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CONSTRUCTION OF A GAS CHROMATOGRAPHY–MASS SPECTROMETRY INTERFACE USING A FUSED-SILICA TRANSFER LINE*

E. WETZEL* and Th. KUSTER
Division of Clinical Chemistry, Department of Pediatrics, University of Zurich, Steinwiesstrasse 75, CH-8032 Zurich (Switzerland)
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SUMMARY

The construction of a versatile automatic interface using a fused-silica capillary as transfer line is described. The heart of the system consists of an effluent splitting device which allows direct and open split coupling of capillary columns with different outer diameters. The construction and technical details are described and the features and advantages of the interface are discussed. The device has been in use in our laboratory for two years and has given excellent performance in different applications [see Th. Kuster and E. Wetzel, *Int. J. Mass Spectrom. Ion Phys.*, 46 (1983) 173].

INTRODUCTION

Since the first report on the coupling of glass capillary columns with a mass spectrometer by Grob and Grob[1] in 1971, various types of interfaces have been described. The characteristics of the different types have been surveyed[2] together with our own demands for an interface which led to the device described here.

EXPERIMENTAL

A Carlo Erba Fractovap 2900 gas chromatograph, equipped with a cold on-column injector and reconstructed for gas chromatographic–mass spectrometric (GC–MS) operation, was employed. The capillary columns, 20 m × 0.3 mm OV-1 and 10 m × 0.3 mm SE-54, were obtained from H. Jaeggi, Labor für Gas Chromatographie, Trogen, Switzerland. The transfer line (300 × 0.12 mm I.D. × 0.24 mm O.D.) was of the fused-silica type, FSN-1M (ICT-Handelsgesellschaft, Frankfort, F.R.G.). Graphpack high temperature connections were used for glass and fused-silica capillaries (Gerstel, Mülheim/Ruhr, F.R.G.), with Silcoset 151 adhesive sealant (I.C.I., Stevenston, U.K.). Precision micro pressure controllers Type ND (Siemens, Karlsruhe, F.R.G.) were employed. The mass spectrometer, Micromass 16-F

* Dedicated to Professor H.-Ch. Curtius on the occasion of his 60th birthday.

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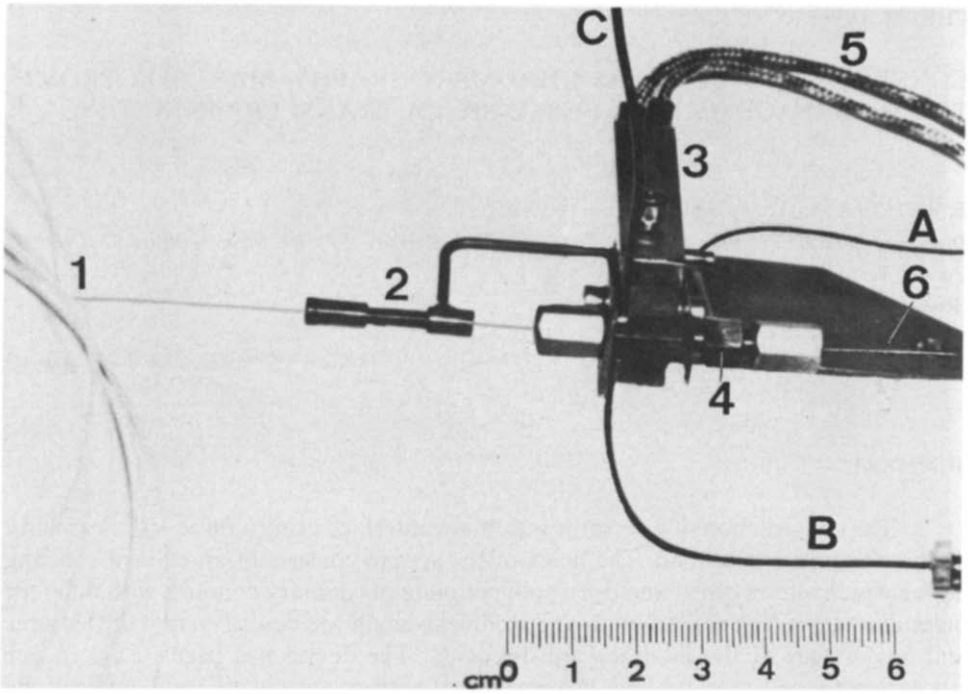

Fig. 1. Photograph of the splitting device. A, B = Scavenger gas (helium) inlets; C = scavenger gas outlet; 1 = GC column; 2 = support for column; 3 = aluminium block; 4 = splitting device; 5 = heater and temperature sensor; 6 = transfer line.

(vacuum generators), was operated with an electron energy of 40 eV (nominal) and an ion source temperature of 200°C. Data system: Finnigan INCOS 2200.

CONSTRUCTION

Splitting device

Fig. 1 shows a photograph of the splitting device mounted on an aluminium block (3). The central part of the device (4) is shown schematically in Fig. 2. The GC column (X) is connected to the mass spectrometer via a coupling capillary (7) and the transfer line (1), both consisting of fused silica. Ideally, the two tubes should fit into each other as mentioned in the figure. At the moment, however, no coupling capillary with a suitable diameter is available and therefore, we used the "guiding tube" (6) to bring the two capillaries of equal diameters as close together as possible. Sealing of the tubes is effected by metal sleeves and graphite packings (2, 8 and 13).

The splitting device works according to a principle introduced by Deans[3]: pneumatically directed flow switching; the eluate flow direction is directed by scavenger gas through inlets A and B. All pressure controllers, manometers and valves are located outside the column oven and are therefore at a constant temperature, which is essential for a constant flow through the system.

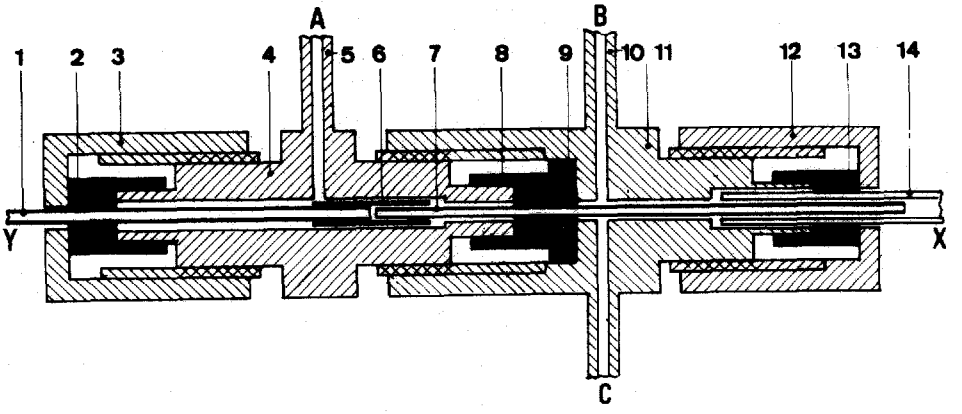

Fig. 2. Diagram of the splitting device. 1 = Transfer line (fused silica, 0.12 × 0.24 mm O.D.); 2, 8, 13 = metal sleeves and graphite packings; 3, 12 = nuts; 4, 11 = stainless-steel blocks; 6 = guiding tube (fused silica, 0.32 × 0.5 mm O.D.); 7 = coupling capillary (fused silica, 0.12 × 0.24 mm O.D.); 9 = graphite vespel seal; 5, 10 = stainless-steel tubes (0.5 × 1.6 mm O.D.); 14 = GC column; A, B = scavenger gas (helium) inlets; C = scavenger gas outlet; Y = connection to mass spectrometer; X = connection to GC column.

Transfer line

Fig. 3 shows the transfer line from the splitting device (Y) to the ion chamber (26). The sealing 2 allows an easy pull-back of the line which is necessary when the ion source has to be exchanged. The capillary is then guided by the inner stainless-steel tube (12) through the gas chromatograph oven wall (8). This tube, which is brazed (at 5) to the steel block (4), leads to the insulating inlet glass capillary 24. The connection of tubes 12 and 14, which have different tube diameters (1.6 and 6.35 mm), is effected in the steel block 14, where 12 is brazed at 13. The inlet capillary is sealed by 6.35-mm graphite ferrules (16 and 19). The two tubes 12 and 24 are surrounded by the outer steel tubing 11 which contains a heating coil in order to allow homogeneous heating of the transfer line. The temperatures in the heating zones 1 (7), 2 (15) and 3 (23) can be set independently and are monitored by platinum sensors (9, 10 and 20) and controlled by thermoregulators. Normally, a slight temperature decrease from the gas chromatograph to the mass spectrometer is favourable; the absolute temperature values, however, depend upon the substances analyzed.

Although fused-silica capillaries are thought to be chemically inert, it is essential to use perfectly deactivated transfer lines and coupling capillaries to avoid adsorptions and decompositions. Different methods of deactivation result in different qualities (see ref. 4 for a detailed discussion). So, Carbowax deactivation, for instance, is not suited to our purposes since the capillaries are not inert long enough due to the high temperatures used. Because our suppliers had no information about deactivation, we evaluated empirically the best commercial capillaries. An easy test of uncoated capillaries is as follows:

(1) Direct connection of the GC column to the flame ionization detector and quality test with the Grob test mixture[5].

(2) Connection of the same column to the detector through a piece of fused-silica capillary (sealing can be performed with Silcoset 151), and quality test.

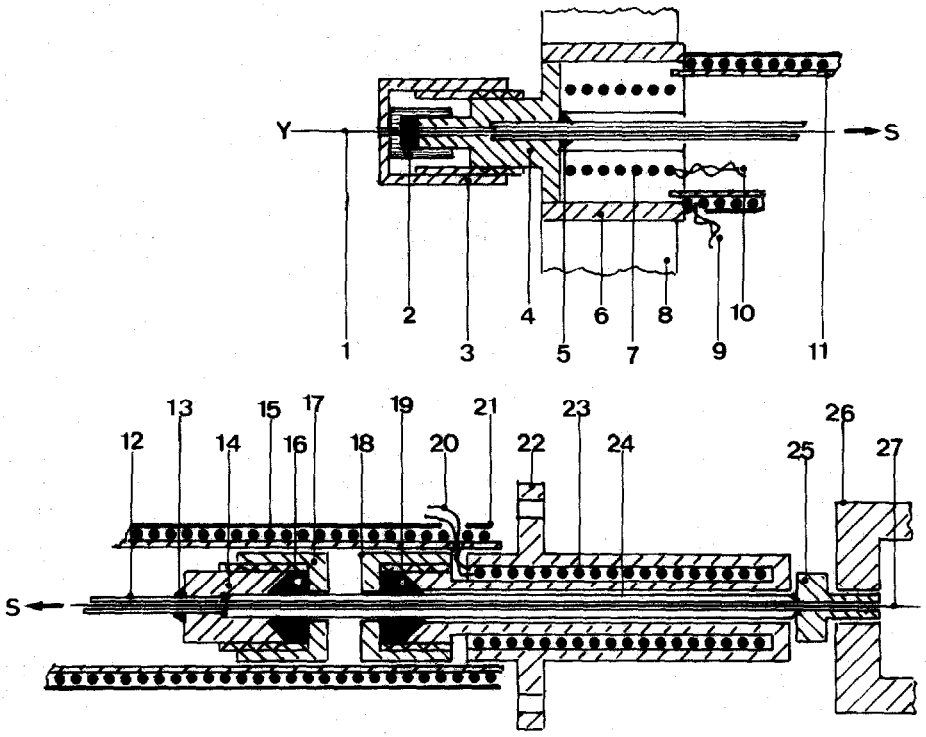

Fig. 3. Diagram of the transfer line. 1 = Transfer line (fused silica, 0.12 × 0.24 mm O.D.): 2 = metal sleeves and graphite packings; 3 = nut; 4 = stainless-steel block mounted at position 7; 5 = brazing position (inner steel tube 12 to block 4); 6 = insulation; 7 = heating zone 1 (cylindrical aluminium block with heating element and platinum sensor); 8 = GC oven wall; 9, 10, 20 = wires, heaters and sensors for the heating zones 2, 1 and 3; 11 = outer stainless-steel tube (15 mm O.D.); 12 = inner stainless-steel tube (0.5 × 1.6 mm O.D.); 13 = brazing position (tube 12 with stainless-steel block 14); 14 = stainless-steel block; 15 = heating zone 2; 16, 19 = graphite ferrules (6.35 mm); 17, 18 = nuts; 21 = insulation (glass fibre tape); 22 = mass spectrometer mounting flange; 23 = heating zone 3; 24 = inlet glass capillary (0.5 × 6.3 mm O.D.); 25 = actuator; 26 = ion chamber; 27 = end of fused-silica transfer line; Y = to gas chromatograph; and S = junction.

(3) The differences in the two chromatograms are an exact measure of the fused silica's quality.

Fig. 4 shows the FID chromatogram obtained with direct connection and Fig. 5 that with a piece of obviously incompletely deactivated fused-silica capillary between the column end and the detector. The latter shows a general decrease in intensity, peak broadening and tailing and the peak for dicyclohexylamine has completely disappeared.

The capillary we chose for our interface was a fused silica sold as needle material for "on column injection" syringes in GC.

OPERATION MODES AND TEST

Fig. 6 shows a diagram of the scavenger gas supply. Exact and reliable flow in the interface is maintained by micro pressure controllers (2–4) and monitored by

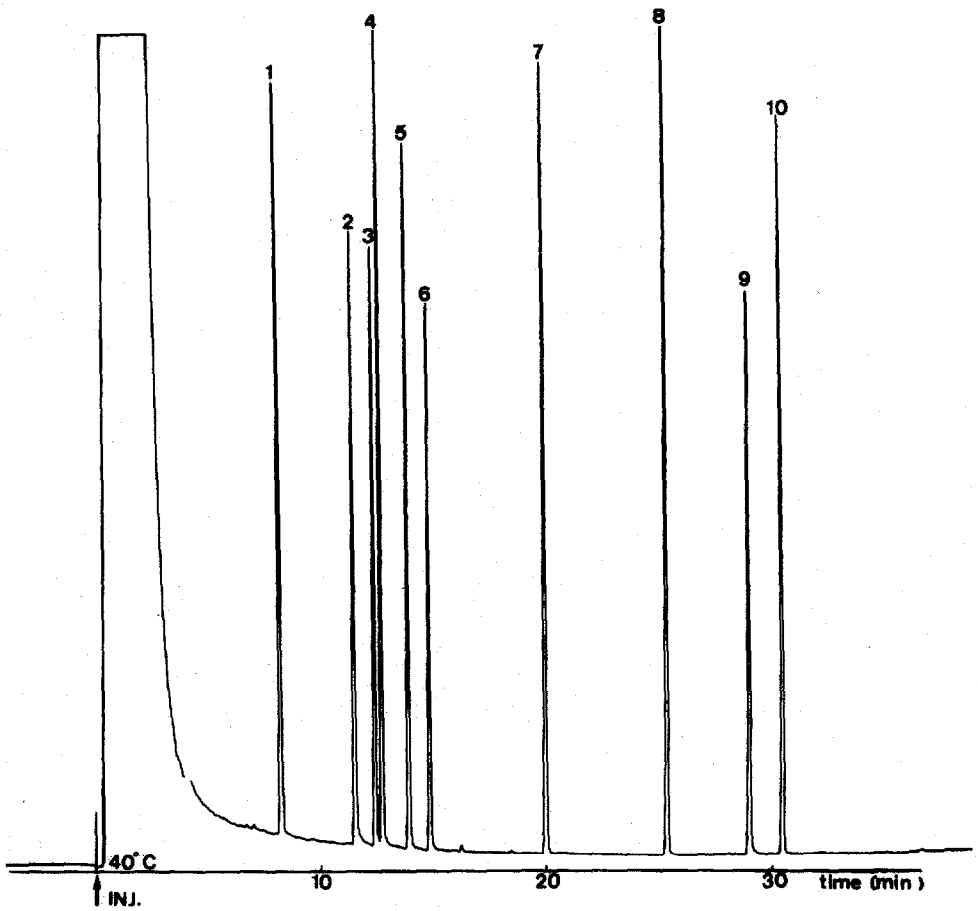

Fig. 4. FID chromatogram of the Grob test mixture[5]. The peak for 2,3-butanediol elutes within the solvent front and is therefore not visible; 2-ethylhexanoic acid was not added to the mixture. Peaks: 1 = decane (5.7 ng); 2 = 1-octanol (7.1 ng); 3 = 2,6-dimethylphenol (6.4 ng); 4 = nonanal (8.0 ng); 5 = undecane (5.7 ng); 6 = 2,6-dimethylaniline (6.4 ng); 7 = C_{10}-acid methyl ester (8.5 ng); 8 = C_{11}-acid methylester (8.3 ng); 9 = dicyclohexylamine (6.3 ng) and 10 = C_{12}-acid methyl ester (8.0 ng) in hexane. Column: 20 m × 0.3 mm I.D. OV-1 glass capillary. Carrier gas: helium, 1.2 bar. Temperature program: 40°C (2 min isothermal) to 140°C at a rate of 2°C per min.

gauges 5–7. The valves 8 and 12 can be operated automatically by a multitimer system. Fig. 7 shows the flow diagram for the different operation modes of the interface.

Fig. 7A denotes direct coupling (transfer of eluate) with the valves 8 and 12 closed. The eluate (large dots) from the GC column is guided directly into the transfer line with the aid of two helium streams (small dots) entering through A and B (each *ca.* 0.1–0.2 ml/min set by valves 3 and 4). It must be added that all these flow values are only estimates, based on the dimensions of the different lines. Measurements of such low flow-rates would be quite difficult. Furthermore, a true determination of the flows would be of limited value since the critical rates depend on the length and the

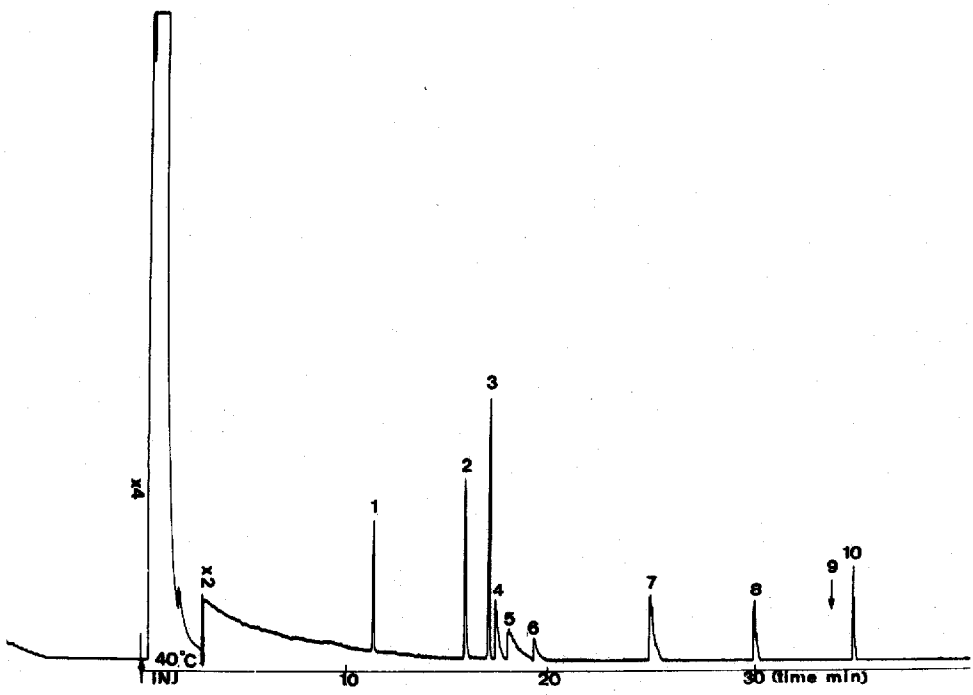

Fig. 5. FID chromatogram of the Grob test mixture[5] using an incompletely deactivated fused-silica capillary (1 m) between the column end and the detector. Conditions as in Fig. 4.

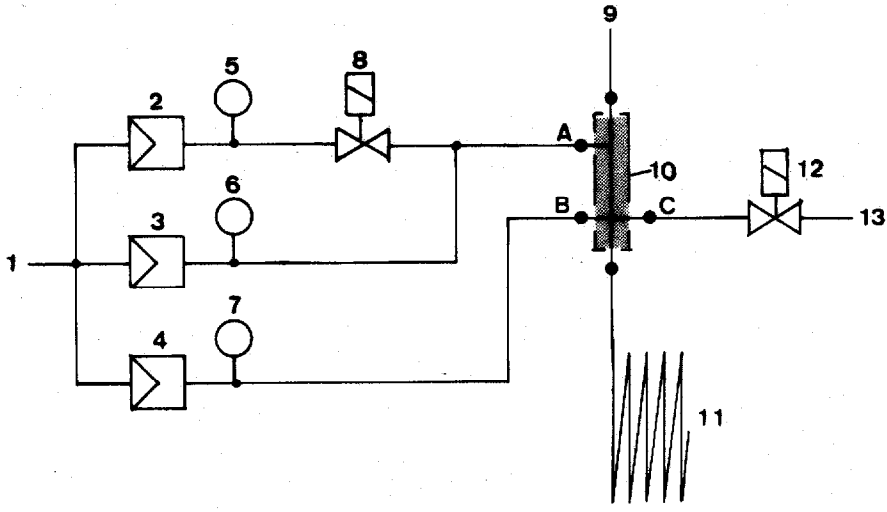

Fig. 6. Diagram of scavenger gas supply. 1 = Helium input; 2–4 = precision micro pressure controllers; 5–7 = precision pressure gauges; 8, 12 = miniature solenoid valves; 9 = connection to mass spectrometer; 10 = splitting device; 11 = GC column; 13 = outlet for helium and eluate; A and B = scavenger gas (helium) inlets; and C = scavenger gas outlet.

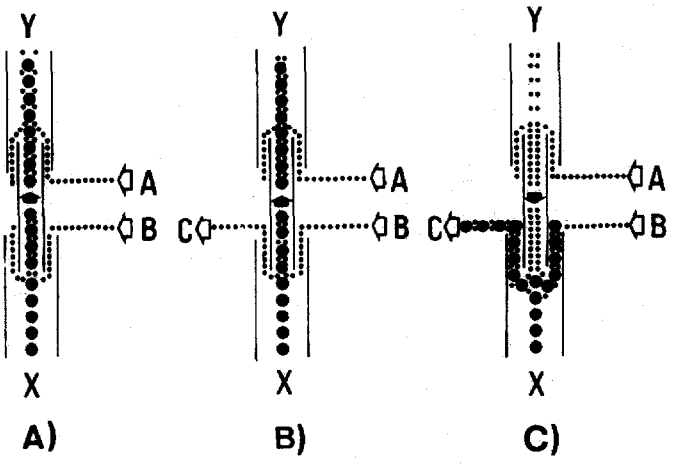

Fig. 7. Flow diagram for direct coupling (A), open split coupling (B) and cut-off mode operation (C). Y = Connection to mass spectrometer; X = connection to GC column; A, B = scavenger gas (helium) inlets; C = outlet (helium and eluate). Open arrows indicate input and output of scavenger gas, whereas filled arrows show the flow direction in the coupling capillary. Large dots represent the eluate, small ones, helium.

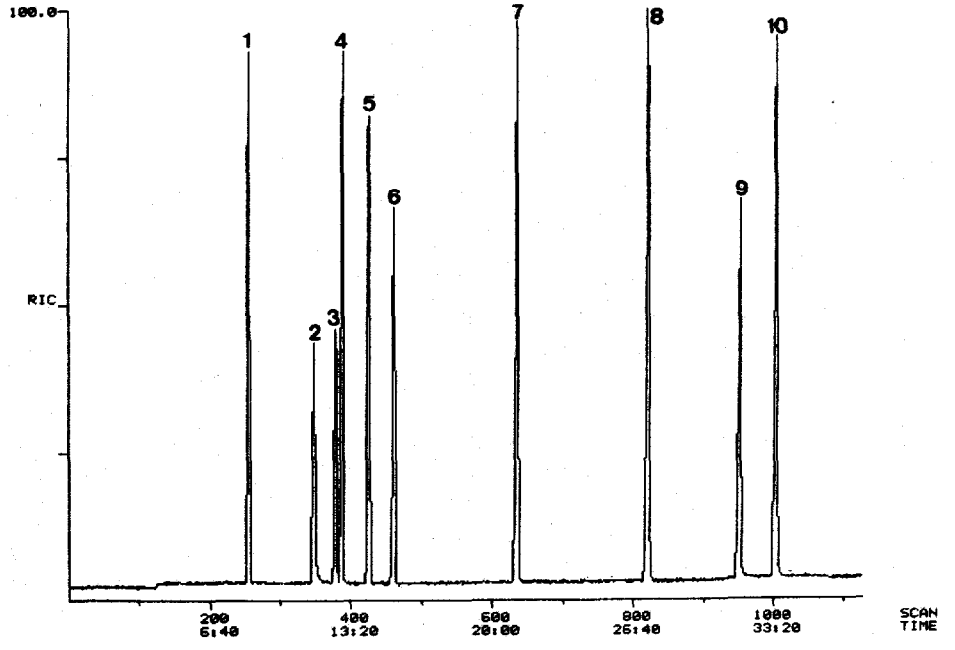

Fig. 8. Total ion current chromatogram of the Grob test mixture[5]. Peak identification and conditions as in Fig. 4.

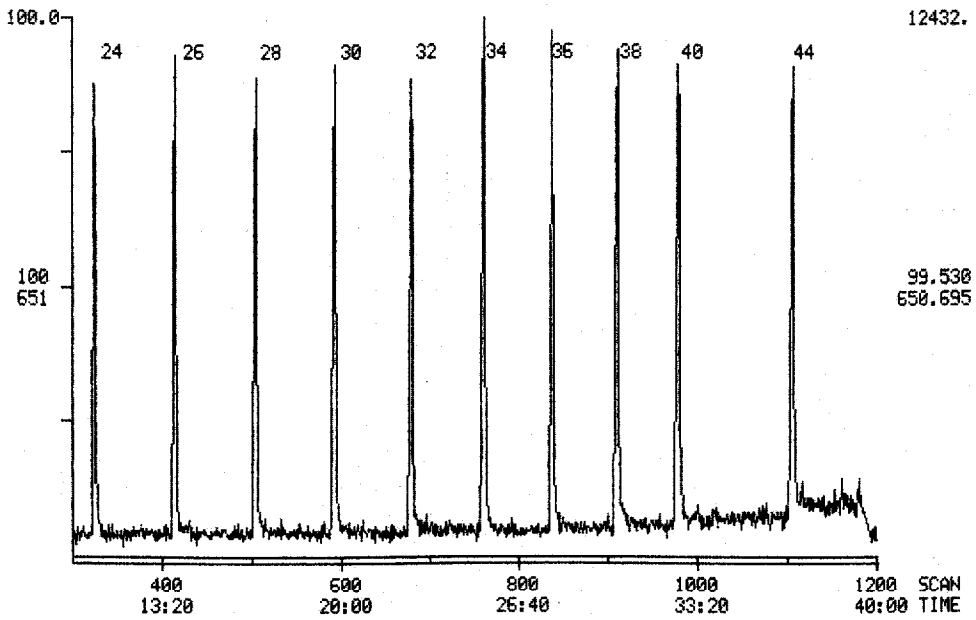

Fig. 9. Total ion currect chromatogram of even-numbered straight-chain alkanes, C_{24}–C_{44} (15 ng each). Column: 10 m × 0.3 mm SE-54 immobilized glass capillary. Carrier gas: helium, 1.0 bar. On-column injection at 40°C, ballasted to 160°C and then programmed to 310°C at a rate of 4°C per min. Temperatures (*cf.*, Fig. 3): heating zone 1, 280°C; heating zones 2, 3 and ion source, 320°C.

dimensions of the transfer line which may be rather different for various types of GC–MS combinations. On the other hand, the mass spectrometer enables an easy experimental access to an optimal flow: when monitoring an ion originating from column bleed, *i.e.*, *m/z* 207, one can change the flow-rates with controllers 2–4 and the intensity variation of this ion is a sensitive indicator of optimal flow-rates.

In the open coupling mode (Fig. 7B) (transfer of eluate), the outlet C is open (magnet valve 12 open) and at atmospheric pressure. The flow at A again is 0.1–0.2 ml/min set by valve 3. The higher flow-rate of around 0.5 ml/min at B (set by valve 4) maintains the system free of air entering through port C. This effects atmospheric pressure at the column end independent of the variable flow through the GC column. The obtained total ion current (TIC) chromatograms therefore show the same retention times as the FID analogues.

In cut-off mode operation (Fig. 7C) (valves 8 and 12 are open for open and direct coupling) the flow at B is further increased to 5 ml/min by valve 2. Now, there is a flow of helium opposite to that from the gas chromatograph and the eluate is split off through outlet C. So, solvents and/or unwanted parts of the chromatogram can be eliminated automatically by setting the desired time intervals by the multitimer system.

Fig. 8 shows a TIC chromatogram of the Grob test mixture[5] obtained under conditions of open split coupling. A comparison with the FID chromatogram in Fig. 4 shows that the separation characteristics of the GC column are fully retained and

that no active sites in the interface can be observed which would give rise to adsorptions and catalytic decompositions.

In order to test the interface for cold spots, we used a mixture of even-numbered straight-chain alkanes, C_{24}–C_{44}. Fig. 9 shows the TIC chromatogram of these compounds. The constant height and the good shape of the peaks indicate that there are no cold spots in the system where the high boiling substances could be adsorbed. In agreement with the observations of Henneberg *et al.*[6], we found drastically decreased intensities and very broad peaks when the temperatures of the ion source and the transfer line were lowered. The most critical part toward temperature changes is the mass spectrometer mounting flange (22 in Fig. 3). An efficient heating of this last part therefore is most important for good results with high boiling compounds as was suggested by Henneberg[7].

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