The Glass Capillary Column in Gas Chromatography. A Tool and a Technique

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Summary

The fact that gas chromatography on glass capillary columns is far from being exploited to its full potential is due to two main reasons: widespread disappointment in poor quality columns and insufficient know-how in the application technique. In order to provide facts about the true situation, general information is given here about performance and durability of a large number of glass capillary columns currently in routine use, some of these for years, at various laboratories. It is emphasized that glass capillaries, as well as the related chromatographic technique and equipment, cannot be successfully considered and handled using the experience gained from packed columns, but should be given particular consideration. The majority of existing glass capillary columns are used for the analysis of complex mixtures. In many instances even extreme separation efficiency may not achieve sufficient resolution. In these cases ancillary techniques may fill the remaining gap. Practical applications of three such techniques, the principles of which are not new, are described; namely, multiple detection, odour analysis, and two-dimensional analysis. A new technique for the introduction of large gaseous samples onto capillary columns is presented with a detailed discussion of its mechanism.

Introduction

It is a well known peculiarity of today's analytical chemistry that a 15 year old method – high resolution gas chromatography – is still far from being exploited to its full potential. In two editorials *Kaiser* [1, 2] describes this situation. To his views I might add the following observations: while in most laboratories high resolution GC has not been introduced (or is already discontinued), there are single institutes – like oases – which base their work on this method to such an extent that many of their best results would not have been accomplished without it. In other words, there seems to be no half way. Where the effort to acquire the basic know-how is pursued until the technique is mastered, there the method is accepted and automatically extended to cover the broadest possible spectrum of application. I shall analyze the reasons for this in some detail.

The Tool

Kaiser [2] states that between theory and practice of high resolution GC there is a gap of 15 years. The main reason undoubtedly is column technology, i. e. obtaining the basic tool of satisfactory quality. A typical and clear analysis of this situation has been given by *German* and *Horning* [3].

Unfortunately, high resolution GC was developed after low resolution GC – the most competent yet exciting report on its early years is still that by *Desty* [4] – and has, therefore, been understood as a simple extension of the latter. While this is true for the theory this holds less for the technique. One unfortunate consequence (others are discussed below) is that in most laboratories, especially in the U.S., there is the predjudice that introducing high resolution GC would firstly mean making capillary columns, as is common practice with packed columns. There is, however, no direct comparison between the two column types as far as their preparation is concerned. Making a glass capillary column with reasonable separation efficiency but with high adsorption activity, poor long term comparability of results and with a short life is not difficult. Normally the first good separations from such columns create some enthusiasm. Then, their drawbacks become evident, their users switch to SCOT or PLOT columns with similar separation efficiency but with far higher loading capacity, or they give up capillary work. Only a few of them continue with good quality purchased columns.

It is typical, on the other hand, that institutes which for years have based their routine work successfully on columns obtained from a specialized manufacturer show no intention of making glass capillaries on their own. They know that making good columns is worth-while only in laboratories willing to concentrate their efforts on the subject. Up to the present time this is the case at a few research institutes with an exceptionally high interest in the method, and without the obligation of calculating the cost of working hours. Besides, there is good evidence that fruitful competition between several manufacturers will arise, providing the user with a reasonable choice of commercial products.

The widespread disappointment arising from poor glass capillary columns has created serious doubt about the subject. To demonstrate the real situation we have asked a limited number of institutes to give us detailed information about the fate (manner of use, performance, durability, ev. cause of failure) of their glass capillary columns. All these institutes have bought and handled their columns according to the quality standards listed earlier [5]. All columns listed in Table I have standard separation efficiencies, e. g., for 50 m × 0.25 mm separation number 50–55 corresponding to 200,000 – 250,000 theoretical plates, for 50 m × 0.35 separation number 40–50 (150,000–200,000). As an essential characteristic their adsorption activity is very low.

From Table I a few observations may be outlined. The life of good glass capillary columns, if properly handled,

Table 1. Performance of arbitrarily selected glass capillary columns

	Stat. Phase	Length (m)	i. D. (mm)	Temp. range (°C)	Operat. time 1)	Remarks 2)	User 3)	Origin 4)
1	Ucon HB 280	34	.32	0–100	8 m	isobutane/isobutene in alcohols	U	G
2	Ucon LB 550	33	.30	0–120	2.5 y	fatty acid esters	U	J
3	Ucon LB 550	120	.38	0–120	4 y	exp. raw cigarette gas phase	B	G
4	Ucon LB 550	100	.34	0–120	2.5 y	acidic, raw cigarette gas phase	B	G
5	XF 1105	50	.33	20–160	6 m		F	J
6	XF 1105	20	.32	20–180	8 m	isomeric olefins	U	G
7	Ucon HB 5100	40	.38	60–170	3 y	various organic subst.	F	J
8	Ucon HB 5100	30	.30	60–180	3 y	permanently coupled to MS	F	J
9	Ucon HB 5100	20	.30	60–180	3 y	various organic subst.	F	J
10	Ucon HB 5100	50	.32	20–185	1 y	exp. raw natural mixtures	G	J
11	Ucon HB 5100	50	.32	20–185	3 y	col. 10 recoated; distilled samples	G	J
12	Ucon HB 5100	20	.34	20–180	2 y	exp. frequent overloaded raw mat.	G	J
13	Ucon HB 5100	20	.34	20–180	6 m	col. 12 recoated; exp. same reason	G	J
14	Ucon HB 5100	50	.31	20–185	2 y	coupled to MS, distilled samples	G	J
15	Ucon HB 5100	20	.31	20–180	2 y	exp. general purpose	G	J
16	Ucon HB 5100	50	.32	20–180	1.5 y	1500 runs 20–180°, distilled mat.	G	J
17	Ucon HB 5100	50	.32	20–180	1 y	exp. heavy head space loading	G	J
18	Ucon HB 5100	20	.29	20–180	1.5 y	exp. large polar samples (glycols)	G	J
19	Ucon HB 5100	20	.33	20–180	6 m	exp. raw extracts	G	J
20	Ucon HB 5100	50	.31	20–180	8 m	exp. MS coupl. cont. overload	G	J
21	Ucon HB 5100	50	.31	20–180	1 y	col. 20 recoated; exp. same reason	G	J
22	Ucon HB 5100	50	.31	20–180	10 m	col. 21 recoated; exp. same reason	G	J
23	Ucon HB 5100	30	.33	20–120	2 y	fatty acid esters	U	J
24	Ucon HB 5100	30	.40	50–180	8 m	terpenes	U	G
25	OS 124	24	.34	60–170	1.5 y	esters of aromatic acids	U	G
26	SF 96	15	.32	20–200	2 y	irradiated N compounds	U	G
27	SF 96	24	.34	20–140	4 y	fatty acid esters	U	J
28	SF 96	50	.32	20–210	2 y	water extracts	E	J
29	OV 101	50	.30	60–230	6 m	general purpose	F	J
30	OV 101	20	.30	20–190	1 y	exp. raw urine extracts	P	J
31	OV 101	50	.31	20–250	9 m	exp. accident, steroids	P	J
32	OV 101	20	.34	20–250	6 m	steroids	P	J
33	OV 101	50	.32	20–240	1.5 y	exp. raw water extracts	E	J
34	OV 101	40	.30	50–200	2 y	plant steroids	U	G
35	Apiezon L	25	.32	60–200	2 y	coupled to MS	F	J
36	Emulphor ON-870	100	.40	20–200	8 m	exp. total cigarette smoke	B	G
37	Emulphor	100	.40	20–200	6 m	col. 36 recoated; tot. cig. smoke	B	G
38	Emulphor	23	.35	80–160	3 y	derivatives of large rings	U	G
39	Emulphor	20	.34	40–180	4 y	irradiation products	U	G
40	Emulphor	16	.35	60–180	3 y	pyridine deriv. kinetic studies	U	G
41	Emulphor	20	.30	100–180	8 m	strongly alcaline, muscarines	U	G
42	OV 17	16	.38	50–160	1 y	irradiation products	U	G
43	XE 60	17	.30	60–170	3 y	alkylated phenols	U	G
44	XE 60	22	.35	40–180	3 y	general purpose	U	G
45	XE 60	40	.34	110–160	2.5 y	isomeric polyolefins	U	G
46	Silar 5 CP	14	.32	60–220	1.5 y	alkyl phenanthrene chinones	U	G

1) m = months; y = years
2) exp. = expired; columns without such indication are still good
3) U = University of Zürich F = Firmenich SA Geneva G = Givaudan Zürich
P = Dept. Pediatrics, University of Zürich E = Federal Inst. Water Res. Zürich
B = F. J. Burrus & Cie, Boncourt
4) G = borrowed from our laboratory J = purchased from H. & G. Jaeggi, 9043 Trogen, Switzerland

is almost unlimited. Most columns listed are still in use with almost unchanged characteristics. A dramatic example is No. 44. This column is in permanent use in the basic course for synthetical organic chemistry. The students are allowed to inject any kind of material, just to get an idea of the composition! On the other hand the most frequent cause of failure becomes very evident, namely frequent heavy loading with raw mixtures, mostly natural extracts, containing almost non-volatile, strongly polar material which accumulates on the column. The trouble totally disappears when distilled samples or samples purified by column chromatography are run. Table I also gives some information about the emphasis on different coatings, e. g. on Ucon HB 5100 as a general purpose phase. The survey is limited, however, by the small number of selected users. In other laboratories, for instance, polar columns with

phases such as FFAP are prevalent. Furthermore Table I gives information exclusively about relatively early work with corresponding long experience. Excellent columns such as OV-1, SE-52, and SE-54 are not listed because they are more recent developments. The most important information given by Table I probably is that, for their users, the columns listed are their constant tools.

The Technique

What has been said about column preparation applies also to the technique of high resolution GC. A great deal of disappointment in many laboratories stems from unsatisfactory technique derived from experience with packed columns. There is again the widespread preconceived idea that what works perfectly with packed columns can be directly transferred to high resolution GC. In addition to the large number of manipulations comprising the procedure itself there are also many details concerning the equipment. The actual unfortunate situation has been accentuated by the great majority of equipment manufacturers who, instead of constructing a gas chromatograph fully suitable for capillary columns, have been advertising their regular models as designed for operation with capillary columns, although high resolution GC is not feasible on them.

An almost inevitable experience upon introducing glass capillary columns to persons well trained with packed columns is the following. The failures which are typical for the introduction period are always due to unsatisfactory technique or unsuitable equipment. They are, however, with surprising regularity, not attributed to these reasons but to the capillary column! This is a further obstacle which makes acceptance of high resolution GC so difficult and slow. The situation becomes more desperate when the same persons do not start their introductory period by using good quality columns but by making columns on their own.

We badly need equipment fully designed for high resolution GC. As soon as it becomes available we shall publish a revised and more detailed version of our technical recommendations [6, 7]. Our experience compels us to stress that starting high resolution GC without being properly introduced to its specific technique, means loss of good will, time and effort.

Two Basic Modes of Application

We have knowledge about the application – mostly routine – of more than 1400 glass capillary columns working all over the world. Without too great a simplification these applications can be attributed to one of two categories.

The scope of the smaller one, comprising about 15 % of the columns, is separation of closely related substances, mostly isomers, as occurs in many special fields of organic chemistry, e. g., investigation of natural products, study of reaction mechanisms, development of new synthetic methods, analysis of the products of photochemistry etc. As examples we cite three papers, the results of which are completely based on high resolution GC separations [8–10].

The larger category, about 85 % deals with complex mixtures as they occur in environmental analysis [11–13], food and flavour chemistry, clinical chemistry [14], analysis of exhaust gases and smoke [15] (arbitrarily selected examples, not a comprehensive survey). In this mode of application it is the excessive number of substances which calls for the highest possible separation efficiency. It is hard to understand why packed columns are still used for such purposes, ignoring the fact that single "peaks" may comprise twenty or more substances.

The most complex mixture we have ever handled is tobacco smoke. Fig. 1 shows a recent separation of the middle fraction, the so-called semi-volatiles (i. e., gas phase and particulate matter not included). The chromatogram presents approximately 800 reproducible signals, a further 200 signals have been omitted on the right. From mass spectroscopy as well as ancillary techniques we know that the average number of substances forming a peak is more than three. Thus the actual number of substances involved in the depicted run is at least 3000. Even the highest available separating power is insufficient to manage this task. Besides, the mixture contains all classes of organic chemicals, e. g., free acids, free bases, free polyols, the simultaneous correct elution of which demands an extremely high column quality. Fig. 1 exemplifies the maximum we can accomplish at the present time combining the best conditions with respect to column, equipment, and chromatographic technique.

For the first mode of application, phase selection and column quality are the decisive prerequisites, since there is little room for ancillary techniques. The opposite is true for the second mode. Here a first separation may still leave many substances unresolved and may present identification problems, especially with minor components. While the principles and potentials of several ancillary techniques have been widely discussed this is less so with their practical realization, especially with high resolution GC. We therefore describe some examples obtained by colleagues or by ourselves. The first example describes an essentially new method.

Direct Injection of Large Head-Space Gas Volumes

Splitless injection of more than 0.1 cm^3 of head space gas onto a capillary column is a well known problem. Trapping on the cooled column (cryogenic technique) or intermediate trapping and concentration are the most common solutions.

We have worked out a new method as a logical extension of what we call "solvent effect" in splitless injection [16]. The mechanism by which a broad sample band, produced by prolonged injection, is condensed on the rear of a large solvent peak, is also applicable to large gaseous samples. Since dissolving them quantitatively in a solvent would not be convenient, it is preferable to inject a suitable amount of solvent and a gaseous sample separately but almost simultaneously. The underlying mechanism is best explained by an example.

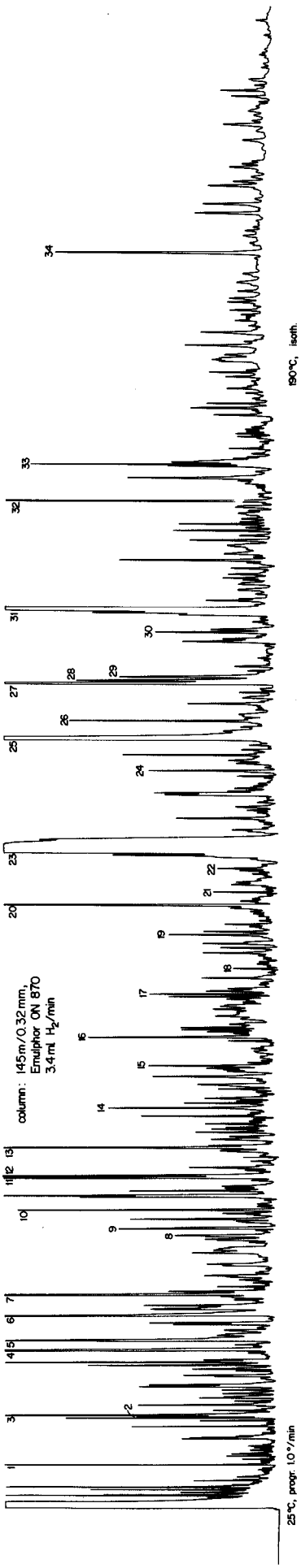

Fig. 1

● Middle fraction (semi-volatiles) of cigarette smoke separated under best available conditions concerning separation and adsorption. Names of some major components see Table II. All gas chromatograms, except Fig. 6, are obtained from gas chromatograph Carlo Erba Mod. 2100.

We prepared a diluted n-octane vapour by injecting 1.0 cm^3 of head space sampled at room temperature over pure n-octane into one liter of air. All further tests were carried out with 1.0 cm^3 of this thousand-fold diluted octane head space gas.

In direct injection, the splitless period – the period during which the column is the only exit from the injection chamber – is a governing parameter. Its significance is best shown by describing the details of our example. The glass capillary column, 50 m × 0.3 mm, coated with silicone oil SF 96, maintained at 35 °C, yielded a carrier flow of 3.0 $cm^3 min^{-1}$ (H_2). A 1.0 cm^3 gas sample should therefore be transferred onto the column within 20 sec. This is confirmed experimentally since the carrier pressure, which is suddenly increased by injecting the 1.0 cm^3 sample, falls to its original value within 20 sec. This does, however, not mean complete transfer of the sample onto the column since extensive mixing of sample gas with carrier occurs. Thus, the splitless period has to be prolonged. As a somewhat arbitrary rule we set it to 60 sec.

As demonstrated by chromatogram A in Fig. 2, even this three-fold period does not assure complete sample transfer. The large initial peak represents volatiles from the laboratory air we used for preparing the head space gas. As expected under these conditions octane appears as broad, flat peak. Its long tail shows a sudden break off, caused by opening the split valve after 60 sec, thus reflecting the end of sample introduction. The area enclosed by the prolonged asymptotic tail and the base-line represents the lost part of the sample.

The outline procedure yielding chromatogram B was the following: close split valve and immediately inject 2.5 mm^3 hexane; after 15 sec inject 1.0 cm^3 head space gas; after further 60 sec open split valve; no further manipulation, in particular no temperature change.

Doubling the interval between hexane and head space injection (chromatogram C) still gives a perfect solvent effect, as is best observed by comparing the octane peak with the surrounding peaks of solvent impurities. When the interval is prolonged to 45 sec (D), the octane peak appears lowered and distorted. The explanation is that about three-quarters of the octane vapor still reaches the area of the large solvent peak where they are perfectly concentrated. The remainder enters the column too late to reach the solvent and keeps, therefore, its distribution over a broad zone. After an interval of 60 sec (E) almost no solvent effect remains. Note that the solvent impurities always appear in perfect peak shape reflecting their simultaneous introduction with the solvent.

Reversing the sequence of injections is a tempting idea. Since the solvent has to be the most volatile substance in the mixture, it is supposed to overtake all other substances when injected last. This should assure full contact with all these substances and, therefore, maximum solvent effect. As chromatograms G and F in Fig. 3 demonstrate, the opposite is true. Even shortening the interval to 5 sec (G) does not help when the solvent is injected after the sample.

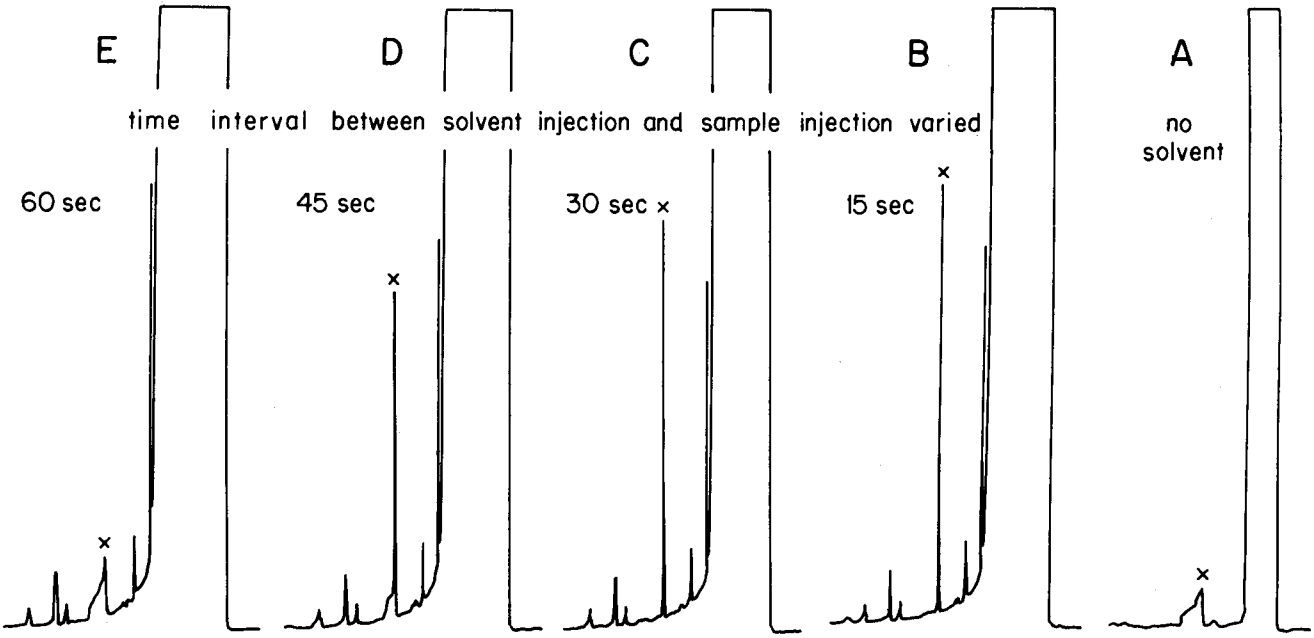

Fig. 2

● 1.0 cm^3 of octane head-space gas injected without splitting. B-E: 2.5 mm^3 hexane injected without splitting prior to sample injection. Column and exact procedure see text. Cross indicates octane peak.

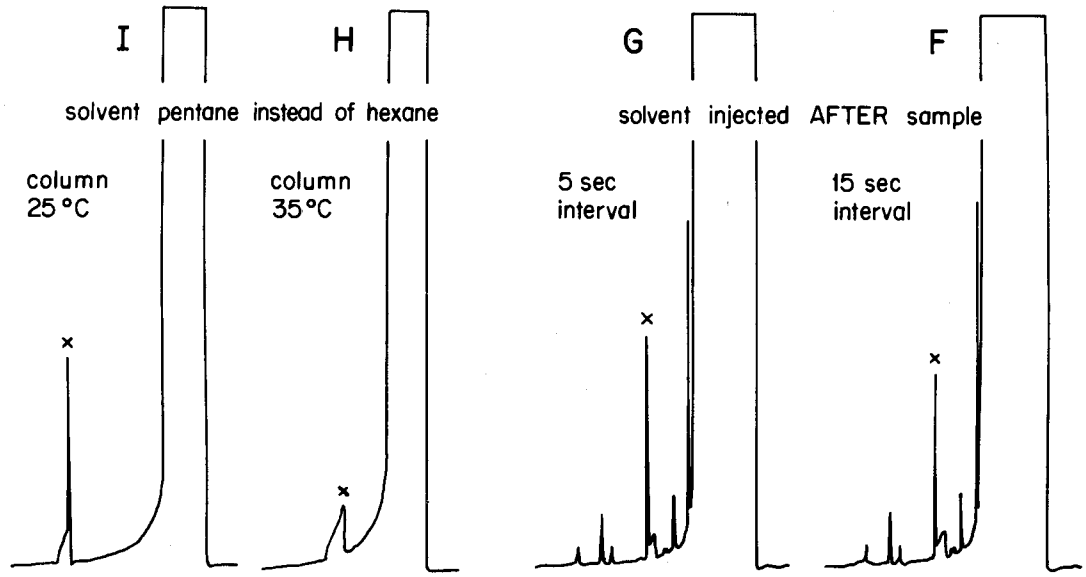

Fig. 3

● Continuation of Fig. 2 F-G: sequence of solvent and sample reversed. H-I: change of solvent.

The reason is obvious. The drastically overloaded solvent peak builds up in the first few meters of the column, a condensed liquid layer which is 20–50 times thicker than the stationary film! Only under these drastic conditions does it exert the solvent effect. The temporarily produced very thick film causes strongly increased retention – and thus concentration – not only for the sample components but also for the solvent itself. This causes the solvent to migrate much slower than expected from its volatility. Thus, when injected last, it remains behind the sample components and starts passing them only when, by sufficient broadening, its local concentration approaches "regular" chromatographic conditions. Under these conditions, however, there is no longer a solvent effect. In the examples F and G only the last part of the long vapour plug of octane is overtaken by the solvent while the latter is still sufficiently concentrated. The first part, which is longer in F, is not influenced by the solvent. This also explains why the distorted part is eluted before the sharp part (in contrast to chromatogram D).

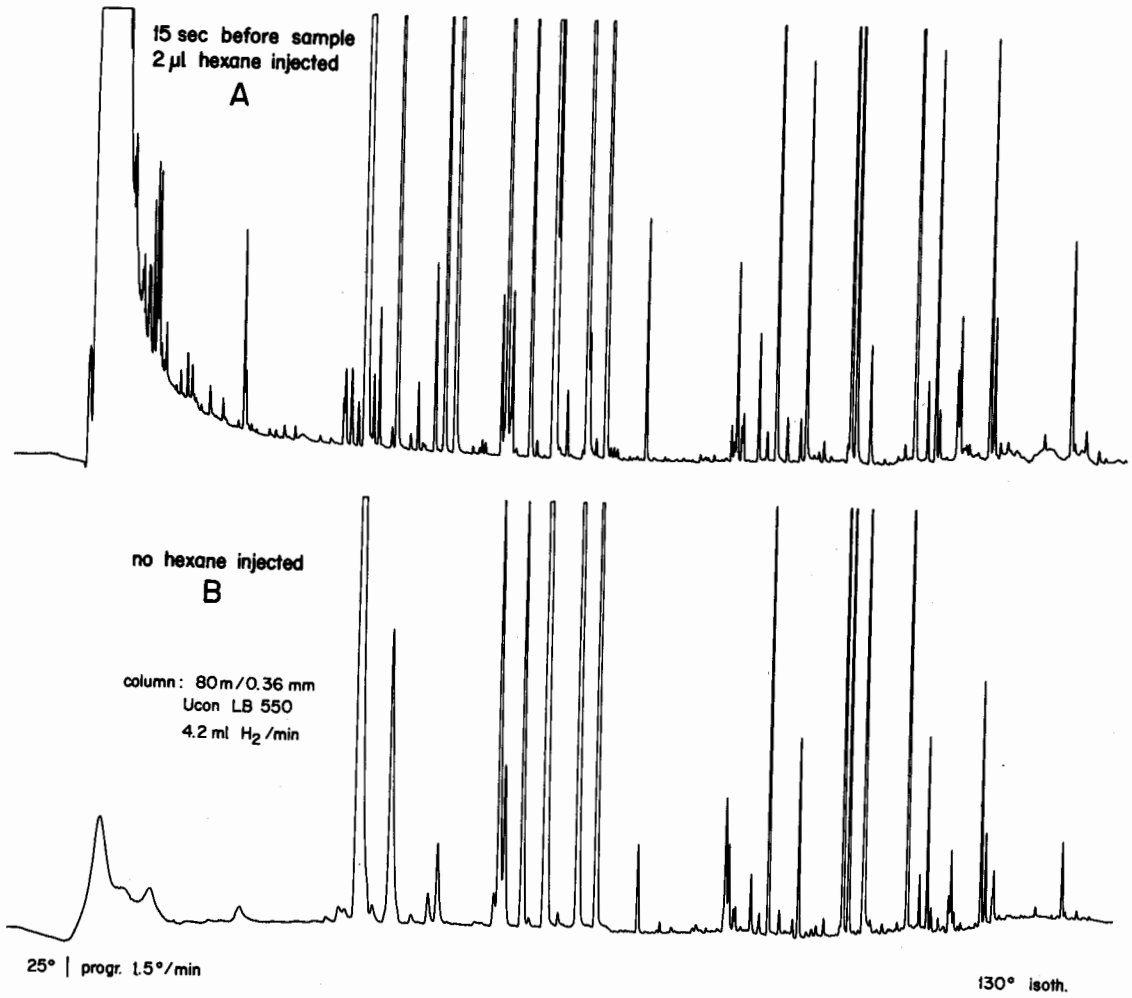

Fig. 4

● 1.0 cm^3 of head-space gas, sampled over dried Italian spices, injected without splitting. Comparison shows application of solvent effect to produce ideal injection conditions for large volume gas samples. Detailed explanation see text.

For runs H and I, Fig. 3, 3.5 mm^3 of pentane, instead of 2.5 mm^3 hexane, were injected 10 sec before the head space injection. Although the main parameters are modified in a sense to enhance the solvent effect, practically no effect is observed when the column is again kept at 35° C (chromatogram H). On the column at room temperature (I) a moderate solvent effect takes place, since pentane is now more retarded and some solvent condensation is built up.

Fig. 4 shows, as a practical example, the analysis of head space gas sampled over a mixture of dry Italian spices. The conditions for both runs were identical except an injection of 2.0 mm^3 of hexane 15 sec prior to the head space injection (1.0 cm^3) in run A. Obviously the difference between the two chromatograms is much more pronounced in the first section. For the heavier substances eluted at least 40° above the temperature of injection, a cold trapping effect concentrates the bands, the more efficiently the lower their volatility. While cold trapping might be considered as perfectly effective, from peak shape as well as from resolution in chromatogram B, the reduced peak heights still result from the unfavorable injection conditions.

Table II. Selected major substances in cigarette smoke

1	toluene	18	naphthalene
2	pyridine	19	methylacetophenone
3	limonene	20	$C_{13}H_{22}O$
4	2,5-dimethylpyridine	21	2-methylnaphthalene
5	3-methylpyridine	22	1-methylnaphthalene
6	tetramethylbenzene	23	nicotine
7	tetramethylbenzene	24	biphenyl
8	indene	25	phenol
9	2-vinylpyridine	26	o-cresol
10	furfural	27	p-cresol
11	tetramethylbenzene	28	m-cresol
12	pentamethylbenzene	29	2-ethylphenol
13	dimethylpyrazole	30	3-ethylphenol
14	pyrrole	31	neophytadiene
15	5-methylfurfural	32	indole
16	propylene glycol	33	3-methylindole
17	furfural alcohol	34	pentacosane

The procedure has proven to be the most direct and quickest way of obtaining full resolution from large head space injections. Only the very earliest sample components may become obscured, i. e., the same substances that are also easily lost by other procedures.

Table III. Major substances in the non-polar fraction of sewage water [22]

1	1,2,4-trichlorobenzene	PCB's	mixture of poly-chlorinated biphenyls
2	1,2,3-trichlorobenzene		
3	1,2,3,5-tetrachlorobenzene	10–34	C-number of n-alkanes
4	1,2,4,5-tetrachlorobenzene		
5	1,2,3,4-tetrachlorobenzene		
6	pentachlorobenzene		

Multiple Detection

Interpreting high resolution gas chromatograms from complex mixtures may be a difficult problem unless a GC/MS run, eventually yielding several hundreds of mass spectra, has been carried out. Valuable preliminary information from a first separation can be obtained when the column effluent is split onto detectors with markedly differing specificity.

Splitting capillary effluents without affecting separation has long been a difficulty which is now solved almost completely by the technique developed by *Etzweiler* and *Neuner-Jehle* [17, 18]. Based on the same technique a capillary split system leading to four different detectors is no problem [19]. An example of dual detection with FID and FPD for capillary columns has been reported by *Zlatkis* and coworkers [20].

Among the detectors suitable for capillary GC the ECD has been critical because of excessive dead volume. A greatly improved ECD developed by *Gay* and *Brechbühler*,

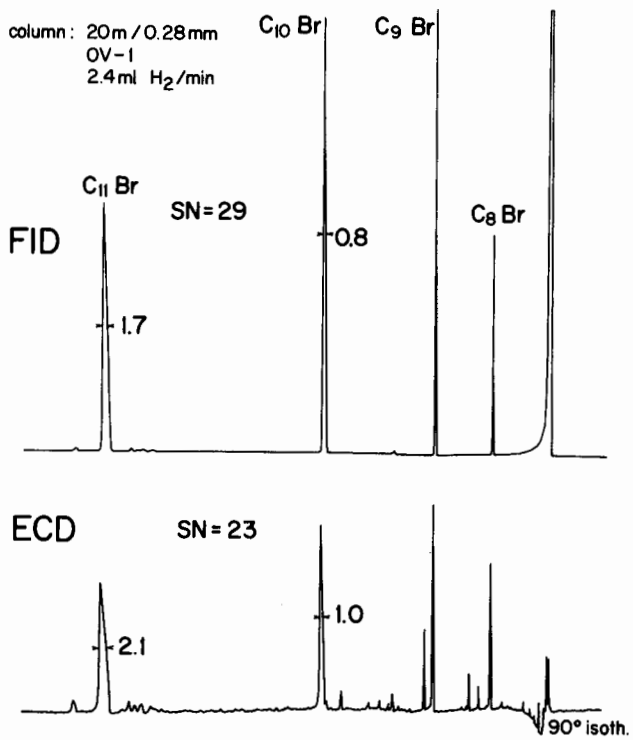

Fig. 5

● Simultaneous detection with FID and new ECD of separated 1-bromoalkanes. SN: separation number. Comparison shows reduced influence of diffusion in ECD.

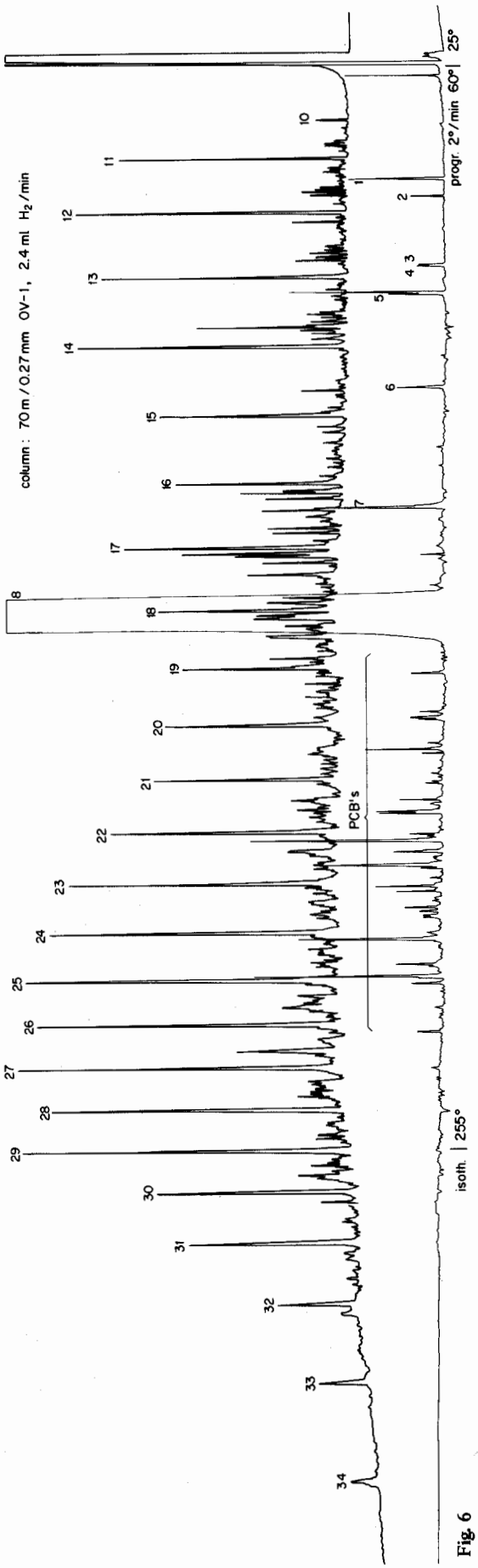

Fig. 6

● Analysis of nonpolar fraction of extract from sewage water, simultaneously recorded with FID and ECD. Identified substances see Table III. Gas chromatograph Carlo Erba, Milano, Mod. 2400 (dual column).

and manufactured by Brechbühler AG, 8902 Urdorf, Switzerland, has recently become available. Its construction and operation will be described in a separate publication [21]. We have tested the new ECD in parallel with an FID. The glass capillary column was attached to one of the vaporizers of a Carlo Erba Mod. 2400 gas chromatograph (dual column). The exit was split, using the above-mentioned platinum capillary technique [17] into FID and ECD. No modification of the apparatus was necessary.

Fig. 5 shows a preliminary separation efficiency test. To get a similar response by both detectors from the same homologous series of substances we used primary bromoalkanes as a test mixture. Both chromatograms in Fig. 5 are produced simultaneously from the same run on the same column with a 1 : 1 split. Additional band broadening can, therefore, derive from the detector system only. While the corresponding loss caused by the commonly used ECD has been around 50 %, it is now about 20 %.

Fig. 6 shows a practical application of simultaneous detection with FID and ECD. The sample, a nonpolar fraction of the extract from a sewage water, was kindly provided by members of the EAWAG [22], together with the corresponding mass spectrometric identifications. Both chromatograms in Fig. 6 have almost nothing in common since the detector responses are strongly complementary. Thus the combined result from simultaneous recording is much more informative than the sum of independent FID and ECD runs.

Organoleptic Odour Detection

In the context of multiple detection, the human nose as a detector of unique selectivity should be considered. Its sensitivity of the ng sec^{-1} level is sufficient for a limited number of substances only. However, substances with strong odour can be detected, and sometimes identified, even as minor components in complex mixtures.

The principle of sensory detection has been mentioned [23] and further developed [24, 25] several years ago. It has also been applied to capillary GC [26, 27]. Nevertheless, its practical use has remained within a surprisingly small number of laboratories.

In our laboratory we carry out odour detection with the same device we use for two-dimensional analysis (Fig. 8, description see next chapter).

As a typical application we report the well elaborated investigation of odorous components of cigarette smoke by *Artho* and *Koch* [28]. From their work, Fig. 7 represents a section (about one-third) of a chromatogram obtained from a 100 m × 0.40 mm glass capillary column coated with Emulphor. Every number means a distinct odour perception. Table IV exemplifies the subjective odour characterisation by reporting 14 out of the total of 126 detectable odours recorded in one run.

Column Switching, Multi-Dimensional Analysis

Both terms have a similar, though not strictly defined meaning. Their common and essential meaning is that

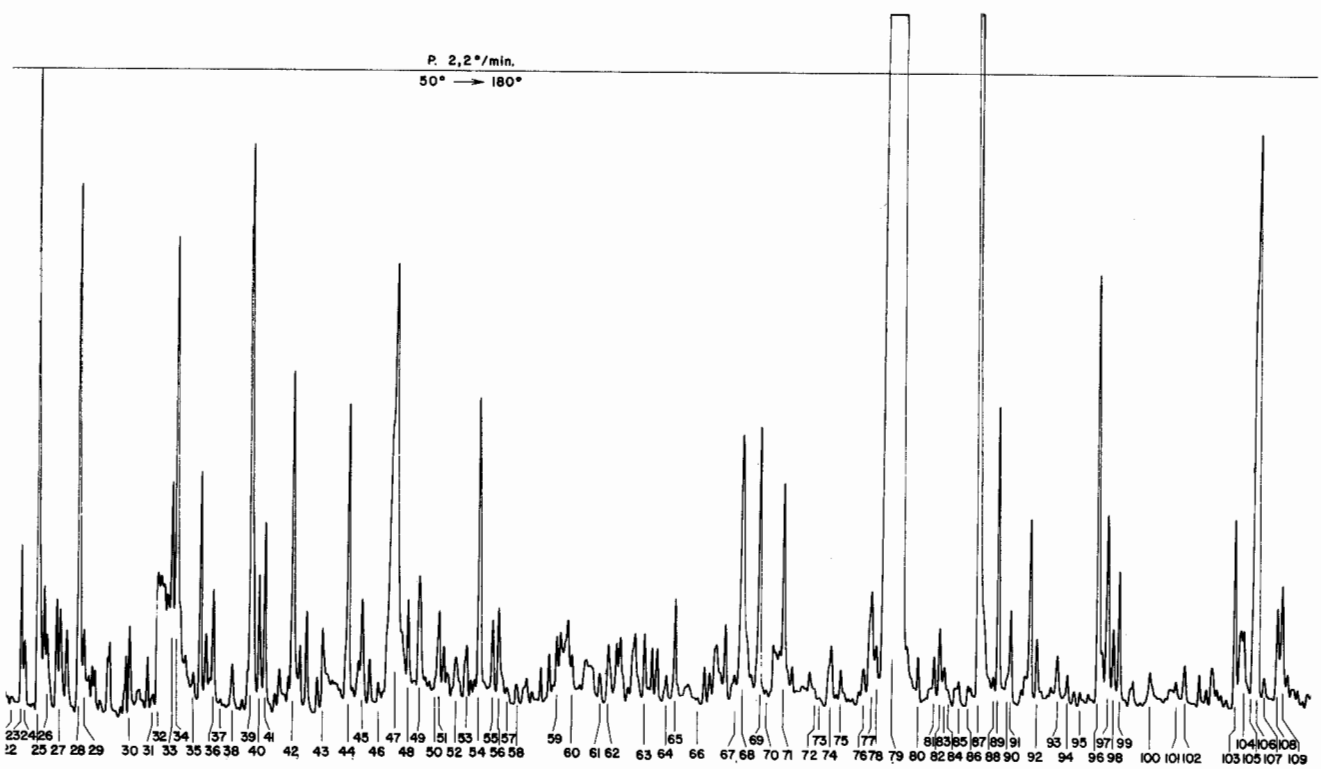

Fig. 7

- Section (about one-third) from gas chromatogram showing semi-volatiles of cigarette smoke. Numbers indicating distinct odour perceptions. From *Artho* and *Koch* [28].

Table IV. Subjective odour characterization for small number of consecutively eluted cigarette smoke components

peak number:	odour:
18	pleasant, very light
19	fresh grass
20	floral
21	pharmaceutical
22	mushroom, intense
23	fresh grass, intense
24	sweet almonds
25	pistachio
26	strongly repugnant
27	chocolate
28	pharmaceutical
29	mushroom
30	strongly repugnant
31	fresh thyme
32	acetic acid, strongly pungent

in a given separation more than one column with different polarities is involved, where one of them is not necessarily a GC column.

As an early example of a classical and successful application the work by a team of *Firmenich & Co.* may be cited [29]. The volatiles of roasted coffee were run on a polar column. Cuts were trapped and re-chromatographed on nonpolar columns. The work brought a break-through in the knowledge of coffee flavour.

Recently *Schomburg* and co-workers [30–32] spent considerable effort on multi-column systems combining backflushing and cutting techniques in an elaborate and partly automated way. In most applications these authors use intermediate trapping followed by a second separation on a glass capillary column. *Kaiser* [33] reports

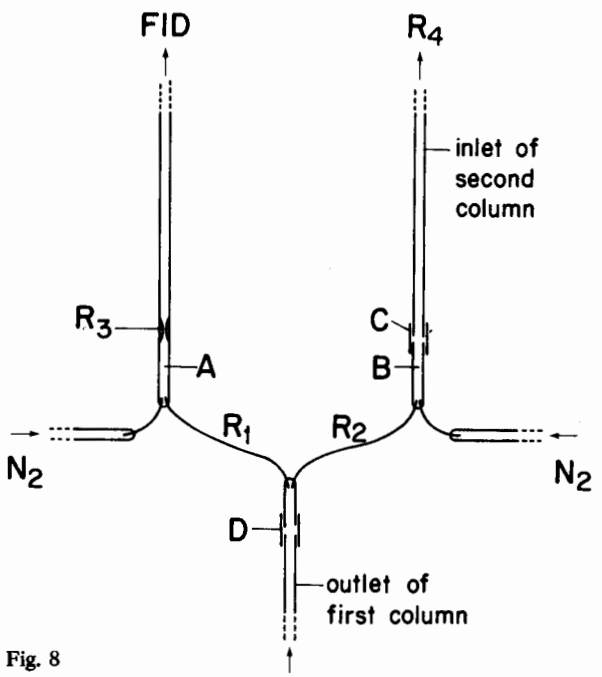

Fig. 8

• Splitting device for controlled transfer of column effluents to FID and to second column respectively. Same device is used for odour detection. Details see text.

that two-dimensional separation is facilitated through the use of separation cassettes.

Our way of dealing with two-dimensional analysis has been to combine two different glass capillary columns without intermediate trapping and without interfering equipment. Both columns are run independently over their full range of programmed temperature control. Fig. 8 shows schematically the column-connection device which is an application of the *Etzweiler/Neuner-Jehle* technique [17]. Single solid lines indicate platinum capillaries (0.3 × 0.1 mm), double lines mean glass capillaries (0.85 × 0.35 mm), push-on connections are made from Teflon shrink tubing WG 24 (Du Pont). While the first glass capillary column is mounted as usual in the oven, the second column is located outside the chromatograph at room temperature. Its inlet end passes the oven walls and is connected at point C, inside the oven, to the split system. With the aid of two independent nitrogen gas supplies controlled pressures can be established in sections A and B, since both lie between restrictions (R_1–R_4). R_1 and R_2 are platinum capillaries, R_3 is a constriction in the glass capillary and is comparable to R_4, which is the resistance of the second column itself. By setting suitable pressures in sections A and B the effluents of the first column can be distributed, with any desired split ratio, between the FID and the second column. The pressures have to be found experimentally for a given pair of columns as well as for a given carrier flow through the first column. The control situation becomes the more manageable, the wider the second column as compared to the first one.

The example shown in Fig. 9 has been obtained in the following way. Diesel oil is run on the first column (chromatogram A), the effluents of which are, at first, fully directed to the FID. The corresponding moderate pressure in section B (0.2 atm) causes a small nitrogen flow through the second column. When the peak of n-dodecane starts being eluted the pressure in section A is raised from 0.1 to 0.3 atm causing about 40 % of the effluents to enter the second column, while 60 % still flow to the FID. These conditions are maintained until the elution of n-tridecane is essentially complete. Thereafter, the pressure in A is changed back to 0.1 atm, totally cutting the sample flow to the second column. A 40 % transfer is again allowed just during the few seconds within which the n-alkanes C_{14}, C_{15}, and C_{16} are eluted. After this point no further sample transfer to the second column occurs. At the end of run A the inlet of the second column is pulled off the Teflon connection. The column is then mounted into a separate GC, and chromatogram B is run.

The transfer to the second column of the n-alkanes C_{12} to C_{16} clearly appears on chromatogram B. In addition, the section between C_{12} and C_{13} is also transferred. The branched alkanes comprising the bulk of this material are again eluted between the same n-alkanes, yielding a similar fingerprint. In addition, this section contains some alkylated benzenes and, as major components, the isomeric methylnaphthalenes. While the former

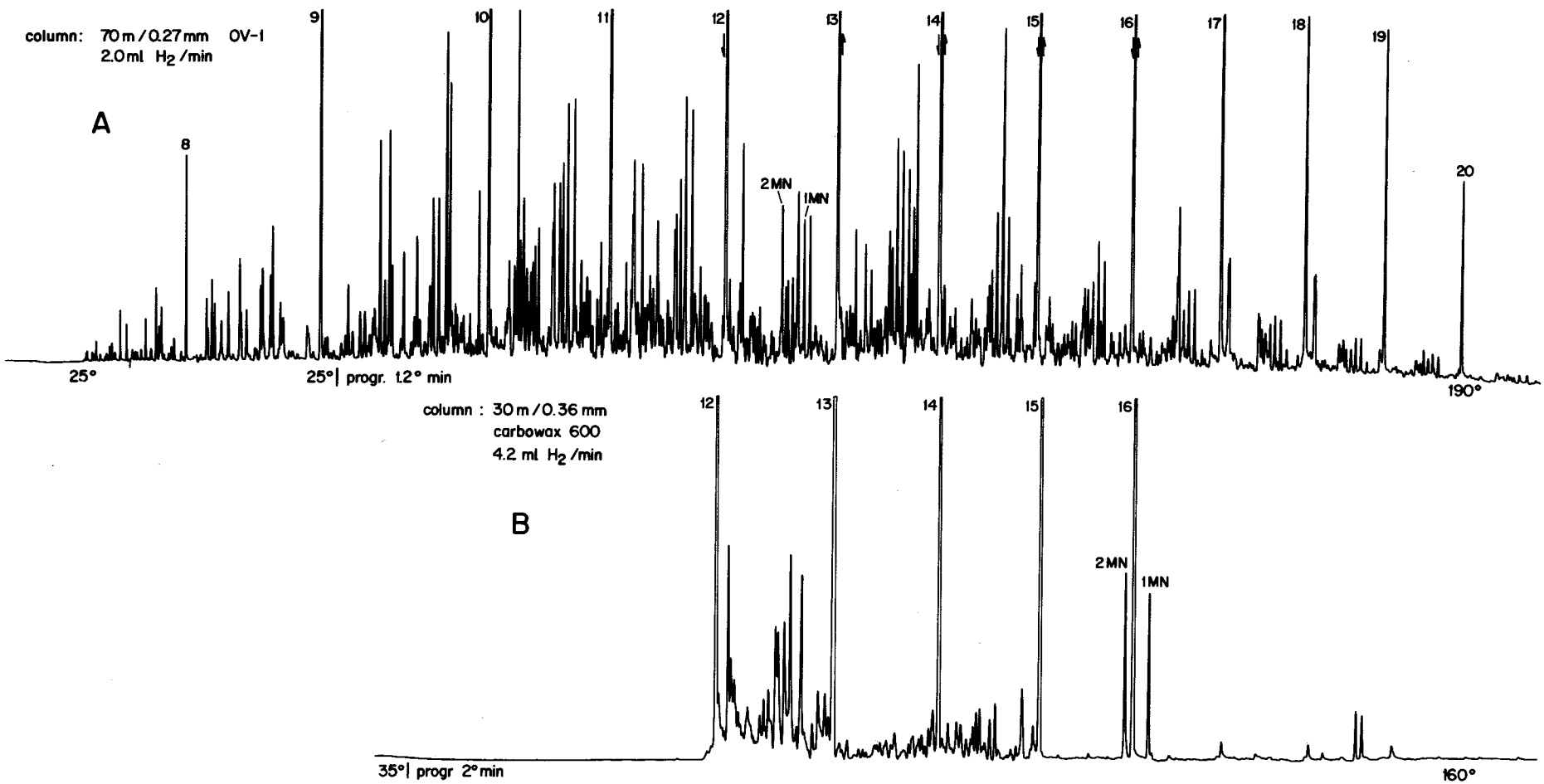

Fig. 9

● Analysis of Diesel oil, partially transferred on, and separately eluted from second column. Arrow down means start, arrow up means end of transfer to second column. Details see text.

appear scattered between C_{13} and C_{15} the latter are eluted as late as C_{16}.

The example has been selected to show best the operation of the technique. It is, on the other hand, not very typical of high resolution technique, since a broad cut comprising two n-alkanes could as well be transferred from a packed column. Normally we transfer just one single peak or a small peak group. The two-dimensional analysis described can, of course, be extended to multi-dimensional analysis by adding further transfer steps.

As we reported five years ago [34] the direct transfer from one column to another yields full efficiency of the second column, provided there is a sufficient temperature difference between two columns. We have recently confirmed this in the following way. We ran on a first column at 80 °C an n-alkane mixture C_{12} to C_{14} that we use to determine the separation number. Half of the column effluents were transferred to a second column kept at room temperature. Elution of the trapped n-alkanes in a separate GC yielded the same separation number as we obtained after regularly injecting (i. e., by a syringe, with stream splitting) the same mixture on the same second column. In other words it makes no measurable difference in separation whether the sample enters the column through the most common injection techniques or as the effluent from a preceding column. We are somewhat surprised by this result, and we do not fully understand the underlying mechanism.

If the transfer technique described would work with both columns at the same temperature, then the method could be greatly simplified since loading and eluting the second column could be carried out in the same oven without touching the column. To have the columns at different temperatures, a dual column chromatograph with two separate ovens would be required.

An essential feature of our transfer technique is its usefulness for GC/MS work. It is a common problem with complex mixtures that poor resolution of neighboring substances may cause severely obscured mass spectra. The interesting, poorly resolved cut, can be transferred to a suitable second column which is then coupled to the MS. The method requires, of course, an easy and rapid coupling technique such as we have been using for a long time with complete success [35].

The same splitting device we use for two-dimensional analysis (Fig. 8), we also use for odour detection. Instead of the inlet of a second column we insert a 15 cm piece of 0.25 mm capillary into the Teflon fitting C. The nitrogen introduced into section B now acts as a makeup gas to increase the flow towards the nose. Since a relatively high flow of 20–50 cm^3 min^{-1} is wanted, the resistance of the short piece is sufficient to allow reasonable splitting conditions. Normally we have about 10 % of the effluents flowing to the FID while the remainder is used for organoleptic detection. Directing 100 % of the effluents to the FID is hardly feasible under these conditions. If it is necessary we close the second exit by pushing a sealed capillary into fitting C.

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