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DETERMINATION OF HYDROCARBONS IN THE PARTS PER 10^9 RANGE USING GLASS CAPILLARY COLUMNS COATED WITH ALUMINIUM OXIDE

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SUMMARY

The properties and limitations of a highly efficient gas chromatographic separation column are described. The column is of importance in the analysis of hydrocarbon emissions as it has the following advantages: high separation efficiency; good detection performance owing to a high signal-to-noise ratio; simultaneous determination of aromatics in the presence of other hydrocarbons in the C_1 - C_9 range in a short time and without the need for a multi-column technique; simple on-line computer connection even in the parts per 10^9 range.

The preparation of the column and its applications and use with suitable measuring equipment are described in detail.

INTRODUCTION

The measurement of hydrocarbons in air is of importance in environmental monitoring. A measurement and evaluation procedure involving gas sampling in the field and subsequent gas chromatographic analysis in the laboratory was elaborated for measuring the emissions in the neighbourhood of refineries and petrochemical plants^{1,2}.

Aluminium was used at an early stage in gas chromatography as a separating agent for hydrocarbons^{3,4}. Considerable improvements in the separation efficiency, in particular a reduction in the tailing effect, were achieved by modifying the aluminium oxide with water⁵⁻⁷, organic liquids⁸ or inorganic salts⁹. The possibility of coating the inner wall of metal capillaries by applying a thin layer of solid material was described by Halász and Horváth¹⁰.

The application of aluminium oxide in packed capillaries was reported by Halász and Heine^{11,12}. Further variations include the generation of oxide layers in aluminium capillaries¹³ and coating the inner walls of the tube by using aqueous or organic dispersions¹⁴⁻¹⁷.

The separation column described in this paper combines the favourable separation properties of aluminium oxide with the advantages of the open capillary tube. Further, the use of glass as a tube material offers a number of additional advantages:

(1) The activity of the glass surface towards the sample components to be analysed is very small. The "irreversible" adsorption and tailing that are observed in metal tubes, particularly with unsaturated or polar substances, does not occur at levels down to the detection limit.

(2) Fine-grained aluminium oxide adheres well to glass surfaces, forming a thin layer even without any auxiliaries. The method of preparation described here produces firmly adhering layers that are non-spalling when the glass is deformed within its elasticity limits.

(3) The coating process can be controlled visually. Failures are immediately apparent and can be corrected.

(4) In addition, glass capillaries can be prepared cheaply in the laboratory by the user, so that the column dimensions and packing materials can be varied at will.

The aluminium oxide layer was applied to the inner wall of the glass capillary from an aqueous dispersion in the form of aluminium hydroxide and converted *in situ* into aluminium oxide by heat treatment. By varying the heat treatment on the one hand and by blocking unwanted activities with potassium chloride on the other, adjustment to the desired separation characteristics can be achieved.

The porous separating phase thus created consists only of inorganic material. Even at high temperature it will not release substances into the carrier gas that will be detected by a flame-ionization detector (FID), so that also in temperature-programmed applications maximal sensitivity is reached even without compensation provisions. The favourable signal-to-noise ratio is increased by small HETP values of the separation system. Hence the automatic evaluation of chromatograms by electronic instruments even at measuring sensitivities as low as $1 \mu\text{g} \cdot \text{m}^{-3}$ per sample can be effected. This allows trace concentrations, for instance in measurements on gaseous emissions, to be determined either directly or after slight enrichment. Fast sampling enables one to resolve rapid fluctuations of emission concentrations according to time, which is not possible with conventional integrating sampling techniques.

EXPERIMENTAL

Apparatus and materials

Measurements are carried out with a conventional gas chromatograph consisting of the following components: an aluminium oxide coated separation column and pre-column, prepared as described below; a flame-ionization detector¹⁸; a pneumatic control unit providing control within about $\pm 1\%$ during 24 h; an air thermostat with electronic control and regulation facilities (isothermal temperature stability $\pm 0.1^\circ$, programmable at at least $20^\circ/\text{min}$); an electrometer amplifier (measuring range up to $1 \cdot 10^{-8}$ A, noise $1 \cdot 10^{-14}$ A, time constant (90% value) for all measuring ranges ≤ 0.5 sec); and an inlet valve (Type 2018 P, Carle Instruments, Fullerton, Calif., U.S.A.).

The amplified detector signal can be fed to a compensation recorder and/or an interface of a data system. Additional equipment required for the analysis includes a micro-stopcock, Type 2 MF 1 (Hamilton, Whittier, Calif., U.S.A.) and a syringe, Type 1010 LL (Hamilton).

Sample input is effected via the pre-column, arranged in the sample loop of the six-way valve (Fig. 1). In this pre-column, the sample is first adsorbed at low temperature and, after heating, passed into the separation column. During the heating phase, a solenoid valve leads the carrier gas through a by-pass, circumventing the pre-column.

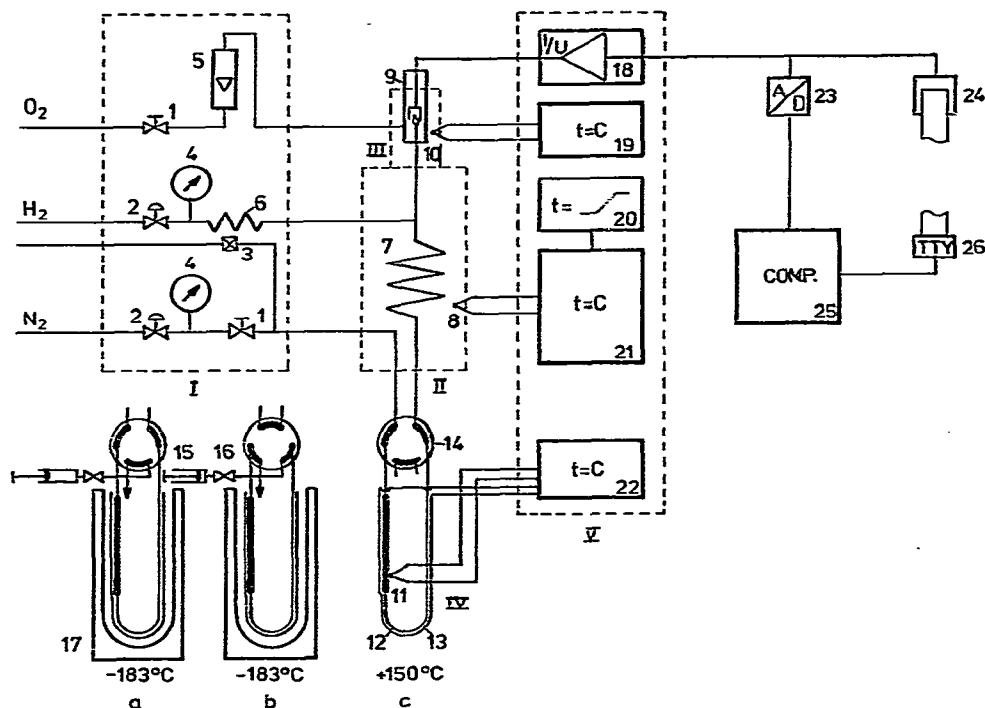


Fig. 1. Schematic layout of the gas chromatographic apparatus. I, Pneumatic supply: 1 = needle valve; 2 = pressure regulator; 3 = solenoid valve; 4 = manometer; 5 = flow meter; 6 = throttle capillary. II, Circulating air thermostat: 7 = separation column; 8 = temperature sensor. III, FID thermostat: 9 = flame-ionization detector; 10 = temperature sensor. IV, Sample inlet and preliminary enrichment: 11 = temperature sensor; 12 = pre-column; 13 = heating conductor; 14 = six-way valve; 15 = gas-tight syringe; 16 = micro-stopcock; 17 = Dewar vessel. V, Power supply: 18 = electrometer amplifier; 19 = power supply and temperature regulator of the FID thermostat; 20 = temperature programmer; 21 = power supply and temperature regulator of the circulating air thermostat; 22 = power supply and temperature regulator of the pre-column; 23 = integrating analogue-digital converter; 24 = recorder; 25 = data evaluation system; 26 = teletype.

To prevent carrier gas and detector supply gases from being contaminated by organic substances, no plastic or rubber material is used in the pneumatic system whenever practicable. Even the diaphragms of the pressure regulators are made of metal.

The connection tubes and constructional units are arranged as to restrict the dead volume to the minimum. The inlet valve is a miniature six-way valve with a Teflon rotating disk of conventional design; the sample loop of this valve is represented by the pre-column.

Pre-column

Aluminium hydroxide (Camag, Muttenz, Switzerland), sieve fraction 0.09–0.10 mm, is used for the production of aluminium oxide (see below).

A 7-cm length of stainless-steel tubing of I.D. 1 mm and 15 cm of stainless-steel tubing of I.D. 0.5 mm are soldered together and bent into an U-shape, as shown in Fig. 2. The tube of I.D. 1 mm is filled to a level of 2 cm with aluminium oxide that has been subjected to a special treatment. The packing is fixed with a wad of quartz-wool.

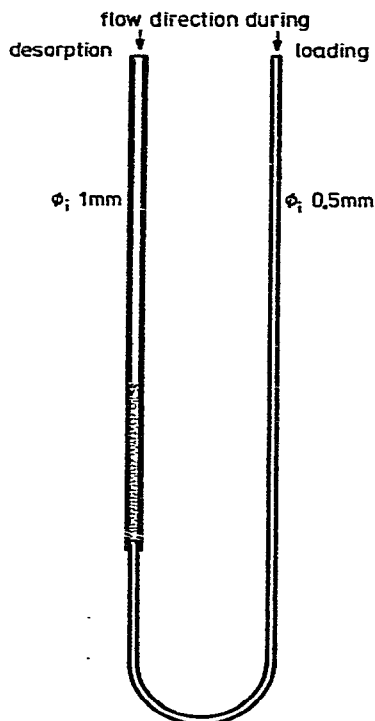


Fig. 2. Pre-column.

Preparing the aluminium oxide for the pre-column. Aluminium hydroxide of grain size 0.09–0.10 mm is heated for 24 h in an open crucible (e.g., nickel) at 400°. Subsequently 3% (w/w) of water is added, followed by heating for 24 h at 300° in a tightly sealed, pressure resistant (100 bar) stainless-steel crucible. The aluminium oxide should fill the stainless-steel container without leaving a dead space.

Separation column

The materials required are as follows: aluminium hydroxide, $\leq 2 \mu\text{m}$ (Camag); Baymal (colloidal aluminium hydroxide; DuPont, Wilmington, Del., U.S.A.); acetic acid, >96%, reagent grade; acetic acid, 1%; nitrogen; and potassium chloride solution, 2% (w/w) solution. The equipment consists of a 1-ml syringe with a Teflon piston (e.g., Hamilton, Type 1001), a nitrogen source with needle valve (filling >100 bar), a

thermostat ($300 \pm 1^\circ$), a pressure regulator (control range 0–3 bar), a glass-drawing machine as described by Desty *et al.*¹⁹ (e.g., Hewlett-Packard, Avondale, Pa., U.S.A.) and an ultrasonic bath.

By means of the glass-drawing machine, a glass tube (Duran 50; Schott and Genossen, Mainz, G.F.R.) is drawn out to a capillary of O.D. ca. 1 mm and I.D. 0.4 mm. This capillary is coiled to give a helix of diameter 12 cm.

Preparation of the coating suspension. Aluminium hydroxide ($\leq 2 \mu\text{m}$) is heated in an open metal crucible (e.g., nickel) for 24 h at 300° . A 20-g amount of the aluminium oxide obtained is mixed with 70 ml of 5% (w/w) Baymal solution and 0.3 ml of acetic acid ($>96\%$) and stirred for about 10 min in an ultrasonic bath. Subsequently, the mixture is filtered through a wire sieve of 300 mesh and allowed to stand for 24 h for ageing. The suspension thus prepared shows thixotropic behaviour.

Coating of the capillary. The glass capillary tube to be coated is connected via a polyethylene capillary tube to a length of about 20 m of glass capillary tube of the same diameter to prevent draining disturbances. Through a polyethylene capillary slipped over the other end of the tube, 0.6 ml of the suspension is forced, by means of the syringe, into the capillary tube, which has previously been rinsed and wetted with 1% acetic acid. The polyethylene tube used for filling is connected to the source of nitrogen. The nitrogen flow pushes the suspension plug through the capillary tube, leaving on the inner wall of the tube a layer of uniform thickness which soon solidifies. To achieve complete coverage of a 65-m length of tube, this procedure must be repeated four times. In order to generate a uniform layer, it is essential to apply the same amount of suspension each time. For the coating procedure, the needle valve connected to the source of nitrogen is adjusted to supply gas at a flow-rate of $4 \text{ ml} \cdot \text{min}^{-1}$. During this step, the pressure drop at the valve must be high compared with that developing at the capillary while coating is effected. A scheme of the filling equipment is shown in Fig. 3. The 20-m length of glass capillary attached for preventing drainage problems can be cleaned from the suspension by flushing with 1% acetic acid and stored for re-use.

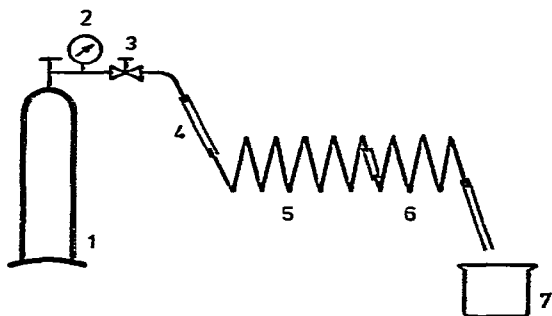


Fig. 3. Coating device. 1 = Storage tank for nitrogen; 2 = manometer; 3 = needle valve; 4 = polyethylene tube; 5 = glass capillary; 6 = auxiliary capillary; 7 = collection vessel.

The coated, moist capillary is stored for at least 10 h and then dried in a flow of nitrogen at ambient temperature. If a nitrogen pressure of 3 bar is applied, drying will take about 1 week. During this time, the whiteness of the coating undergoes changes, allowing one easily to follow the process visually. The nitrogen flowing

through the capillary is water-saturated after having travelled for a short distance, which implies that even small temperature fluctuations along the column will cause condensation, destroying the coating. Storage of the drying columns in well isolated containers, *e.g.*, made of polystyrene, will prevent this effect. After complete drying at ambient temperature the column is heated in a flow of nitrogen for 3 h at 300°. During this treatment, the coating becomes solid, insoluble and activated. The amount of aluminium oxide introduced into the capillary is determined by differential weighing. It can be varied within a wide range by altering the coating parameters, such as modifying the viscosity of the suspension by varying the volume of acetic acid added or by the addition of water, varying the nitrogen flow-rate or varying the amount of suspension introduced in each particular instance. Table I shows the coatings obtained by the above procedure under the same conditions and the reproducibility of the coating strength.

TABLE I
COATINGS ON SEPARATION COLUMNS

Column No.	Inner diameter (mm)	Length (m)	Al ₂ O ₃ coating (mg·m ⁻¹)
1	0.40	67	5.8
2	0.40	70	5.4
3	0.40	69	5.7
4	0.40	71	5.1
5	0.40	69	5.6
6	0.40	61	5.3
7	0.40	58	5.9
8	0.40	56	5.5
9	0.40	64	5.4
10	0.40	69	5.4
Average			5.5
Standard deviation			±0.24

For activity reduction, the capillary thus prepared is rinsed twice, without intermediate drying, with 2 ml of 2% (w/w) potassium chloride solution. The potassium chloride solution is forced through the column by applying a nitrogen pressure of 2 bar. After drying at ambient temperature with nitrogen (3 bar pressure) and heating for 1 h at 300° under a flow of nitrogen, the column is ready for use.

Sample injection

Sampling for measurements on emissions in air in the field is effected as described earlier¹, using glass gas collection vessels specially developed for this purpose.

Afterwards, in the laboratory, a sample of 10 cm³ or more is drawn from the gas collection vessel using a gas-tight syringe. About 2 cm³ of the sample gas are used to scavenge the feed lines to the inlet valve at position (a) in Fig. 1. After switching to position (b), exactly 8 cm³ are passed into the pre-column. The pre-column is refrigerated by immersion in liquid oxygen. During these steps, the solenoid valve 3 is opened.

Subsequently the coolant is removed, the inlet valve switched to position (c) and the pre-column electrically heated to 150°. The solenoid valve 3 is closed, thus allowing the sample components to be desorbed and passed by the flow of carrier gas

into the separation column. At the moment the solenoid valve is shut, the temperature programme and data evaluation system are started. Fig. 4 shows a time-sequence chart of the analysis. The syringe equipped with injection needle and micro-stopcock, if not in use, is permanently flushed with hydrocarbon-free nitrogen.

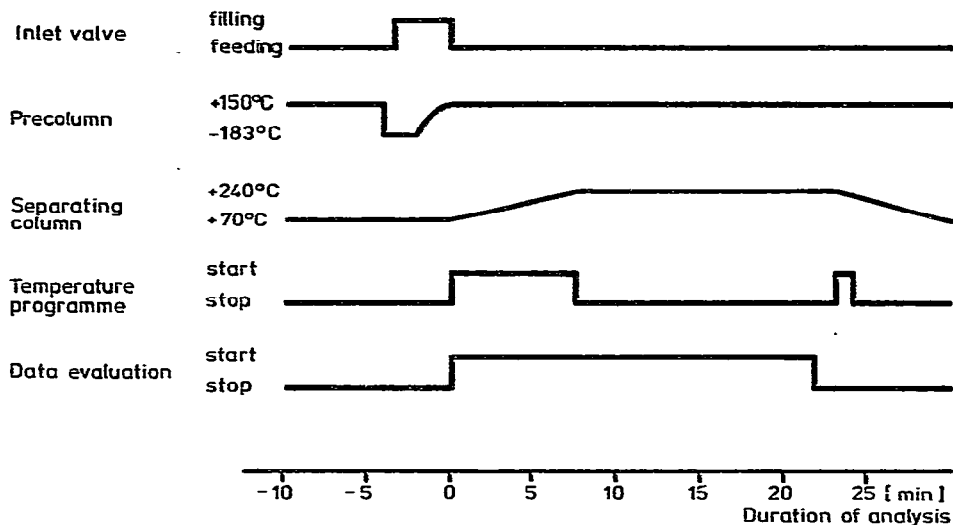


Fig. 4. Temporal sequence of the analysis.

Purity control of the carrier gas is carried out, as mentioned above, under conditions identical with those of the analysis. In position (a) in Fig. 1 carrier gas is passed through the cooled pre-column for 5 min (*ca.* 50 ml), followed by desorption and analysis, as described above. Hydrocarbon peaks must not appear during this procedure.

RESULTS AND DISCUSSION

Example of a measurement

Fig. 5 shows the chromatogram of a mixture of C_1 – C_9 hydrocarbons in air, the concentrations of the different components being approximately 0.003 – $0.5 \text{ mg} \cdot \text{m}^{-3}$. As can be seen, $0.014 \text{ mg} \cdot \text{m}^{-3}$ of benzene, for instance, after a net retention time of about 11 min, yields a readily measurable signal, and $0.008 \text{ mg} \cdot \text{m}^{-3}$ of *n*-octane gives a signal more than ten times the background noise.

Fig. 6 is the corresponding computer print-out of the results. The values were measured during real-time analysis in an HP 3354 laboratory data system (Hewlett-Packard), which was also used for the subsequent evaluation and documentation. For quantitative evaluation, the analyser system was calibrated with a methane–nitrogen mixture of known methane concentration, applying a previously described procedure¹.

Statistical evaluation

A test mixture similar to that shown in Figs. 5 and 6 was analysed ten times

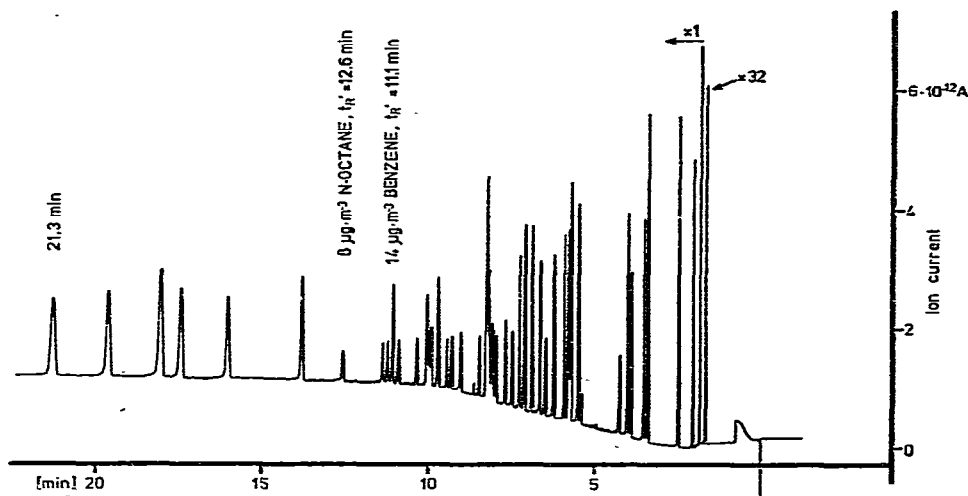


Fig. 5. Analysis of a test mixture using a glass capillary column coated with Al_2O_3 . Length, 71 m; I.D., 0.40 mm; coating, $5.1 \text{ mg} \cdot \text{m}^{-1}$ of Al_2O_3 ; temperature programme, $70\text{--}240^\circ$ at $20^\circ \cdot \text{min}^{-1}$. Assignment: see Fig. 6.

consecutively. The mean value, standard deviation and relative standard deviation are given in Table II. Standard deviations for a concentration range of $0.003\text{--}0.5 \text{ mg} \cdot \text{m}^{-3}$ are usually between 2 and 10%. They increase, as is usual with this type of analysis, with decreasing concentration and increasing peak width.

Test of applicability of the apparatus to trace analysis

It is well known that active solids, when considering relatively rapid chromatographic processes, tend to retain "irreversibly" portions of organic substances. The amounts retained are generally small. Consequently, when dealing with high-concentration samples, the resulting error is included within the analytical error and thus is not discovered. However, the amounts involved in the analytical procedure considered here are extremely small. Only $8 \cdot 10^{-11} \text{ g}$ of a given substance will enter the separation column if its concentration in the injected sample is $0.01 \text{ mg} \cdot \text{m}^{-3}$. The above-mentioned errors under these circumstances can reach a high percentage of the measured value.

It is therefore imperative to check the method of measurement for its applicability to all classes of substances to be analysed. The test procedure used here has been described earlier¹. It involves the analysis of known but different amounts of the substance in question and checking for systematic deviations of the measured from the true value. The different test mixtures were prepared by using a Telab pump (Type BF 411/30 + 30 K + H 1/30 + H 2/50; Telab-Labor & Technik, Homburg, G.F.R.) in a dynamic procedure¹. Table III lists the true values and the analytical results for 10 fillings of a test mixture, their averages, their standard deviations, and their deviations from the true values. When the pre-columns and separation columns were prepared by the method described above, no substantial errors were encountered for concentrations down to a few micrograms per cubic metre. Deviations from the true values are of the same order as the standard deviation.

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RETENTIONSZEIT MINUTEN	FLAECHE COUNT	KONZENTRATION MG/CEM	KOMPONENTE
1.65	13254	.511	METHAN
1.82	520	.020	AETHAN
2.05	541	.221	AETHEN
2.50	726	.328	PROPAN
3.44	919	.036	CYCLOPROPAN
3.55	614	.024	PROPEN
3.99	424	.017	AETHIN
4.04	769	.032	ISO-BUTAN
4.29	276	.311	N-BUTAN
5.47	83	.023	TR-BUTEN-2
5.56	667	.026	BUTEN-1
5.78	744	.029	ISO-BUTEN
5.83	748	.029	2.2-DIMETHYLPROPAN
5.97	593	.023	CIS-BUTEN-2
6.28	607	.024	ISO-PENTAN
6.52	304	.012	N-PENTAN
6.71	422	.017	PROPIN
6.93	574	.022	BUTADIEN-1.3
7.14	694	.024	3-METHYLBUTEN-1
7.29	520	.020	TR-PENTEN-2
7.53	255	.010	PENTEN-1
7.73	287	.011	CIS-PENTEN-2
8.00	276	.011	2.2-DIMETHYLBUTAN
8.11	299	.012	METHYLCYCLOPENTAN
8.17	425	.017	CYCLOHEXAN
8.24	564	.022	2-METHYLPENTAN
8.32	731	.029	3-METHYLPENTAN
8.43	251	.010	BUTIN-1
8.52	238	.009	N-HEXAN
8.69	80	.003	>C5-VERBINDUNG
9.11	256	.011	TR-HEXEN-2
9.37	200	.008	HEXEN-1
9.51	206	.008	CIS-HEXEN-2
9.77	485	.019	2.2-DIMETHYLPENTAN
9.96	249	.010	3.3-DIMETHYLPENTAN
10.33	233	.009	2.3-DIMETHYLPENTAN
12.11	480	.019	2-+3-METHYLHEXAN
10.41	200	.008	N-HEPTAN
12.95	212	.008	TR-HEPTEN-2
11.13	348	.014	BENZOL
11.26	200	.008	HEPTEN-1
11.42	195	.008	CIS-HEPTEN-2
12.60	217	.008	N-OKTAN
13.82	587	.023	TOLUOL
16.04	821	.032	N-NONAN
17.46	984	.039	ETHYLBENZOL
13.10	1422	.056	M-+P-XYLOL
19.67	1186	.046	O-XYLOL
21.29	1256	.049	CUMOL
	3957	.155	SUMME C4-VERBINDUNGEN
	3325	.130	SUMME C5-VERBINDUNGEN
	6605	.258	SUMME VERBINDUNGEN >C5
	3593	.141	SUMME C5-AROMATEN
	36890	1.443	SUMME KW

Fig. 6. Print-out of the analytical results for a test mixture, produced by the HP 3354 laboratory system. Hydrocarbon concentrations are given in $\text{mg} \cdot \text{m}^{-3}$.

TABLE II
REPRODUCIBILITY TEST

10 repeated analyses of the same mixture (test results in $\text{mg} \cdot \text{m}^{-3}$, \bar{x} = arithmetic mean; s = standard deviation; ν = relative standard deviation or coefficient of variation).

Hydrocarbon	Number of replicate experiment										\bar{x}	s	ν (%)
	1	2	3	4	5	6	7	8	9	10			
Methane	0.515	0.534	0.524	0.538	0.517	0.511	0.503	0.520	0.512	0.516	0.5190	0.0106	2.0
Ethane	0.020	0.021	0.020	0.020	0.021	0.020	0.020	0.020	0.021	0.020	0.0203	0.0005	2.5
Ethene	0.018	0.019	0.019	0.020	0.018	0.021	0.019	0.018	0.018	0.020	0.0190	0.0011	5.8
Propane	0.028	0.028	0.027	0.027	0.029	0.028	0.028	0.029	0.028	0.028	0.0280	0.0007	2.5
Cyclopropane	0.036	0.036	0.034	0.033	0.035	0.036	0.036	0.035	0.036	0.036	0.0353	0.0011	3.1
Propene	0.024	0.024	0.023	0.022	0.024	0.024	0.024	0.024	0.024	0.025	0.0238	0.0008	3.4
Ethyne	0.017	0.017	0.016	0.015	0.017	0.017	0.017	0.017	0.017	0.017	0.0167	0.0007	4.2
Isobutane	0.031	0.030	0.029	0.029	0.030	0.030	0.030	0.030	0.030	0.030	0.0299	0.0006	2.0
<i>n</i> -Butane	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.011	0.0110	0.0000	0
<i>trans</i> -2-Butene	0.005	0.004	0.004	0.003	0.004	0.003	0.004	0.005	0.004	0.004	0.0040	0.0007	17.5
1-Butene	0.029	0.028	0.024	0.021	0.029	0.026	0.028	0.027	0.028	0.029	0.0269	0.0026	9.7
Isobutene	0.030	0.029	0.027	0.025	0.030	0.029	0.029	0.030	0.029	0.029	0.0287	0.0016	5.6
2,2-Dimethylpropane	0.029	0.029	0.028	0.027	0.029	0.029	0.029	0.029	0.029	0.028	0.0286	0.0007	2.5
<i>cis</i> -2-Butene	0.023	0.023	0.022	0.020	0.023	0.023	0.023	0.023	0.023	0.023	0.0226	0.0010	4.4
Isopentane	0.024	0.024	0.024	0.023	0.024	0.024	0.024	0.023	0.024	0.024	0.0238	0.0004	1.7
<i>n</i> -Pentane	0.011	0.013	0.012	0.010	0.013	0.012	0.012	0.012	0.011	0.013	0.0119	0.0010	8.4
Propyne	0.017	0.017	0.015	0.013	0.018	0.017	0.017	0.017	0.018	0.017	0.0166	0.0015	9.0
1,3-Butadiene	0.021	0.021	0.018	0.017	0.022	0.022	0.022	0.022	0.022	0.022	0.0209	0.0019	9.1
3-Methyl-1-butene	0.026	0.026	0.022	0.019	0.025	0.024	0.025	0.025	0.026	0.026	0.0244	0.0023	9.4

DETERMINATION OF HYDROCARBONS IN THE ppb RANGE

<i>trans</i> -2-Pentene	0.020	0.021	0.016	0.020	0.020	0.021	0.020	0.020	0.0198	0.0015	7.6
1-Pentene	0.010	0.010	0.008	0.010	0.010	0.010	0.011	0.011	0.0099	0.0009	9.1
<i>cis</i> -2-Pentene	0.012	0.012	0.009	0.011	0.011	0.011	0.012	0.011	0.0110	0.0009	8.2
2,2-Dimethylbutane	0.010	0.012	0.010	0.011	0.011	0.011	0.011	0.010	0.0106	0.0007	6.6
Methylcyclopentane	0.011	0.012	0.012	0.012	0.011	0.010	0.010	0.010	0.0112	0.0009	8.0
Cyclohexane	0.012	0.015	0.015	0.015	0.013	0.014	0.012	0.011	0.0138	0.0018	13.0
2-Methylpentane	0.021	0.022	0.021	0.022	0.022	0.022	0.022	0.021	0.0224	0.0020	8.9
3-Methylpentane	0.027	0.027	0.024	0.029	0.028	0.025	0.027	0.028	0.0267	0.0016	6.0
1-Butyne	0.006	0.006	0.006	0.006	0.006	0.006	0.007	0.008	0.0064	0.0007	10.9
<i>n</i> -Hexane	0.009	0.010	0.008	0.009	0.009	0.009	0.009	0.009	0.0092	0.0006	6.5
<i>trans</i> -2-Hexene	0.010	0.008	0.008	0.009	0.011	0.009	0.010	0.010	0.0093	0.0009	9.7
1-Hexene	0.008	0.008	0.007	0.008	0.008	0.008	0.009	0.008	0.0081	0.0006	7.4
<i>cis</i> -2-Hexene	0.008	0.010	0.010	0.008	0.008	0.009	0.008	0.008	0.0085	0.0010	11.8
2,2-Dimethylpentane	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.0188	0.0006	3.2
3,3-Dimethylpentane	0.010	0.010	0.009	0.010	0.010	0.010	0.010	0.010	0.0099	0.0003	3.0
2,3-Dimethylpentane	0.009	0.009	0.008	0.009	0.009	0.009	0.009	0.009	0.0089	0.0003	3.4
2- + 3-Methylhexane	0.019	0.019	0.018	0.019	0.019	0.019	0.019	0.019	0.0188	0.0004	2.1
<i>n</i> -Heptane	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.008	0.0080	0.0000	0
<i>trans</i> -2-Heptane	0.009	0.009	0.008	0.008	0.008	0.008	0.009	0.008	0.0085	0.0005	5.9
Benzene	0.013	0.014	0.015	0.014	0.014	0.014	0.014	0.014	0.0140	0.0007	5.0
1-Heptene	0.008	0.008	0.007	0.008	0.008	0.008	0.008	0.008	0.0076	0.0007	9.2
<i>cis</i> -2-Heptene	0.007	0.007	0.006	0.007	0.007	0.007	0.007	0.007	0.0072	0.0006	8.3
<i>n</i> -Octane	0.007	0.008	0.008	0.008	0.007	0.008	0.008	0.007	0.0076	0.0005	6.6
Toluene	0.025	0.024	0.024	0.023	0.023	0.023	0.023	0.023	0.0240	0.0016	6.7
<i>n</i> -Nonane	0.033	0.032	0.032	0.032	0.033	0.035	0.032	0.031	0.0322	0.0013	4.0
Ethylbenzene	0.037	0.033	0.036	0.039	0.036	0.036	0.039	0.036	0.0364	0.0017	4.7
<i>p</i> - + <i>m</i> -Xylene	0.052	0.052	0.052	0.056	0.053	0.052	0.053	0.053	0.0527	0.0013	2.5
<i>o</i> -Xylene	0.047	0.046	0.048	0.046	0.045	0.046	0.046	0.044	0.0456	0.0014	3.1
Isopropylbenzene	0.045	0.047	0.049	0.049	0.049	0.049	0.049	0.047	0.0481	0.0015	3.1

TABLE III
COMPARISON OF TRUE CONCENTRATIONS WITH VALUES MEASURED ON TEN DIFFERENT ANALYTICAL RUNS

Test substance	True value ($\mu\text{g}\cdot\text{m}^{-3}$)	Measured value ($\mu\text{g}\cdot\text{m}^{-3}$)										Average measured ($\mu\text{g}\cdot\text{m}^{-3}$)	Standard deviation ($\mu\text{g}\cdot\text{m}^{-3}$)	Difference between true and average measured values ($\mu\text{g}\cdot\text{m}^{-3}$)
		1	2	3	4	5	6	7	8	9	10			
Ethyne	8	9	8	8	8	8	8	8	9	9	8	8.4	± 0.5	-0.4
	33	33	32	31	34	32	33	31	31	31	32	32.2	± 1.0	+0.8
	163	161	160	159	156	158	159	160	160	164	165	160.3	± 2.7	+2.7
2-Butene	19	20	18	19	19	18	18	18	20	20	18	18.9	± 0.9	+0.1
	78	77	77	79	77	80	76	79	77	77	76	77.5	± 1.4	+0.5
	399	409	407	401	407	409	401	404	412	412	407	406.9	± 3.9	-7.9
Cyclohexane	34	33	32	35	36	30	35	32	30	31	31	32.5	± 2.2	+1.5
	143	138	141	143	140	141	140	142	138	142	143	140.8	± 1.8	+2.2
	354	354	359	371	358	365	360	358	369	369	357	361.7	± 5.7	-7.7
Benzene	27	28	28	29	28	28	28	28	28	30	27	28.4	± 1.0	-1.4
	120	120	118	115	121	118	117	116	117	118	115	117.5	± 2.0	+2.5
	294	300	302	301	293	300	297	299	293	295	302	298.2	± 3.5	-4.2
Octane	5	6	6	5	5	6	5	5	4	5	5	5.2	± 0.6	-0.2
	49	46	48	47	47	47	47	47	49	46	51	47.5	± 1.5	+1.5
	145	147	143	149	149	143	143	145	150	150	146	146.5	± 2.9	+1.5

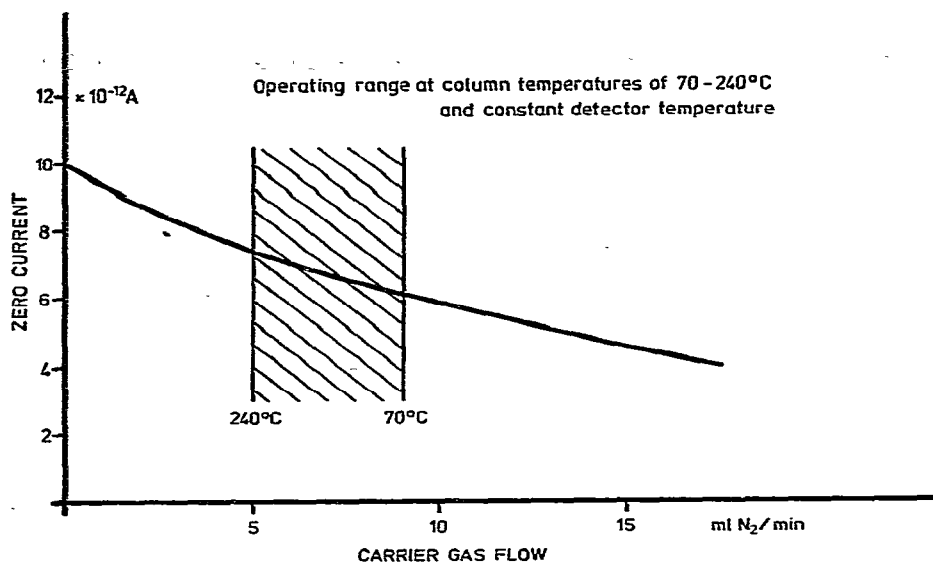


Fig. 7. Zero current of the FID at different carrier gas flow-rates. Combustion gas: H_2 , $20 \text{ ml} \cdot \text{min}^{-1}$. Scavenging gas: O_2 , $500 \text{ ml} \cdot \text{min}^{-1}$. Detector temperature: 250° .

Introduction of the sample

The high separation capability of the capillary column used, of course, becomes apparent only if the hydrocarbons enriched from the sample are introduced into the separation system as highly concentrated as possible. *i.e.*, diluted with as small volumes of carrier gas as possible. For this reason, the flow of carrier gas is switched off before heating the loaded pre-column, as described above. If not, double peaks,

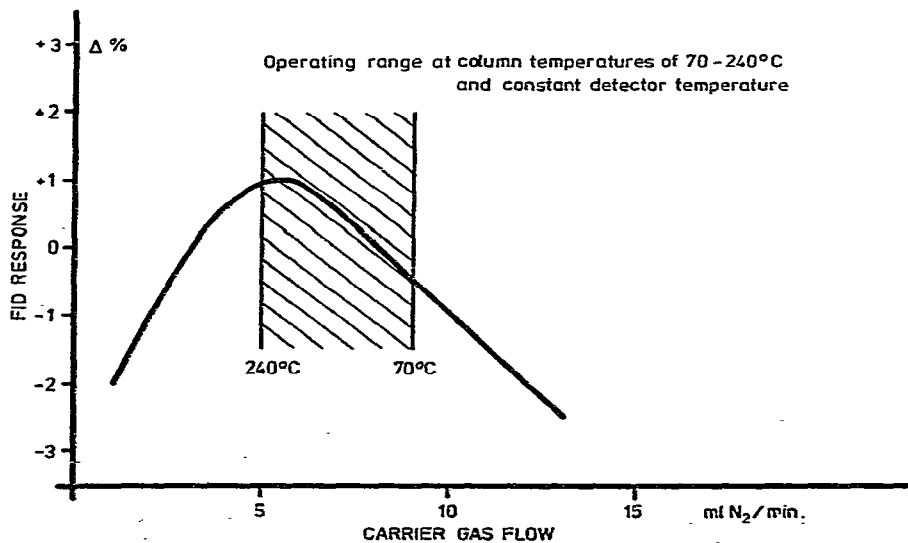


Fig. 8. Change of FID response at different carrier gas flow-rates. Combustion gas: H_2 , $20 \text{ ml} \cdot \text{min}^{-1}$. Scavenging gas: O_2 , $500 \text{ ml} \cdot \text{min}^{-1}$. Detector temperature: 250° .

TABLE IV

KOVÁTS RETENTION INDICES MEASURED ON TEN DIFFERENT SEPARATION COLUMNS

Inlet pressure: 2 bar. Column temperature: 50–210°.

Test substance	Column No.									
	1	2	3	4	5	6	7	8	9	10
Acetylene	375	376	372	376	375	376	373	374	375	376
Isobutene	454	453	453	458	457	457	455	457	454	458
Pentyne	547	543	545	549	546	550	548	548	544	548
2-Hexene	625	624	623	626	625	626	625	624	626	626
2,2-Dimethylpentane	668	667	667	668	668	668	667	668	667	668
Benzene	734	735	737	737	736	737	736	736	737	736
Toluene	834	835	833	834	834	834	835	834	834	835

peak broadening and tailing will occur. These difficulties are avoided, as can be seen in Fig. 5, by the method of sample introduction described here, *viz.*, with stopped gas flow during heating.

Detector

As illustrated in Fig. 5, the zero current of the detector increases with increasing temperature (70–240°) by about $1.1 \cdot 10^{-12}$ A. This phenomenon is not caused by "bleeding", *i.e.*, an increased release of organic matter from the separation column

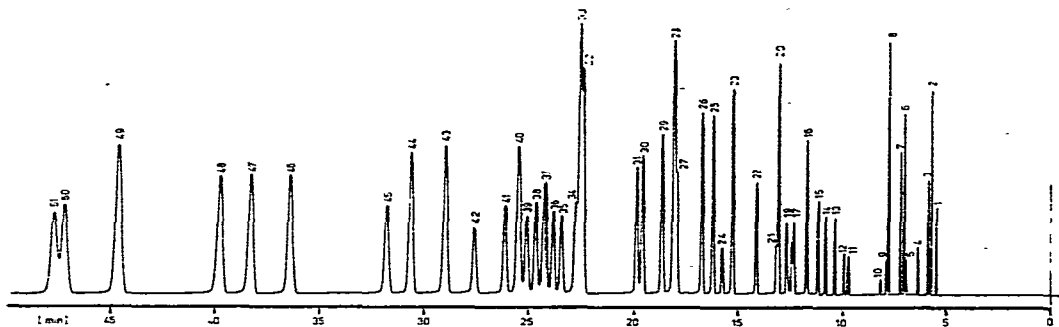


Fig. 9. Analysis of test mixture using a glass capillary coated with Al_2O_3 . Length, 71 m; I.D., 0.40 mm; Al_2O_3 coating, $5.1 \text{ mg} \cdot \text{m}^{-1}$; column temperature, 130°; inlet pressure, 2 bar. Peaks: 1 = methane; 2 = ethane; 3 = ethene; 4 = propane; 5 = cyclopropane; 6 = propene; 7 = acetylene; 8 = propadiene; 9 = isobutane; 10 = *n*-butane; 11 = *trans*-2-butene; 12 = 1-butene; 13 = isobutene; 14 = *cis*-2-butene; 15 = 2,2-dimethylpropane; 16 = methylcyclobutane; 17 = cyclopentane; 18 = isopentane; 19 = 1,2-butadiene + propyne + *trans*-1,2-dimethylcyclopropane; 20 = 1,1-dimethylcyclopropane; 21 = *n*-pentane; 22 = *cis*-1,2-dimethylcyclopropane + 1,3-butadiene; 23 = ethylcyclopropane; 24 = 3-methyl-1-butene; 25 = cyclopentene; 26 = *trans*-2-pentene; 27 = 2-methyl-2-butene; 28 = 1-pentene + methylenecyclobutane; 29 = 2-methyl-1-butene; 30 = *cis*-2-pentene; 31 = 3-methyl-1,2-butadiene; 32 = 2-butyne; 33 = 2,2-dimethylbutane + 1,1,2-trimethylcyclopropane; 34 = methylcyclopentane + 3,3-dimethyl-1-butene; 35 = ethylcyclobutane; 36 = cyclohexane; 37 = 1-butyne + 2,3-dimethylbutane; 38 = 2-methylpentane; 39 = 3-methylpentane; 40 = 1,2-pentadiene + 2,3-pentadiene; 41 = vinylcyclopropane; 42 = *n*-hexane; 43 = *trans*-4-methyl-2-pentene + isopropylcyclopropane; 44 = 2-methyl-1,3-butadiene; 45 = 1-methylcyclopentene; 46 = 4-methyl-1-pentene; 47 = *cis*-1,3-pentadiene; 48 = *trans*-1,3-pentadiene; 49 = 3-methyl-1-butyne; 50 = isopropylacetylene; 51 = 2-pentyne.

at higher temperature levels, as is usually the case, but by the reduction in the flow of nitrogen (viscosity increase) to the detector as a consequence of the increasing column temperature. This relationship is a well known and more or less pronounced phenomenon, depending on the detector geometry. The general lay-out of the detector used was described elsewhere¹⁸. Fig. 7 shows the zero current of the detector as a function of the carrier gas flow-rate.

It would require complicated equipment to keep the carrier gas flow-rate constant when capillary columns and rapid temperature changes are involved. On the other hand, the small zero drift does not interfere with the evaluation of chromatograms by manual or modern electronic auxiliaries. Therefore, the carrier gas flow-rate need not be kept constant.

Not only the baseline current, but also the response of a flame-ionization detector, depends on the flow-rate of nitrogen and the ratio of hydrogen to nitrogen in the flame²⁰. Depending on the geometry of the detector, this may lead to extensive deviations in response and should be checked carefully. The influence on response

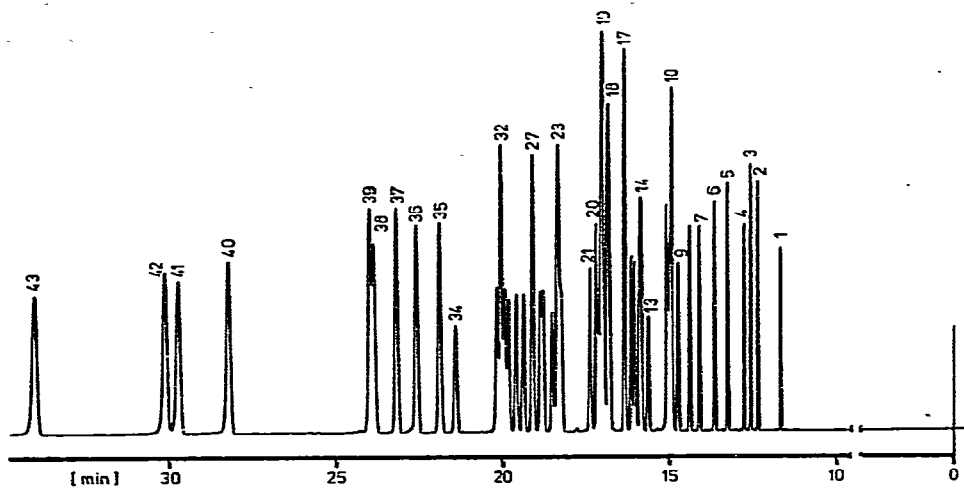


Fig. 10. Analysis of test mixture using a glass capillary coated with Al_2O_3 and squalane. Length, 129 m; I.D., 0.25 mm; coating, Al_2O_3 $0.6 \text{ mg} \cdot \text{m}^{-1}$; squalane $0.3 \text{ mg} \cdot \text{m}^{-1}$; column temperature, 100° ; inlet pressure, 5 bar. Peaks: 1 = *n*-pentane; 2 = 2-methylpentane; 3 = 3-methylpentane; 4 = *n*-hexane; 5 = 2,2-dimethylpentane; 6 = 2,2,3-trimethylbutane; 7 = 2-methylhexane; 8 = 3-methylhexane; 9 = *cis*-2,5-dimethyl-3-hexene; 10 = 2,2,4-trimethylpentane + *trans*-2,2-dimethyl-3-hexene; 11 = *trans*-2,5-dimethyl-3-hexene; 12 = benzene + *n*-heptane; 13 = 2,4,4-trimethyl-1-pentene; 14 = 2,4,4-trimethyl-2-pentene + 2,2-dimethylhexane; 15 = *cis*-2,2-dimethyl-3-hexene; 16 = 2,5-dimethylhexane; 17 = 2,4-dimethylhexane + 1,1,3-trimethylcyclopentane; 18 = *trans*-2-methyl-3-heptene + 2,2,3-trimethylpentane; 19 = *trans*-4-ethyl-2-hexene + 3,3-dimethylhexane + 2,5-dimethyl-1-hexene; 20 = 3,4-dimethyl-1-hexene + *trans*-6-methyl-3-heptene; 21 = *trans*-3,4,4-trimethyl-2-pentene; 22 = 3-methylheptane; 23 = *cis*-4-methyl-3-ethyl-2-pentene + 3,4-dimethylhexane; 24 = 3-ethyl-3-hexene; 25 = 2-methyl-1-heptene; 26 = 3-methyl-3-ethylpentane; 27 = 2-methyl-3-ethyl-2-pentene + 1-octene; 28 = *trans*-3-octene; 29 = 2-methyl-2-heptene; 30 = *n*-octane; 31 = toluene; 32 = *trans*-2-octene + *trans*-1-methyl-2-ethylcyclopentane; 33 = 1,1-dimethylcyclohexane; 34 = *trans*-1,3-dimethylcyclohexane; 35 = isopropylcyclopentane; 36 = *cis*-1-methyl-2-ethylcyclopentane; 37 = *n*-propylcyclopentane; 38 = 4-vinylcyclohexene; 39 = ethylcyclohexane; 40 = ethylbenzene; 41 = *p*-xylene; 42 = *m*-xylene; 43 = *o*-xylene.

in the range 5–10 ml·min⁻¹ of nitrogen, shown in Fig. 8, was less than $\pm 1\%$ with the detector used. For this and the above reasons, stabilization of the supply of carrier gas to the detector was omitted.

Column

The lifetime of a properly treated column can be several years. A column in use in our laboratories for 18 months has shown no signs of deterioration.

The column described is a powerful tool for measurements relating to emission problems owing to its ability to analyse in one run hydrocarbons from methane to cumene at very low concentrations, with a high separation efficiency for the low-boiling components such as methane, ethane and ethylene.

The Kováts retention indices of several polar substances from ten different separation columns prepared by the same procedure, as listed in Table IV, show that the separation behaviour of the columns is satisfactorily reproducible.

Other applications

The separation column with an aluminium oxide coating described here is applicable not only in trace analyses but, of course, also in the analysis of sample components with concentrations in the per cent range. Fig. 9 shows an example of such an application. In this instance, a test mixture containing C₁–C₆ hydrocarbons in higher concentrations in the percent range was fed into the column. A good separation is obtained, regardless of the concentration.

Figs. 10 and 11 show chromatograms of test mixtures obtained with aluminium

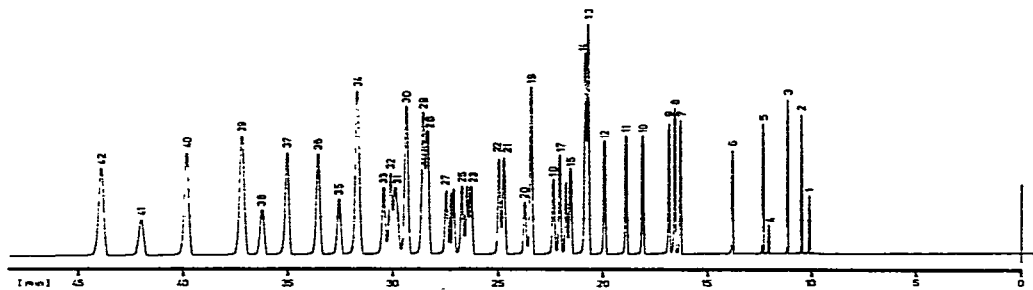


Fig. 11. Analysis of test mixture using a glass capillary coated with Al₂O₃ and Carbowax. Length, 125 m; I.D., 0.25 mm; coating, Al₂O₃ 0.5 mg · m⁻¹, Carbowax 0.3 mg · m⁻¹; column temperature, 100°; inlet pressure, 5 bar. Peaks: 1 = *n*-heptane; 2 = *n*-octane; 3 = *n*-nonane; 4 = benzene; 5 = *n*-decane; 6 = toluene; 7 = ethylbenzene; 8 = *p*-xylene; 9 = *m*-xylene; 10 = isopropylbenzene; 11 = *o*-xylene; 12 = *n*-propylbenzene; 13 = 4-ethyltoluene; 14 = 3-ethyltoluene; 15 = *tert.*-butylbenzene; 16 = isobutylbenzene; 17 = 1,3,5-trimethylbenzene; 18 = *sec.*-butylbenzene; 19 = styrene + 2-ethyltoluene + 1-methyl-3-isopropylbenzene; 20 = 1-methyl-4-isopropylbenzene; 21 = neopentylbenzene; 22 = 1,2,4-trimethylbenzene; 23 = 1,3-diethylbenzene; 24 = 1-methyl-2-isopropylbenzene + 1-methyl-3-*n*-propylbenzene; 25 = 1-methyl-4-*n*-propylbenzene; 26 = 1,4-diethylbenzene; 27 = *n*-butylbenzene; 28 = 1-methyl-3-*tert.*-butylbenzene; 29 = 1,3-dimethyl-5-ethylbenzene; 30 = 1-methyl-4-*tert.*-butylbenzene + 1,3-diethylbenzene; 31 = α -methylstyrene; 32 = 1-methyl-2-*n*-propylbenzene + *tert.*-pentylbenzene; 33 = 1,2,3-trimethylbenzene; 34 = 1,3-diisopropylbenzene + 1,4-dimethyl-2-ethylbenzene; 35 = 1,3-dimethyl-5-isopropylbenzene; 36 = 1,2-dimethyl-4-ethylbenzene; 37 = 1,2-diisopropylbenzene + indane; 38 = 1,3-dimethyl-2-ethylbenzene; 39 = 1-methyl-3,5-diethylbenzene + 1,4-diisopropylbenzene; 40 = *n*-pentylbenzene + 1,2-dimethyl-3-ethylbenzene; 41 = 1,2,4,5-tetramethylbenzene; 42 = 1,2,3,5-tetramethylbenzene.

oxide capillaries coated additionally with squalane or polyethylene glycol. It is evident that aluminium oxide is suitable as a base for these two organic separation phases. It is well known that these substances do not adhere well to untreated glass.

These few examples are intended to show that with the separation system described, viz., glass capillaries coated with aluminium oxide, a large number of variations is possible. However, also the operator is not relieved from his responsibility of adapting the separation system to the particular sample under investigation.

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