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DIRECT HEADSPACE GAS CHROMATOGRAPHY WITH FUSED-SILICA CAPILLARY COLUMNS AND MULTIPLE SIMULTANEOUS DETECTION

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SUMMARY

Some direct headspace analyses of industrial waste water samples, polymers and foods, are illustrated. These analyses have been performed with automatic high-resolution gas chromatography dedicated instrumentation, including fused-silica columns and various multidetector configurations. The use of fused-silica columns also permits the convenient use of an improved and simple effluent splitter. This splitter can be adapted to any position of the oven and also permits varying the splitting ratio.

INTRODUCTION

Headspace analysis is now widely recognized as one of the most useful and important auxiliary techniques in gas chromatography (GC). In fact, its features of simplicity, speed and the elimination of preliminary sample preparation make it an invaluable analytical method for the determination of volatile constituents, even at trace levels, in products of very complex nature.

The complexity of these mixtures requires the use of capillary columns because of their high separating efficiency, great sensitivity and low bleed. However, the qualitative and quantitative determination of specific components at ppb* levels requires the use of selective detectors. For instance, the analysis of aromas and environmental pollutants must often be performed with different types of detectors.

In such cases, the use of individual detectors, in a given sequence, unduly prolongs operations, because the entire system has to be reconditioned each time they are changed and the analysis must be repeated. For these reasons, the use of multiple detection can provide the following benefits. (i) The analysis time is drastically reduced, since several items of specific information are obtained simultaneously after a single injection. This is particularly useful in cases of product identification by fingerprints. (ii) Bands of trace components, which may be affected by adjacent bands of major components are better resolved. In practice, therefore, multidetector operations may improve selectivity, provide additional information for the

* Throughout this article, the American billion (10^9) is meant.

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confirmation and identification of certain components and increase the number of detectable substances[1,2].

The use of glass capillary columns, combined with the headspace technique and multidetector operations has previously been reported[3,4]. In this paper we will illustrate some headspace analyses performed with fused-silica columns which, by virtue of their characteristics of flexibility and ease of handling, greatly facilitate the use of this technique.

EXPERIMENTAL

Fig. 1 shows the automatic system used for the direct GC analysis of headspace samples. It consists of a dedicated capillary gas chromatograph with sub-ambient temperature capability, coupled with an automatic headspace sampler.

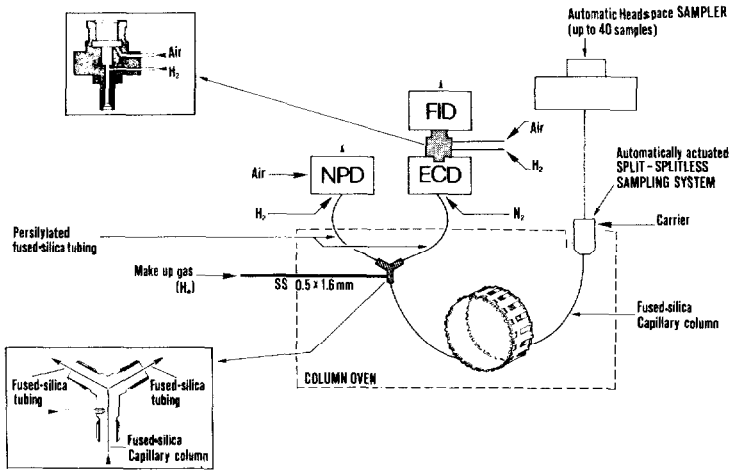

Fig. 1. Headspace configuration with multidetector system. ECD = Electron-capture detector; FID = flame ionization detector; NPD = nitrogen–phosphorus detector; SS = stainless steel.

Sample withdrawal and injection operations in the split or splitless mode are automatically performed by a thermostatted gas-tight syringe. This injection system is completely independent of the capillary column head pressure and can therefore operate without any problems when the pressure in the vial is higher than the column head pressure.

Multidetector configurations

The particular design of the gas chromatograph also permits different multidetector configurations to be easily arranged in series and/or in parallel. The connection of the non-destructive electron-capture detector in series with the flame ionization, flame photometric and nitrogen–phosphorus detectors is performed through an easily attached adapter, which can also be used for connection to a photoionization detector. This adapter is provided with two independent lines for auxiliary gases (see Fig. 2). Moreover, when fused-silica capillary columns are used, the geometry of the electron-capture detector permits the column end to be pushed upwards

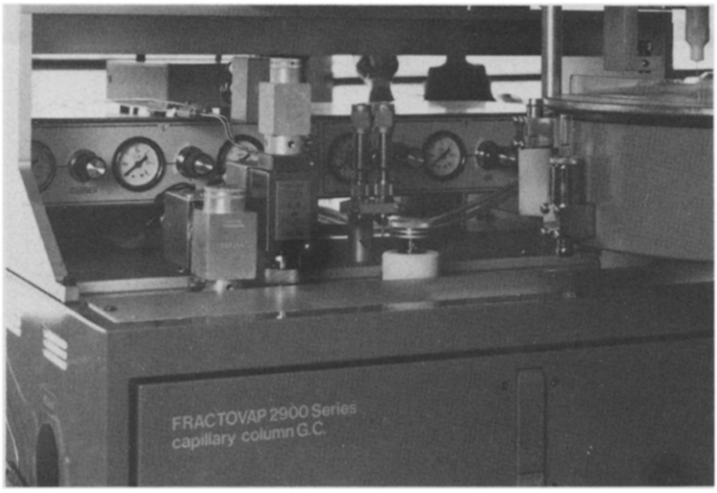

Fig. 2. Nitrogen–phosphorus–electron-capture–flame ionization detector assembly.

directly into the flame ionization detector, therefore avoiding contact of the column effluent with the electron-capture detector.

This configuration has been tested in the headspace analysis of a tap-water sample containing traces of chlorinated hydrocarbons and known amounts of toluene and *m*-xylene. Chromatograms reproduced in Fig. 3 demonstrate that there is no significant loss of efficiency and sensitivity for aromatic hydrocarbons with the series connection of electron-capture and flame ionization detectors.

The parallel detector configuration requires a capillary column effluent splitter. In previous papers[3,4] we reported the use of a glass-lined T-piece with a fixed splitting ratio, usually 1:1. The effluent splitter employed here consists of a specially designed metal Y-piece provided with an inlet for the make-up gas line. It allows the fused-silica capillary column to be easily connected to two detectors through connector arms made from persilanized uncoated fused-silica capillaries (see Fig. 4). Our effluent splitter features the following advantages. (i) Variable effluent splitting ratios are achievable simply by varying the length and internal diameter of the two arms. (ii) The two arms are easily and correctly positioned without any overlap of the same into the Y-piece. (iii) The arms are easily and quickly replaced without removing the whole piece. (iv) A portion of the column can be led outside the column oven for eventual auxiliary operations, such as sniff detection.

The efficiency of the splitting system has been tested by the headspace analysis of a standard solution of 30 ppm of ethyl acetate in water, equilibrated at 50°C. This analysis was performed by the simultaneous detection with two flame ionization detectors in parallel, by use of a fused-silica capillary column (MEGA), coated with 1.5-μm JXR (methylsiloxane polymer), at 63°C.

Splitting ratios have been varied by using arms of different sizes, as shown in Table I.

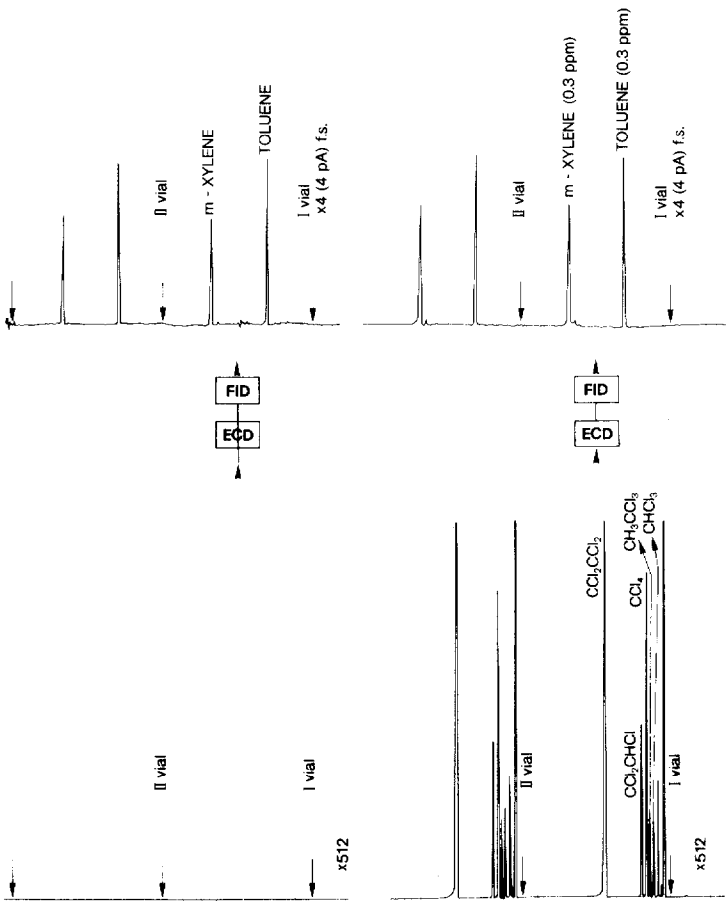

Fig. 3. Headspace analysis of tap-water. Multidetector configuration: electron-capture–flame ionization detectors. Fused-silica capillary column: MEGA, 25 m × 0.32 mm. Column temperature: 58°C. Detector temperature: 200°C.

TABLE I

EXAMPLES OF OUTLET SPLITTING ACHIEVABLE BY FUSED-SILICA CAPILLARY ARMS OF DIFFERENT SIZES

Side	*Length (cm)*	*I.D. (mm)*	*Peak area (counts)**	*Ratio L/R*
L	20	0.32	51,415	0.93
R	20	0.32	55,316	
L	20	0.32	87,212	5.81
R	20	0.26	15,008	
L	20	0.32	96,200	10.69
R	40	0.26	8995	
L	20	0.32	105,010	13.12
R	20	0.22	8006	

* Mean of five values (S.D. 2%).

* Throughout this article, the American billion (10^9) is meant.

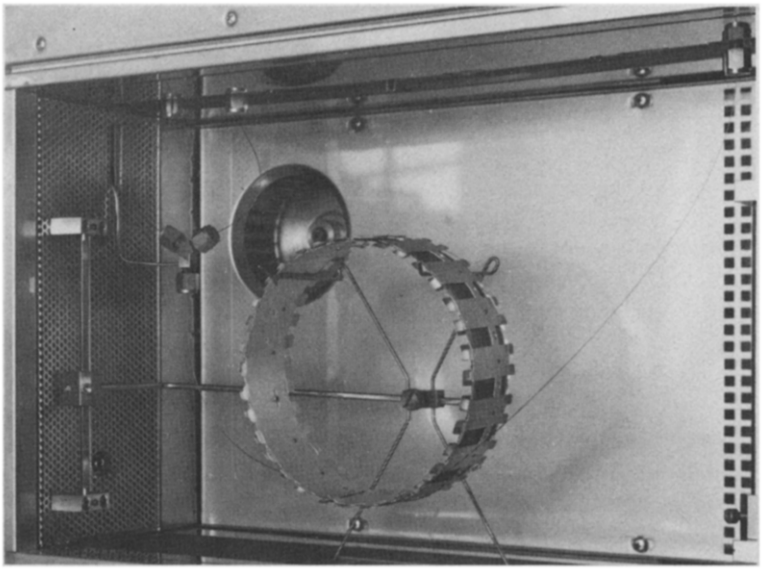

Fig. 4. Assembly of the fused-silica capillary column with the effluent splitter in the GC oven.

APPLICATIONS

The proposed analytical system is suitable for numerous applications, such as the analysis of the aroma of beverages, foods and natural products, volatile residues in polymers and volatile pollutants in water[4–6].

In this paper, examples of applications such as the determination of residual volatile constituents in polystyrene, the analysis of industrial waste waters and the volatile profiles obtained from tomato paste samples, are described.

Residual volatiles in polymers

The high standard of purity required for commercial polymers, particularly with respect to their content of monomers and volatile residues due their potential toxicity or undesirable odours, requires the use of analytical techniques capable of detecting these residual components at extremely low levels.

Fig. 5 shows the chromatogram of a polystyrene bead sample. The sample was finely ground in a special grinder at −20°C before head space analysis. This determination was performed with a flame ionization detector and a mixed stationary phase fused-silica capillary which permitted, in addition to the determination of the residual styrene monomer, also other volatile residues to be detected at the ppm level.

Volatile pollutants in industrial waste water

Purification of industrial waste waters is a problem of fundamental importance for environmental pollution control. From the analytical point of view, due to the large number of components and their low concentrations, a high efficiency system coupled with multiple selective detectors is a must.

Fig. 6 shows the headspace analysis of industrial waste water samples before

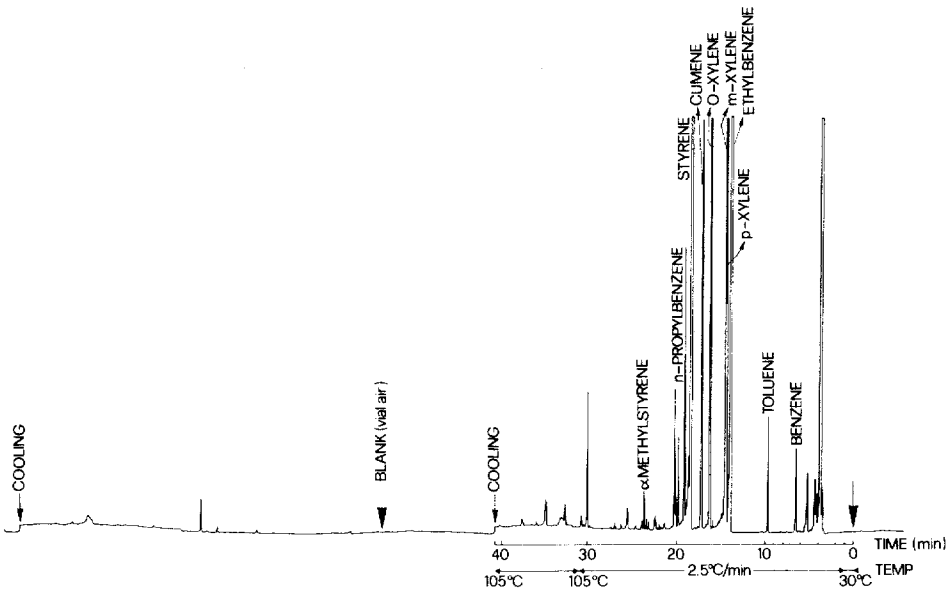

Fig. 5. Headspace analysis of polystyrene. Intrument: FTV 2900 + HS Sampler Model 250. Detector: flame ionization. Column: fused-silica capillary, 25 m × 0.32 mm, with mixed phase (1:1) C 20M and OV-1. Carrier gas (hydrogen) flow-rate: 1.2 ml/min. Sample: 1.5 g at 80°C. Equilibration time: 4 h.

and after biological purification. The multidetector configuration used in this case (electron-capture–flame ionization-photoionization) with a 1:1 splitting ratio has permitted chlorinated hydrocarbons to be determined by the electron-capture detector while the other volatile organic components have been detected by the flame ionization detector. The use of a photoionization detector (HNU Systems), in series with the electron-capture detector, has resulted in a higher sensitivity than the use of a flame ionization detector for toluene and *m*-xylene and provided the confirmation of aromatic hydrocarbons or other constituents for which the photoionization detector gives a selective response.

Fig. 7 shows the analysis of an industrial waste water containing pyridine. In this case the electron-capture–flame ionization–nitrogen–phosphorus combination has permitted the selective determination of the nitrogen compounds.

Sodium sulphate was added to the sample to increase the concentration of volatile constituents in the gas phase of the headspace.

Volatile profiles from foods

The characterization of a product by direct headspace analysis can also often represent a rapid and advantageous method for quality control of foods.

Fig. 8 shows volatile profiles of tomato pastes, both natural and simmered with aromatic herbs and spices. The addition of aromatic substances is conformed by the different profiles obtained by a single analysis performed with a capillary column and an electron-capture–flame ionization–flame photometric detector configaration.

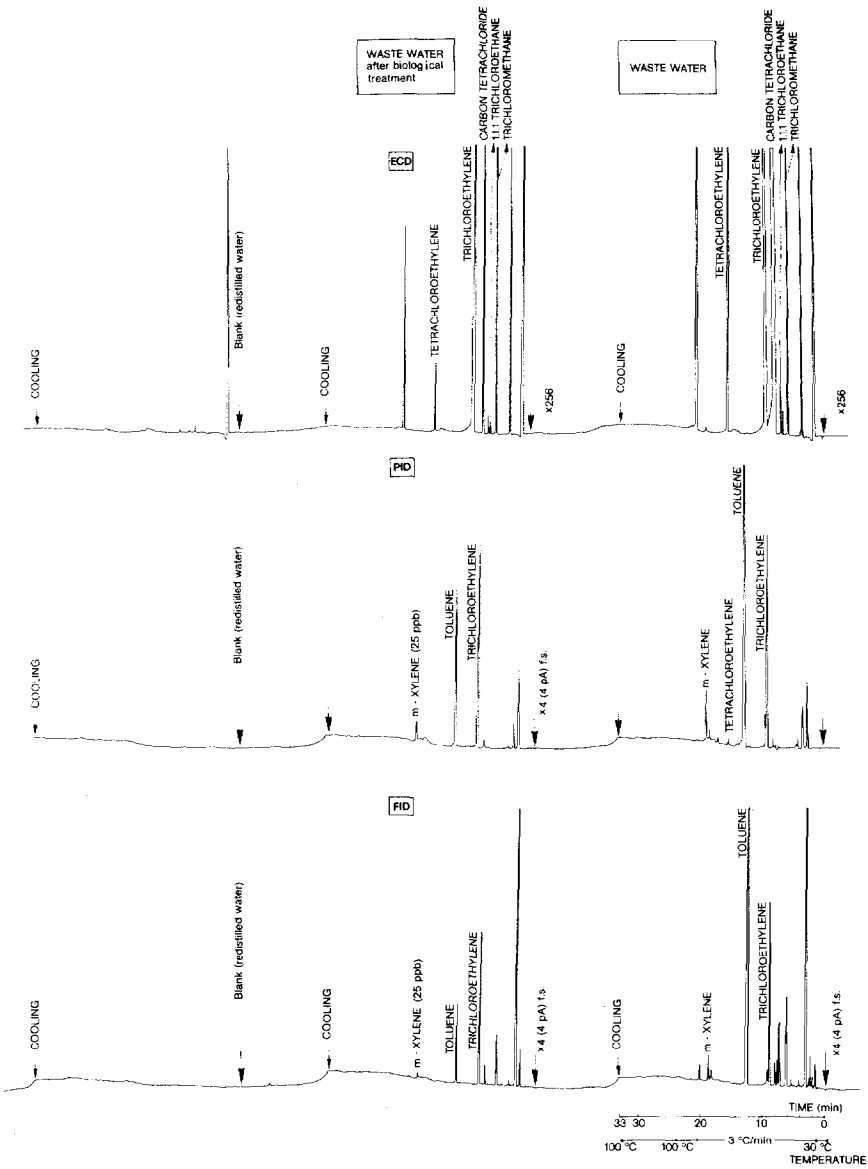

Fig. 6. Headspace analysis of industrial waste water. Instrument as in Fig. 5. Multidetector configuration: electron-capture–photoionization in series, flame-ionization in parallel. Column: fused-silica capillary, MEGA, 25 m × 0.32 mm, 1.5-μm JXR. Carrier gas: hydrogen. Detector temperature: 200°C. Equilibrium temperature: 50°C. Equilibrium time: 30 min. Headspace gas volume injected: 1.5 ml (splitter mode 1:4).

CONCLUSIONS

The combined use of the headspace technique and high resolution GC may be extremely valuable for the solution of complex analytical problems strictly related to the particular nature of the products to be investigated.

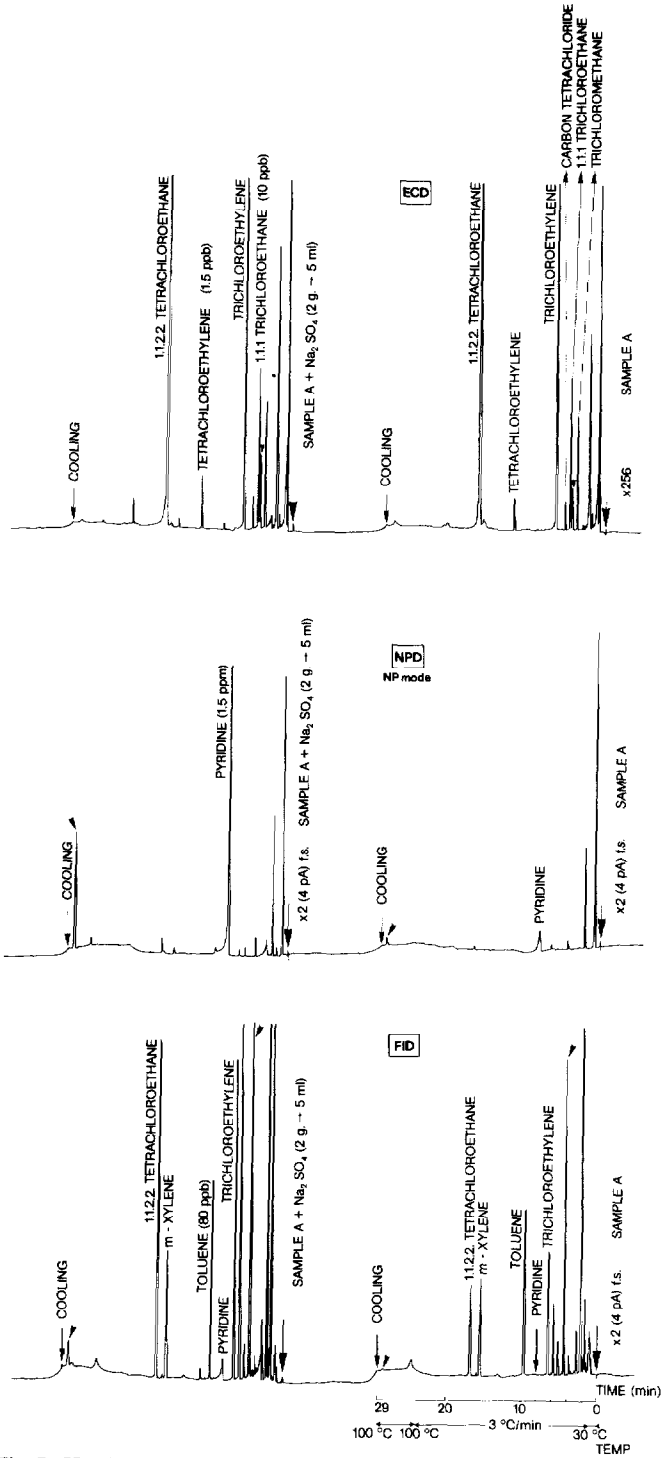

Fig. 7. Headspace analysis of industrial waste water. Instrument: as in Fig. 5. Multidetector configuration: electron-capture–flame ionization in series, nitrogen–phosphorus in parallel. Column as in Fig. 6. Carrier gas: Helium. Detector temperature: 200°C. Water sample: 5 ml at 50°C. Equilibrium time: 30 min. Headspace gas volume injected: 1.5 ml (splitter mode: 1:4).

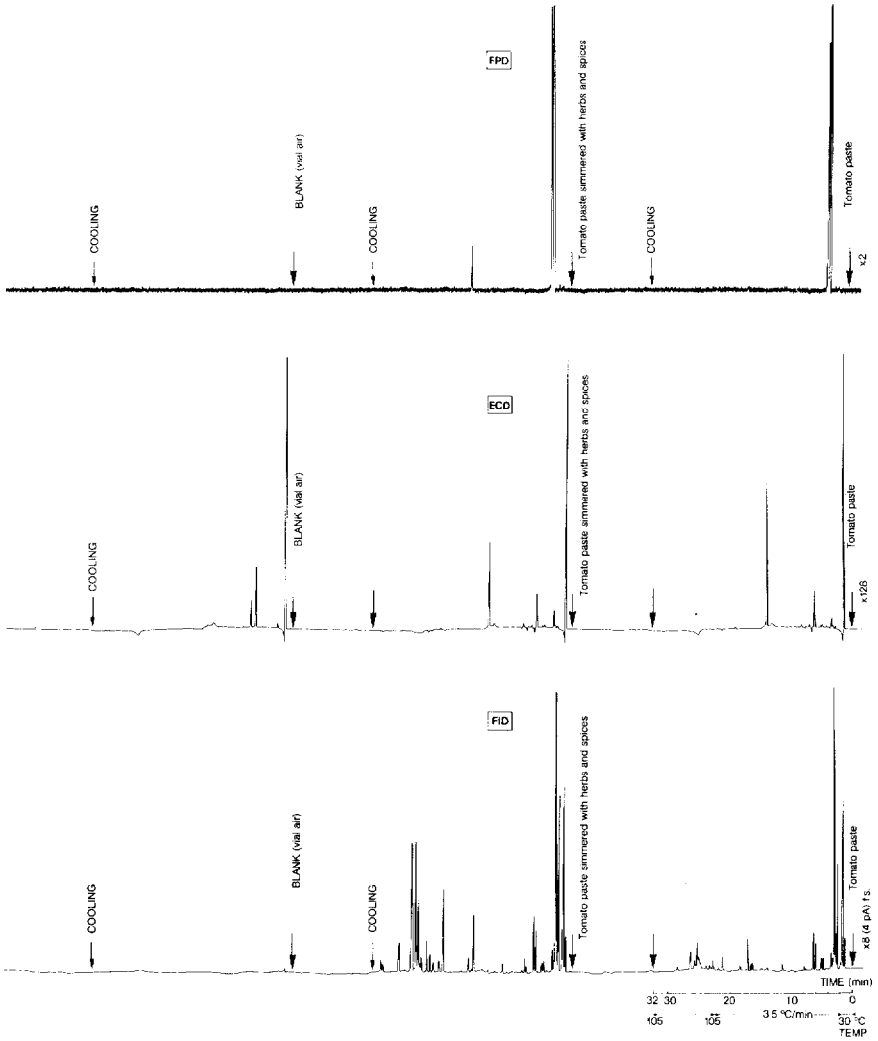

Fig. 8. Headspace analysis of tomato paste. Instrument as in Fig. 5. Multidetector configuration: electron-capture–flame ionization in series, flame photometric in parallel. Column as in Fig. 6. Carrier gas: hydrogen, 2 ml/min. Detector temperature: 200°C. Sample: 1 g at 60°C. Equilibrium time: 1 h. Headspace gas volume injected: 2 ml (splitter mode 1:4).

Fused-silica capillary columns, by virtue of their flexibility, also favour multiple detector operations which can facilitate identification and determination of specific components at ppb levels.

Full automation of the analytical system makes this technique particularly attractive for routine analysis especially in the environmental field and quality control.

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