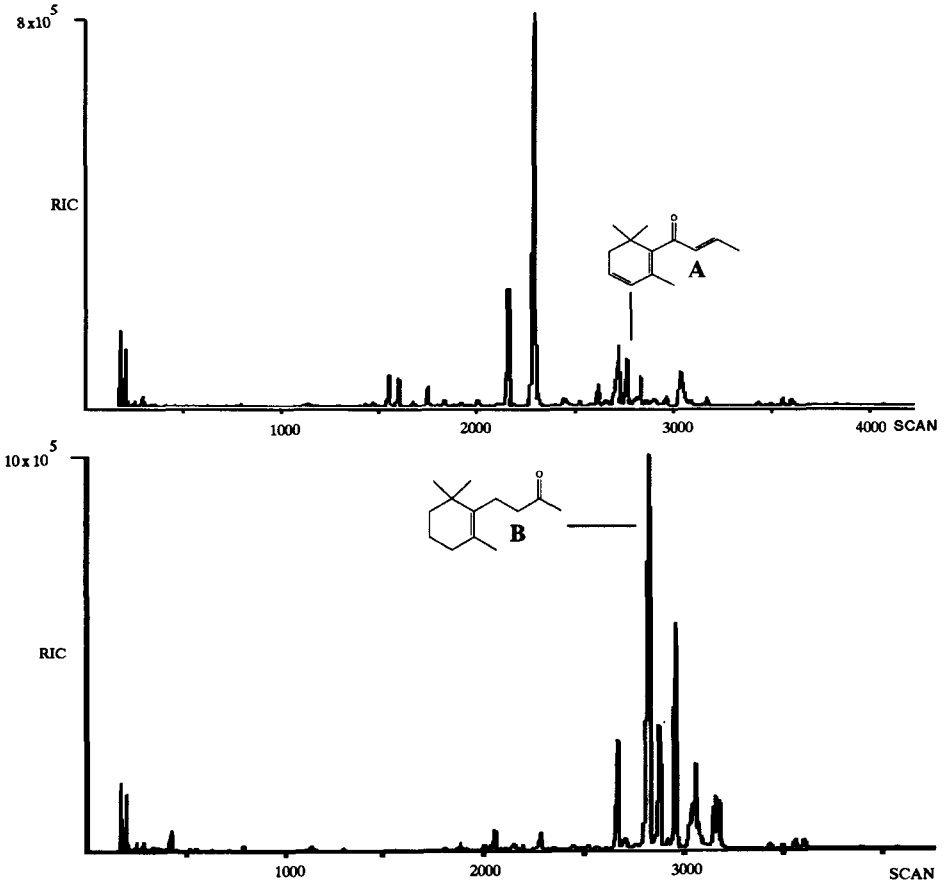

Fig. 3. Reconstructed ion chromatograms (RIC) of thermally desorbed volatiles from sorption tube A (upper trace) and sorption tube B (lower trace). Odorous compounds identified by simultaneous sniffing–MS monitoring: (A) β-damascenone and (B) 7,8-dihydro-β-ionone.

typical odour impressions resembling tropical fruits were recorded near the retention of the major component hexyl hexanoate (I 1375–1435). The effluents in this retention range were cut into a FFAP column (column II) and two regions of sensorial interest (A, "fresh fruity, gooseberry-like"; B, "powerful fruity, apricot-like"; see Fig. 2) were enriched on two different sorption traps using the micropreparative system described previously [5].

Thermal desorption of the enriched volatiles and subsequent MS analysis revealed that β-damascenone (A) (see Fig. 3, $R_{I\ CW\ 20\ M}$ 1797, $R_{I\ SE\text{-}54}$ 1380, m/z 69, 121, 41, 105, 91, M^+ 190) and 7,8-dihydro-β-ionone (B) (see Fig. 3, $R_{I\ CW\ 20\ M}$ 1807, $R_{I\ SE\text{-}54}$ 1431, m/z 43, 121, 41, 93, 161, M^+ 194) were responsible for these flavour impressions. Both volatiles are known ingredients of yellow passion fruit flavour, but could not be detected in our study by direct GC–MS analysis of an extract from nearly 1 kg of passion fruit because of its low concentration level.

Compound B was identified by Winter and Klöti [12] in an extract of 539 kg of yellow passion fruit juice; compound A was detected in yellow passion fruits after distillation for 2 h at pH 3 by Tressl and Engel [13]. Liberation of both C_{13}-norterpenoids from glycosidically bound precursors was presumed [13]. In contrast to our findings, the odour of compound A has been described as "fruity, rose-like" [14]. A "fruity-berry" odour comparable to that detected in the passion fruit extract was also observed during the investigation of cape gooseberry [15]. After micropreparative enrichment, thermal desorption and sniffing–MS monitoring, β-damascenone could also be identified.

CONCLUSIONS

The arrangement described has proved to be invaluable in the GC–MS analysis of compounds present at trace levels, especially in biological systems. A 500–1000-fold increase in the signal-to-noise ratio can be obtained with thermal desorption and splitless transfer on the capillary column as compared with solvent elution of sorption traps containing enriched substances and subsequent splitless liquid sample injection. When applied to the analysis of sensorially relevant components at trace levels, MS monitoring of the eluate in addition to the sniffing facilities is indispensable for identification purposes. If a deliberately unbalanced total transfer system is used, sniffing of the whole eluate and of each separated component can also be performed. In this instance an additional connection of the sniffing mask to D1 or D2 as indicated with dashed lines in Fig. 1 is necessary.

The ease of changing between multi-dimensional operation and thermal desorption allows maximum flexibility with regard to different analytical tasks.

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