DUAL COLUMN–DIFFERENTIAL FLAME IONIZATION DETECTOR SYSTEM AND ITS APPLICATION WITH PACKED AND GOLAY TYPE COLUMNS*

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In gas–liquid partition-chromatography, bleeding of the liquid phase is usually unavoidable. Every liquid phase has a certain vapor pressure at a given temperature and because the gas in the column is constantly moving, the column effluent always contains a certain amount of this vapor.

Since gas chromatographic detectors usually respond to any substance other than the inert gas (and certainly to any organic material), substrate bleeding will result in a detector background signal. However, if column temperature and carrier gas flow rate are unchanged during analysis (*isothermal operation*), the rate of bleeding is constant. Thus, the background signal—due to substrate bleeding—is also kept constant and can therefore electrically be compensated.

The situation is different when the column temperature is constantly raised (*programmed temperature operation*). Since the vapor pressure of any substance increases exponentially with temperature, the rate of bleeding is not constant any more but will increase during the program. This will result in a continuous (and exponential) base line drift with both thermal conductivity and ionization detectors. The sample component peaks will be superimposed over this drifting base line making peak identification and the quantitative evaluation of the chromatogram practically impossible.

THE INFLUENCE OF LIQUID PHASE BLEEDING

In order to demonstrate the effects of substrate bleeding on background current, a column was prepared with squalane liquid phase. The column dimensions were 3 ft. × 0.085 in. I.D. (0.125 in. O.D.) and it consisted of 15 wt.-% squalane on Chromosorb W, 80–100 mesh. The column was placed in a gas chromatograph equipped with a flame ionization detector and the carrier gas (helium) flow was kept constant during the whole investigation at 15.5 ml/min (uncorrected value, at column outlet). The recorder base line was adjusted to zero at room temperature, and then the temperature of the column was raised in steps of 25° from 50° up to 175° and the background current from the detector was recorded after the base line reached equilibrium. The results are given in Table I and plotted in Fig. 1. This graphical presentation results

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TABLE I

BACKGROUND SIGNAL OF SQUALANE COLUMN AT DIFFERENT TEMPERATURES WITH 15.5 ml/min* CARRIER GAS (He) FLOW

Column temperature (°C)	*Background signal (recorder deflection) (× 10^{-12} A)*
50	0.14
75	0.29
100	0.94
125	12.5
150	93.0
175	810.0

* Uncorrected value measured at column outlet.

in a curve similar to the actual base line drift during programmed temperature operation.

The ordinate (*i.e.* the background) of Fig. 1 is expressed in two different ways: the scale on the left gives the background signal in ampères while the scale on the right indicates full scale deflection at different attenuations on a 5 mV recorder giving the approximate magnitude of base line drift during programmed temperature operation with the given flow rate. For example, the background signal at 150° was $93 \cdot 10^{-12}$ A. With the system used, $2.5 \cdot 10^{-12}$ A signal corresponds to full scale deflection at attenuation × 1; thus, full scale deflection with *e.g.* attenuation × 500 corresponds to $1250 \cdot 10^{-12}$ A. This means that the programming of this particular column from room temperature up to 150° with the given flow rate, using attenuation × 500 would result in 7.4% base line drift. However, with attenuation × 50, the same programming would result in a 74% base line drift since with this attenuation, full scale recorder deflection is equal to $125 \cdot 10^{-12}$ A.

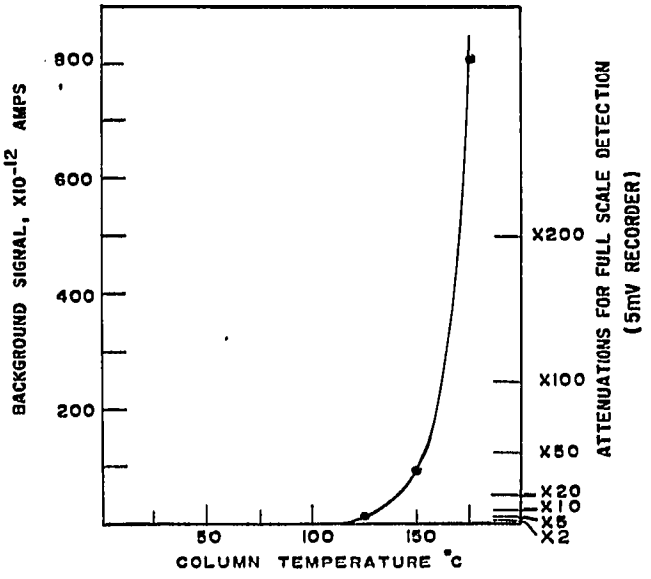

Fig. 1. Background signal of a packed column with 15 wt.-% squalane on Chromosorb W, 80–100 mesh. Column dimensions: 3 ft. × 0.085 in. I.D. Carrier gas (He) flow rate: 15.5 ml/min.

This short calculation means that the base line drift during programmed temperature operation is less significant when low detector sensitivities are used; at high sensitivities, however, it makes the analysis practically impossible.

Another conclusion can be made when the measured values are compared with the vapor pressure data of squalane. According to the literature, usually the temperature corresponding to 0.1 mm Hg vapor pressure is considered as the maximum operating temperature of a gas chromatographic column[1]. Fig. 2 gives the vapor

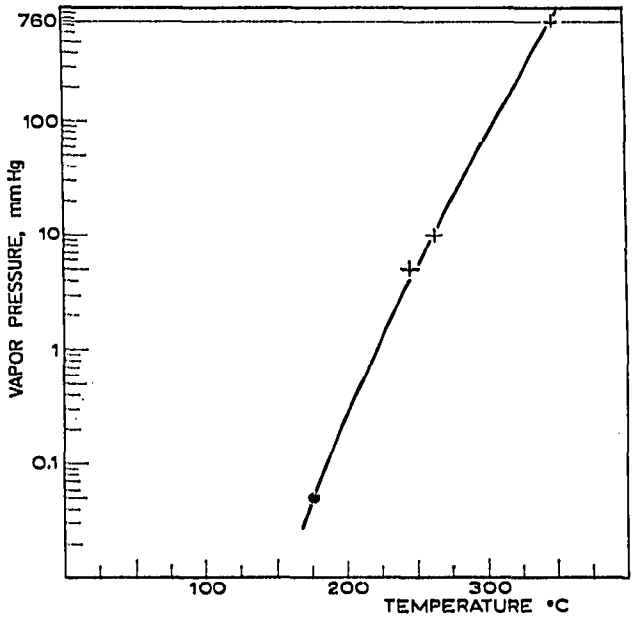

Fig. 2. Vapor pressure curve of squalane. Data marked with + are from Ref. 2 while the value corresponding to 0.05 mm Hg is from Ref. 3.

pressure curve of squalane[2,3]. According to this, a vapor pressure of 0.1 mm Hg corresponds to about 185°. However, it is clear from Fig. 1 that a squalane column could not be programmed higher than about 125–130° if the high sensitivity of the flame ionization detector is utilized. Thus, maximum temperature values reported in the literature are only valid with thermal conductivity detectors, under isothermal conditions.

DUAL COLUMN OPERATION

In 1961, EMERY AND KOERNER[4,5] introduced a new approach for the elimination of base line drift when the column temperature is programmed. In their system, a second column parallel to the analytical column is bleeding at identical rate into the reference side of the thermal conductivity detector. Since the output of such detector bridge is a measure only of the differences in thermal conductivity in the two chambers, it will be zero except when sample components enter the sensing cell. Thus, the base line drift due to substrate bleeding can be eliminated.

The only limitation of their system is that since it is utilizing a thermal conductivity detector, its sensitivity is restricted by the detector itself and some of the advantages of base line compensation are lost although otherwise, it can be used with practically any type of liquid phase[6]. Therefore, TERANISHI *et al.*[7] substituted *two*

identical flame ionization detectors (FID) for the katharometer feeding their output into a differential amplifier.

An alternate approach is the use of a *differential* flame ionization detector with a single output feeding one amplifier. In such system, differential amplifiers and complicated controls are avoided: the single output from a differential FID eliminates the problems associated with matching high megohm input resistors and designing complex zero suppression circuitry.

In this paper, such a system is briefly described and its application is illustrated.

APPARATUS

Fig. 3 gives the simplified electrical circuitry of the differential detector. Two flames housed within a single chamber are oppositely polarized by two 300 V batteries; the other terminal of each battery is connected to amplifier ground. A platinum screen acting as a common collecting electrode for each flame is connected to the input of an electrometer amplifier. Since both flames are oppositely polarized and commonly connected to the electrometer amplifier, the circuit is equivalent to a differential ampèremeter. The current appearing at the input of the electrometer is the difference

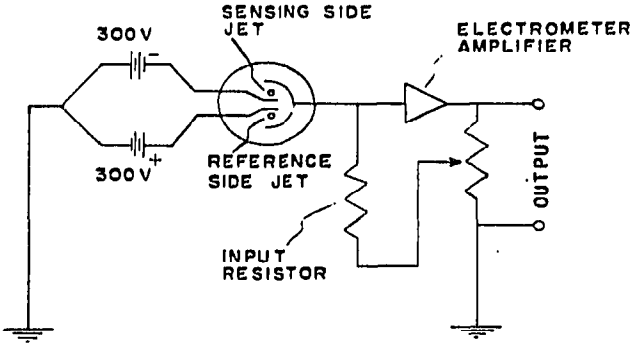

Fig. 3. Simplified electrical circuitry of the differential flame ionization detector system.

between the signals generated in the sensing and reference flames. Whereas signals from the sensing flame tend to decrease the current at the electrometer amplifier, signals from the reference flame tend to increase this current. The net result is a measure only of the difference on the two generated signals. The differential voltage developed across the input resistor is amplified by the electrometer amplifier and recorded on a suitable recorder connected to the output. The amplifier used is a negative feedback amplifier which is capable of driving both galvanometric and potentiometric recorders.

Fig. 4 shows a more detailed view of the detector. The jets are made of stainless steel tubes of 0.020 in. I.D. and are connected directly to the detector base with internal Swagelok fittings. Platinum wires running vertically in close proximity to the flames serve as the polarizing electrodes; these electrodes pass insulated through the detector base. The common collecting electrode is constructed of fine mesh platinum screening. An ignitor coil is placed between the jets for ignition of the hydrogen flames. Filtered air is purged into the detector through a sintered stainless steel disc to insure smooth air flow within the chamber. The combustion products and excess air escape through vents in the top of the detector cover.

The detector construction described shows no electrical communication between the two flames; therefore, shielding or separate detector chambers are not needed. Due to the symmetrical relationship of the electrode pairs, both flames exhibit equal sensitivities after initial optimization of gas flows. The presence of grounded jets and ignitor does not affect detector response. The detector is insensitive to gross temperature changes and may be programmed up to 400°.

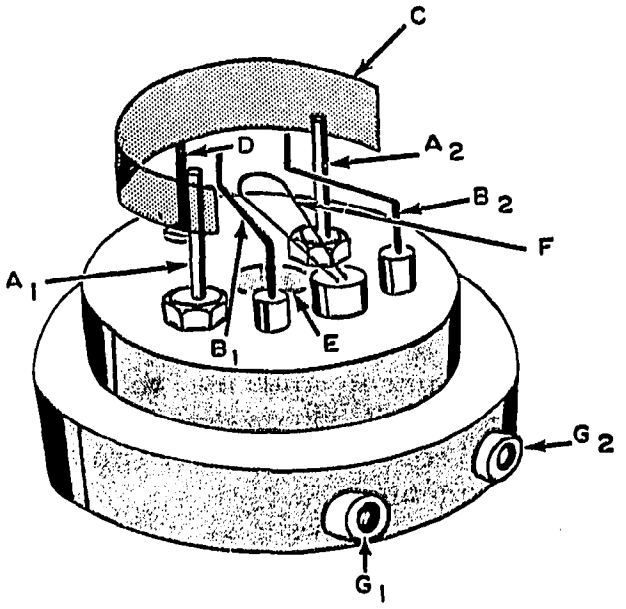

Fig. 4. View of the differential flame ionization detector (cover removed). (A_1, A_2) jets; (B_1, B_2) polarization electrodes; (C) common collecting electrode; (D) connection to electrometer input; (E) air filter disk; (F) ignitor; (G_1, G_2) column connections.

The symmetrical construction of the detector allows each flame to be used separately (but not simultaneously) as a single flame ionization detector. In this case, the hydrogen flow through the unused jet is shut off.

The described differential FID is incorporated into a gas chromatographic system* shown schematically in Fig. 5. Individual proportional flow controllers with needle valve adjustment are used to independently balance column flows. The system has dual injection ports housed within a single block which can be heated up to 500°. The columns are enclosed in a high velocity circulated air bath oven compartment capable of operation up to 400°. The effluents of each column proceed to effluent splitters which allow a specified percentage of the flow to enter the detector, the remainder of which vents to atmosphere for sample collection, auxiliary detection (*e.g.* additional hot wire or electron capture detector, etc.) or discard. The vents may also be plugged to allow full column flow to the detector. The detector jets, as described previously, are housed within a single chamber and supplied with externally regulated hydrogen gas. A needle valve and snubber is installed in each hydrogen line for establishing the desired flow rates. Externally regulated filtered air provides the necessary oxygen for the flame and purges the combustion products from the detector chamber.

* The system described is the Model 800 gas chromatograph of the Perkin-Elmer Corporation, Norwalk, Conn. All analyses reported in this paper were performed with this instrument.

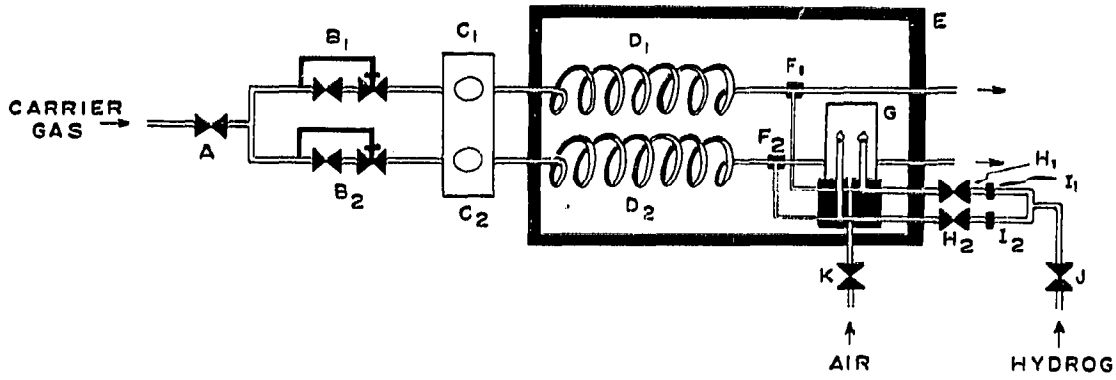

Fig. 5. Flow scheme of a dual column–differential FID gas chromatograph. (A) carrier gas pressure regulator; (B_1, B_2) flow controllers with needle valve adjustment; (C_1, C_2) sample introduction ports; (D_1) analytical and (D_2) reference columns; (E) column oven compartment; (F_1, F_2) column effluent splitters; (G) differential flame ionization detector; (H_1, H_2) needle valves; (I_1, I_2) snubbers; (J) hydrogen pressure regulator; (K) air pressure regulator.

The dual injection ports permit special applications of the system. In this way, both columns can be used alternately for separation. It is also possible to install two *different* columns into the instrument and use them alternately, operating the differential FID as a single detector. Two consecutive analyses on different columns can be carried out under identical conditions, greatly simplifying *e.g.* relative retention time or retention index measurements.

COMPENSATION OF LIQUID PHASE BLEEDING

The compensation of liquid phase bleeding is carried out by the adjustment of the reference carrier gas flow. The columns are stabilized at the initial temperature of the program and the base line is electrically zeroed. Now, the oven is programmed up to the maximum temperature; as a result, a base line drift will be observed which will level off at the end of the program. The flow through the reference column is now adjusted to rezero the recorder base line. After this procedure, the instrument is cooled down and can be used for actual analysis.

Fig. 6 illustrates base line compensation of a 6 ft. × 0.085 in. I.D. packed column with SE-30 liquid phase. The column was programmed from 75 to 355° at 20°/min and then cooled to 75°. The chromatogram shows the actual base line with single column operation and also, base line compensation with dual columns.

APPLICATIONS

Dual column–differential FID systems can be used in practically all applications where programmed temperature operation over a wide range is necessary. The following examples illustrate some typical applications of the system described.

Figs. 7 and 8 demonstrate the analysis of a high boiling sample containing trace components. Two 6 ft. × 0.085 in. I.D. columns containing Apiezon L on hexamethyldisilazane (HMDS) treated Chromosorb W, 80–100 mesh were used in both single and dual column mode. The samples consisted of high boiling aromatics. Peaks 4 and 5 corresponded to approximately $6 \cdot 10^{-9}$ g each. Since attenuation × 5 was used, the minimum detectable limit for this sample with 1 μl injection is about 1 p.p.m. in the

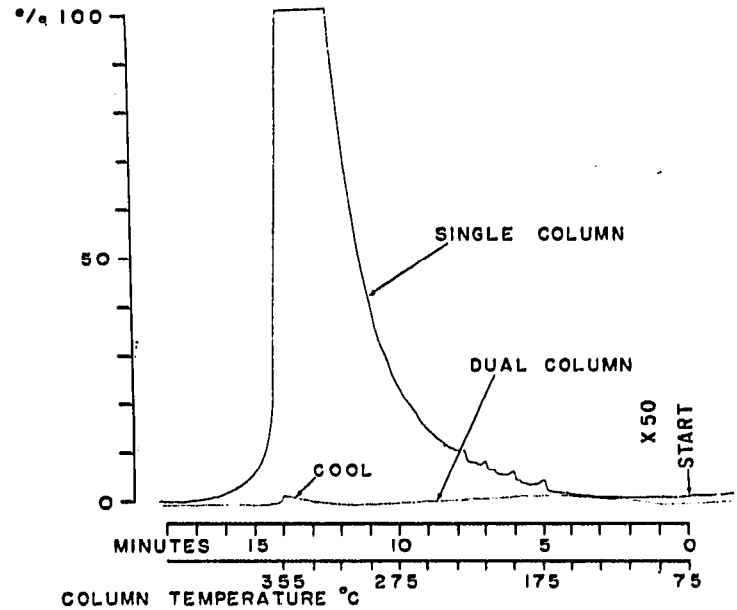

Fig. 6. Single *versus* dual column base line stability under heating and cooling. Each column 6 ft. × 0.085 in. I.D. containing 1.5 wt.-% SE-30 silicone gum rubber on Chromosorb W, 80–100 mesh. 5 mV recorder with attenuation × 50; full scale response corresponds to $1.25 \cdot 10^{-10}$ A.

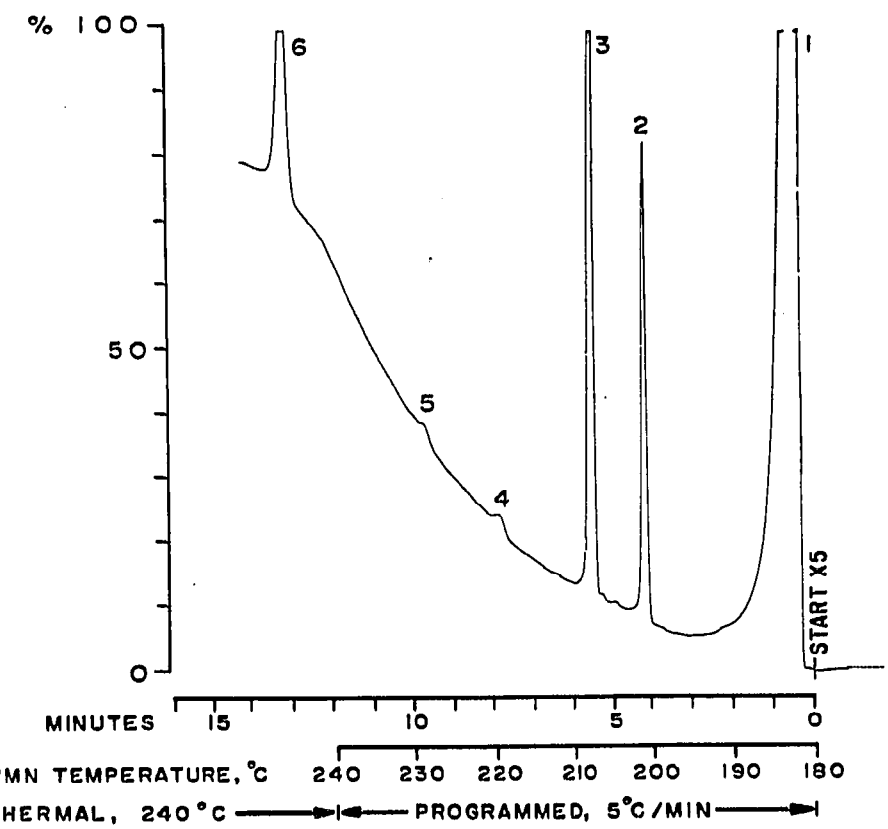

Fig. 7. Analysis of a high boiling aromatic sample. Single column operation. 6 ft. × 0.085 in. I.D. column containing 8 wt.-% Apiezon L on HMDS-treated Chromosorb W, 80–100 mesh. Injection block: 260°. Sample: 1 μl solution. Peaks: 1 = benzene (b.p. 80°) (solvent); 2 = biphenyl (b.p. 255°); 3 = 2,3-dimethylnaphthalene (b.p. 268°); 4 = fluorene (b.p. 298°); 5 = anthracene (b.p. 354°). Peaks 4 and 5 correspond to approximately $6 \cdot 10^{-9}$ g each. 5 mV recorder with attenuation × 5; full scale response corresponds to $1.25 \cdot 10^{-11}$ A.

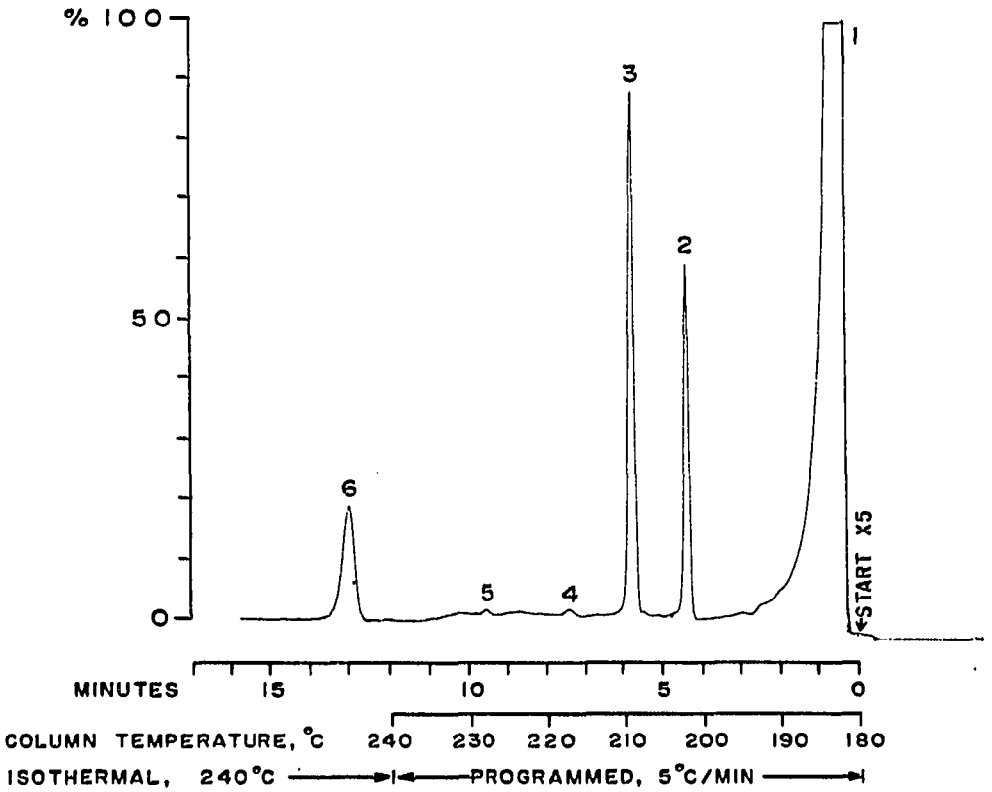

Fig. 8. Analysis of a high boiling aromatic sample. Dual column operation. Each column, conditions, sample and peaks as given in Fig. 7.

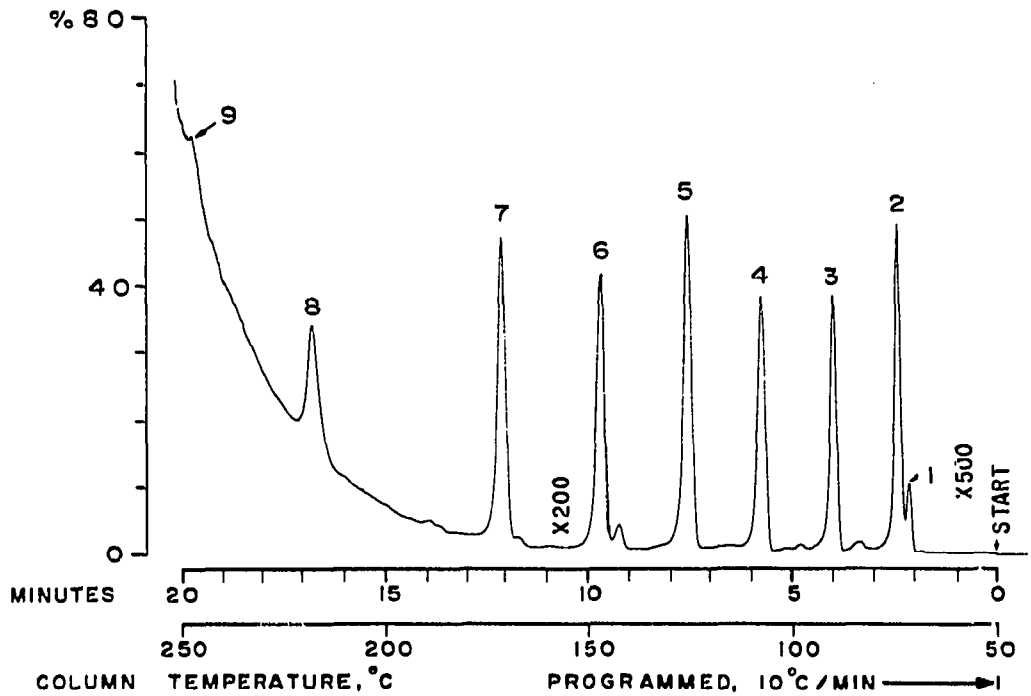

Fig. 9. Analysis of halogenated hydrocarbons. Single column operation. 6 ft. × 0.085 in. I.D. column containing 10 wt.-% DC-550 phenylsilicone oil on Chromosorb W, 80–100 mesh. Sample: 0.02 μl mixture. Peaks: 1 = chloroform (b.p. 61°); 2 = 1-chlorobutane (b.p. 78°), 3 = 1-chloropentane (b.p. 108°); 4 = 1-chlorohexane (b.p. 132°); 5 = 1-chloroheptane (b.p. 159°); 6 = *o*-dichlorobenzene (b.p. 180°); 7 = hexachlorobutadiene (b.p. 215°); 8 = 1-iodo-3-nitrobenzene (b.p. 280°); 9 = hexachlorobenzene (b.p. 326°). 5 mV recorder with given attenuations; with attenuation × 200, full scale response corresponds to $5 \cdot 10^{-10}$ A.

sample. However, if higher sample volumes were used or the flow rate of the carrier gas increased, concentration in the p.p.b. range could also be detected.

Figs. 9 and 10 compare the results of the analysis of a wide range halogenated hydrocarbon mixture. Using a single column, it is difficult to judge whether the base line disturbance at 20 min is a peak. With dual column operation, this peak—corresponding to a small amount of hexachlorobenzene (b.p. 326°)—can clearly be

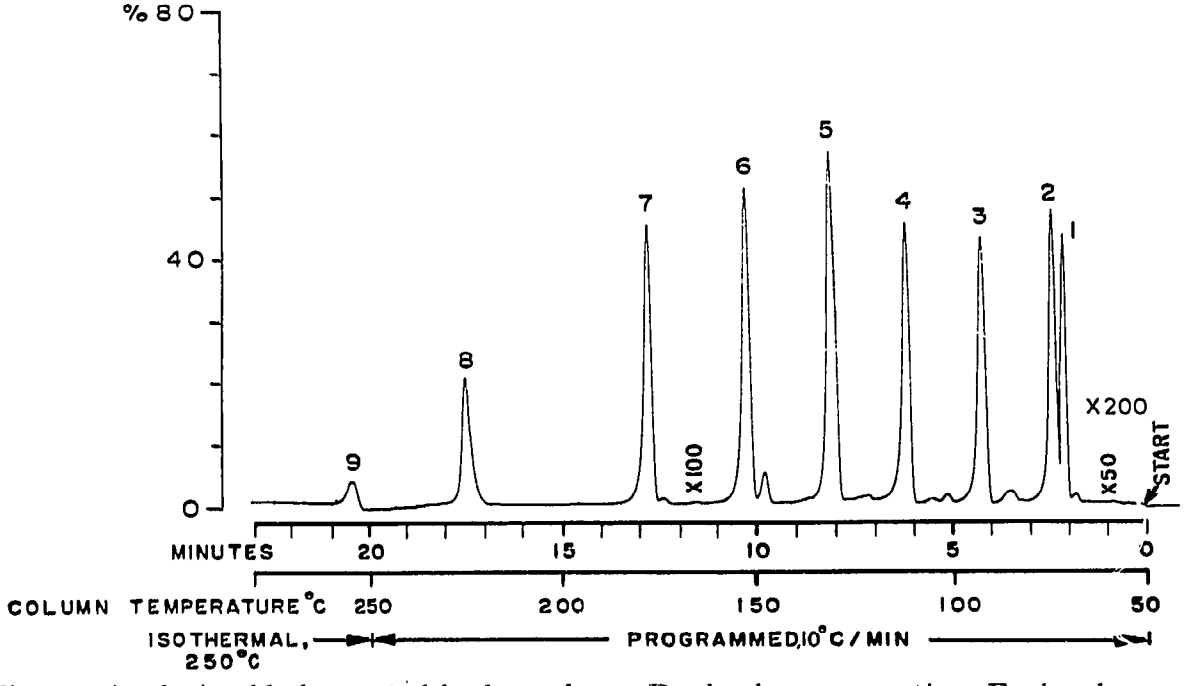

Fig. 10. Analysis of halogenated hydrocarbons. Dual column operation. Each column, conditions, sample and peaks as given in Fig. 9.

distinguished. For this analysis, the DC-550 phenylsilicone oil was heated 25° higher than its maximum recommended temperature[8].

A recent publication[9] showed some interesting comparative chromatograms on the analysis of higher fatty acid methyl esters. Under isothermal conditions, at 180°, erucic acid methyl ester emerged in about 67 min; using temperature programming and dual column operation, this time could be reduced to 23 min without significant loss in the resolution of the stearate–oleate pair.

The dual column analysis of a mixture of high boiling condensed ring aromatics is shown in Fig. 11. The Apiezon L columns were relatively new and except for the usual preconditioning at 200° for a few hours, no special conditioning took place. The columns were heated higher than the recommended maximum operating temperature, without any observable base line drift.

Fig. 12 is a typical example for the analysis of another high boiling sample. In this case, Versamid 900, a long chain linear polyamid (a product of the Chemical Division of the General Mills Corporation, Hensakee, Ill.) was used as liquid phase and programmed up to 275°.

Dual column operation is interesting not only at high temperatures but can also be applied at any temperature if the relatively high bleed rate of the column makes it necessary. Fig. 13, for example, shows the analysis of two beer head space gas samples.

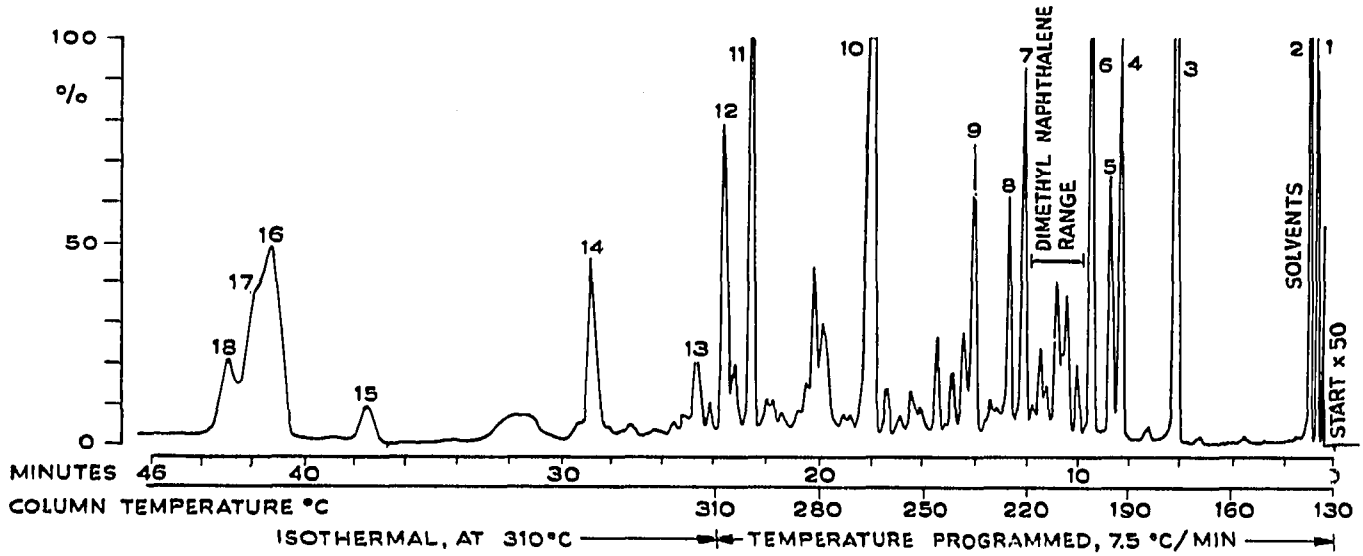

Fig. 11. Analysis of a neutral creosote oil with added polycyclic substances. Dual column operation. Two 6 ft. × 0.085 in. I.D. columns containing 8 wt.-% Apiezon L on HMDS-treated Chromosorb W, 80–100 mesh. Injection block: 350°. Sample: 0.2 μl of a benzene–toluene solution. Peaks: 1,2 = solvents; 3 = naphthalene (b.p. 218°); 4 = 2-methylnaphthalene (b.p. 245°); 5 = 1-methylnaphthalene (b.p. 240–243°); 6 = biphenyl (b.p. 254–255°); 7 = acenaphthene (b.p. 277°); 8 = diphenylene oxide (b.p. 288°); 9 = fluorene (b.p. 295–298°); 10 = phenanthrene (b.p. 340°) + anthracene (b.p. 354°); 11 = fluoranthene (b.p. 384°); 12 = pyrene (b.p. 394°); 13 = 1,2-benzofluorene (b.p. ~ 407°); 14 = chrysene (b.p. 448°); 15 = perylene (b.p. ~ 460°); 16 = 1,2-benzpyrene (b.p. 493°); 17 = 3,4-benzpyrene; 18 = 1,2-benzoperylene. 5 mV recorder with attenuation × 50; full scale response corresponds to $1.25 \cdot 10^{-10}$ A.

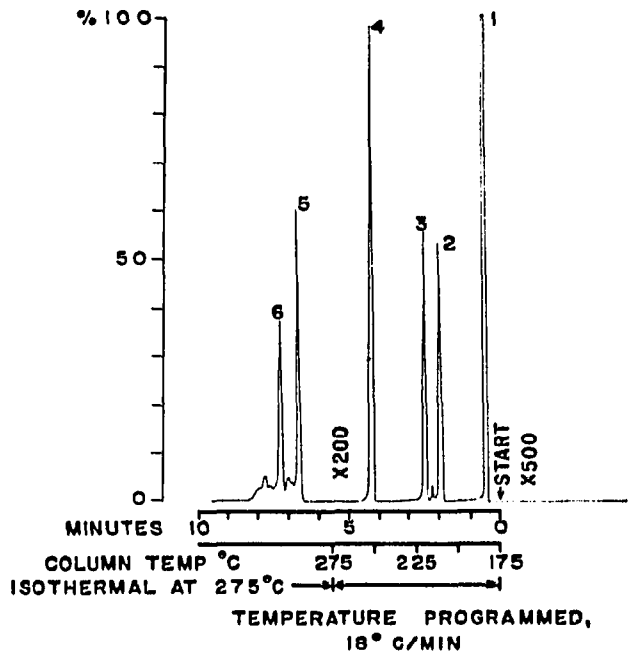

Fig. 12. Analysis of a phthalate mixture. Dual column operation. Two 6 ft. × 0.085 in. I.D. columns containing 2 wt.-% Versamid 900 on HMDS-treated Chromosorb W, 80–100 mesh. Injection block: 350°. Sample: 0.5 μl solution in acetone. Peaks: 1 = acetone (solvent); 2 = dimethyl phthalate (b.p. 282°); 3 = diethyl phthalate (b.p. 296°); 4 = dibutyl phthalate (b.p. 340°); 5 = dioctyl phthalate (b.p. 384°); 6 = dinonyl phthalate (b.p. 420–440°). 5 mV recorder with given attenuations; with attenuation × 200, full scale response corresponds to $5 \cdot 10^{-10}$ A.

Although Carbowax type columns can usually be heated isothermally higher than 120°, they have a relatively high bleed rate at the sensitivities used when programming and therefore, they would show a significant base line drift under single column condition. These two chromatograms also illustrate the reproducibility of dual column operation.

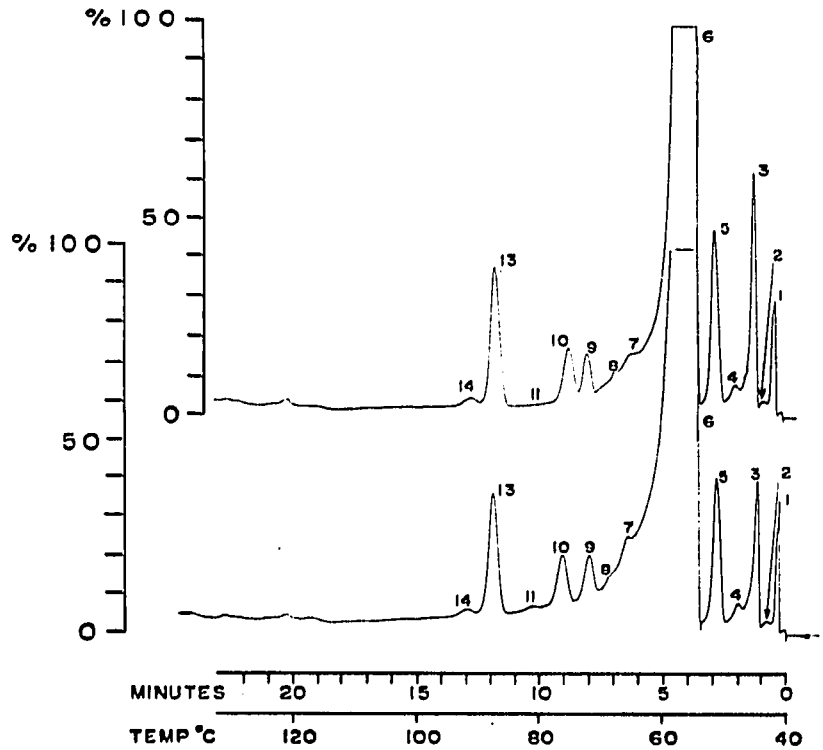

Fig. 13. Analysis of beer head space gas samples. Dual column operation. Two 6 ft. × 0.085 in. I.D. columns containing 8 wt.-% Carbowax 1540 on Chromosorb W, 80–100 mesh. Sample: 3 ml gas. Identified peaks: 1 = acetone; 3 = acetaldehyde; 5 = ethyl acetate; 6 = ethanol; 9 = isobutanol; 13 = isoamyl alcohols. 5 mV recorder with attenuation × 5; full scale response corresponds to $1.25 \cdot 10^{-11}$ A.

CAPILLARY (GOLAY) COLUMNS

Dual column systems can easily be adopted for use with open tubular (Golay) columns. When working with these columns of "capillary" dimensions (0.010 in. I.D.), the flow rates are usually less than 5 ml/min. Such low flows prevent the use of standard flow controllers. It was found, however, that base line compensation is possible using independent pressure regulation on each column. A previous paper[10] showed that under proper conditions, the change in the carrier gas flow during programming does not influence the quantitative analysis if constant pressure drop is maintained through the column, when working with FID.

The modification of the standard system for operation with capillary columns is shown in Fig. 14. The reference capillary column is connected directly to an independent source of regulated carrier gas. A linear stream splitter is installed between one injection port and the analytical capillary column. The outlet of this split system is connected to the second injection port normally used for the reference column. Split ratios are easily obtained by inserting various gauge calibrated needles into the septum of the second injection port.

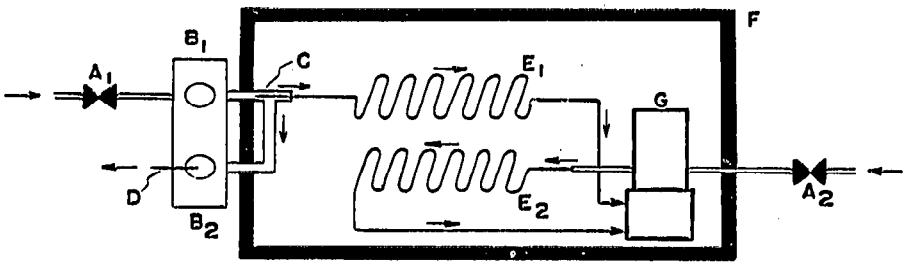

Fig. 14. Flow scheme of the dual column–differential FID gas chromatograph for capillary columns. (A_1, A_2) carrier gas pressure regulators in the analytical and reference gas lines; (B_1) sample introduction port; (B_2) injection block in the former reference line; (C) linear stream splitter; (D) interchangeable restrictor at vent; (E_1, E_2) analytical and reference columns; (F) column oven compartment; (G) differential FID, the construction of which is identical to that shown in Fig. 5.

The technique of dual column compensation with capillary columns is identical to that described previously for packed columns except for the use of pressure regulation in place of flow controllers. With Golay columns of larger diameters, standard flow regulators can again be utilized.

Figs. 15 and 16 illustrate the difference between uncompensated single column and compensated dual columns when analyzing commercial gasoline. The columns used were 150 ft. × 0.010 in. I.D. and coated with squalane.

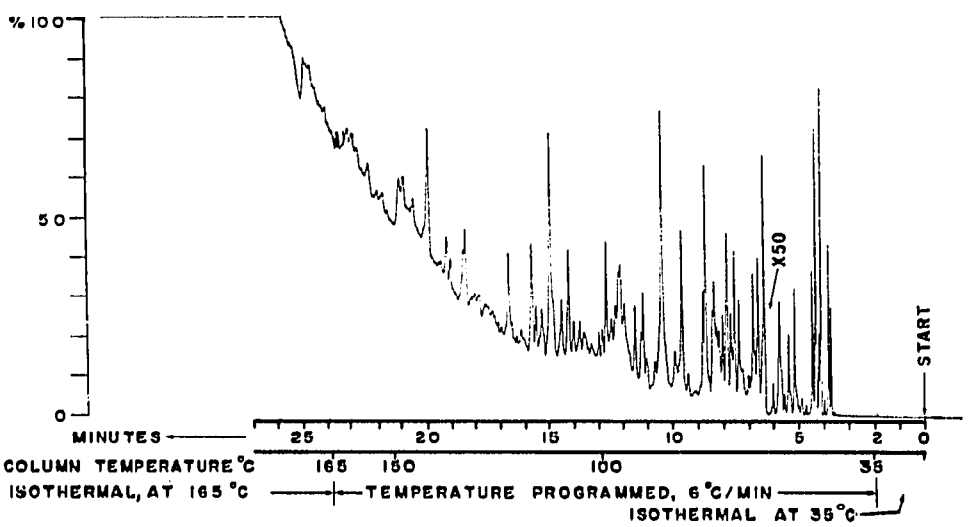

Fig. 15. Analysis of a commercial gasoline sample. Single column operation. 150 ft. × 0.010 in. I.D. capillary column coated with squalane as liquid phase. Injection block: 240°. Sample: 1 μl, split ratio about 1 : 500. 5 mV recorder with given attenuations; with attenuation × 50, full scale response corresponds to $1.25 \cdot 10^{-10}$ A.

QUANTITATIVE ASPECTS

In order to demonstrate the quantitative accuracy of a dual column–differential flame ionization detector system, a mixture of fatty acid methyl esters with known concentration was selected. The sample was a standard of the National Institutes of Health, obtained from the Applied Science Laboratories, University Park, Pa. The conditions were as follows:

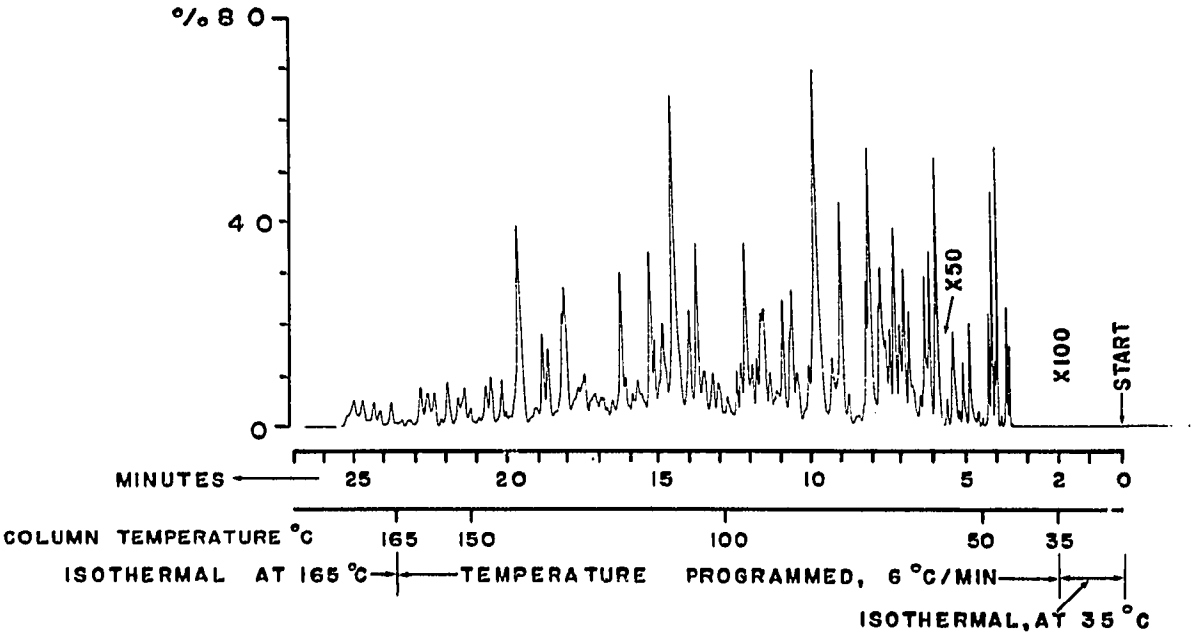

Fig. 16. Analysis of a commercial gasoline sample. Dual column operation. Each column, conditions and sample as given in Fig. 15.

Column: 6 ft. × 0.085 in. I.D. packed columns containing 8 wt.-% butanediol succinate on Chromosorb W, 80–100 mesh.

Injection block temperature: 300°.

Column temperature: (a) Isothermal at 180°.
(b) Programmed 150–210° at 2°/min.
(c) Programmed 150–210° at 4°/min.

Sample volume: 0.2 μl.

Gas inlet pressures and flow rates: (a) Carrier gas (He): 50 p.s.i.g., 30 ml/min.
(b) Air: 40 p.s.i.g., 500 ml/min.
(c) Hydrogen: 12 p.s.i.g., 33 ml/min.

Table II summarizes the analytical results. The isothermal and programmed results show a deviation of less than 0.5 %. The table also compares the analytical results with the original composition of the sample; these results confirm again that—as

TABLE II

QUANTITATIVE ACCURACY OF A DUAL COLUMN–DIFFERENTIAL FLAME IONIZATION DETECTOR SYSTEM

	Composition of sample (wt.-%)	*Isothermal at 180°*		*Programmed 150–210° at 2°/min*		*Programmed 150–210° at 4°/min*	
		Peak area (%)	*Deviation (%)*	*Peak area (%)*	*Deviation (%)*	*Peak area (%)*	*Deviation (%)*
Methyl myristate	11.83	12.08	+0.25	11.83	—	12.02	+0.19
Methyl palmitate	23.62	24.06	+0.44	23.74	+0.12	24.00	+0.38
Methyl palmitoleate	6.84	6.39	−0.45	6.60	−0.24	6.53	−0.31
Methyl stearate	13.09	12.58	−0.51	13.09	—	12.44	−0.65
Methyl oleate	44.62	44.89	+0.27	44.74	+0.12	45.01	+0.39

shown in a previous paper[11]—in the analysis of fatty acid methyl esters with flame ionization detection, the relative peak area values are very close to the actual concentration by weight of the sample when analyzing methyl esters with relatively high carbon number.

ACKNOWLEDGEMENTS

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SUMMARY

The influence of liquid phase bleeding on the analytical results and the possibilities for its compensation in programmed temperature for chromatography were discussed. A new differential FID was described; the dual column system incorporating this detector allows the use of both packed and open tubular (Golay) columns. The application of the system to a few problems was shown and its quantitative accuracy was demonstrated.

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