GAS CHROMATOGRAPHY, EXPERIMENTAL STUDIES ON THE FLOW RATE EFFECTS OF CARRIER GAS AND APPLICATION OF THE METHOD TO HYDROCARBON ANALYSIS OF SOME NATURAL GASES IN TURKEY

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ABSTRACT. — First section of this publication covers the method of Gas Chromatography generally, the second section includes our experimental studies on the flow rate effects of carrier gas and the third section describes the way of application of that method to hydrocarbon analysis of some natural gases in Turkey by using a Beckman Gas Chromatograph.

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GAS CHROMATOGRAPHY

Chromatography is a physical method of separation in which the components to be separated are distributed between two phases. One of these phases constitutes a stationary bed of a large surface area, the other is a fluid or a gas that percolates through or along the stationary bed.

Chromatography was first employed by Tswett, a Russian botanist, in 1906, for separating components of plant pigments. Since he obtained discrete bands of colored materials, he termed his method «chromatography». This name obviously became a misnomer when the methods were applied to colorless materials, but it was so firmly established that it was irreplaceable. In 1931, Kuhn and Lederer used Tswett's technique successfully for the separation of carothens and xantophylls on a preparative scale.

Gas-liquid partition chromatography was first used by James and Martin in 1952 for the separation and analysis of mixtures of volatile fatty acids.

Gas Chromatography as a convenient method for the separation and analysis of gases and volatile materials has been accepted extensively in the field of chemistry.

Chromatographic methods have the advantages that the separating equipment itself is simpler, the operation is easier and it is considerably less time-consuming.

The main uses of chromatography in the laboratory are :

a) as an analytical method for identifying the constituents of a mixture qualitatively and determining them quantitatively,

b) as a research method for determining certain physical quantities, such as partition, coefficients and adsorption isotherms,

c) as a preparative procedure for isolating components from mixtures.

As an analytical method, chromatography has been accepted extensively during recent years. Chromatography has most of the advantages of the physical methods of separation. It is carried out in such a manner that no constituents of the mixture are lost and no new substances are formed by chemical reactions. Consequently, if a substance has been isolated by that method, it is almost certainly present in the original sample.

Basically, chromatography consists of a two-phase system. The components of the mixture are distributed over two phases. One phase is fixed and is termed as stationary phase, the other phase is mobile and is termed as moving phase.

The stationary phase may be :

(1) A solid having adsorptive properties. In this case the method is termed «adsorption chromatography».

(2) A liquid. Methods of this type are referred to as «partition chromatography». In this case the liquid stationary phase is generally distributed over an inert solid support in order to give it a large surface area.

The moving phase may be:

(1) A liquid

(2) A gas (or vapor)

These consist of four possible basic systems of chromatography. These are shown as follows:

Solid stationary phase «Adsorption chromatography»	**1. Liquid moving phase «Liquid-solid chromatography» (L.S.C.)**
	2. Gaseous moving phase «Gas-solid chromatography» (G.S.C.)
Liquid stationary phase «Partition chromatography»	**1. Liquid moving phase «Liquid-liquid chromatography» (L.L.C.)**
	2. Gaseous moving phase «Gas-liquid chromatography» (G.L.C.)

Basically, all chromatographic methods where the moving phase is a gas (or vapor) are termed as «gas chromatography». This method includes «gas-solid chromatography» and «gas-liquid chromatography».

All the chromatographic separations are based on the transportation of a sample mixture (moving phase) through a column constituting a stationary phase. In gas chromatography, the volatile components of the sample are distributed between an inert gas phase (carrier gas) and a stationary phase.

Furthermore, chromatography may also be classified according to techniques and a subdivision may be made again as to the methods of removing the separated sample components from the column. These techniques are referred to as «development». There are three general, methods of development which have been used extensively. These are displacement, frontal analysis and elution analysis.

This article is restricted to gas chromatography as a class and elution analysis as the method of development.

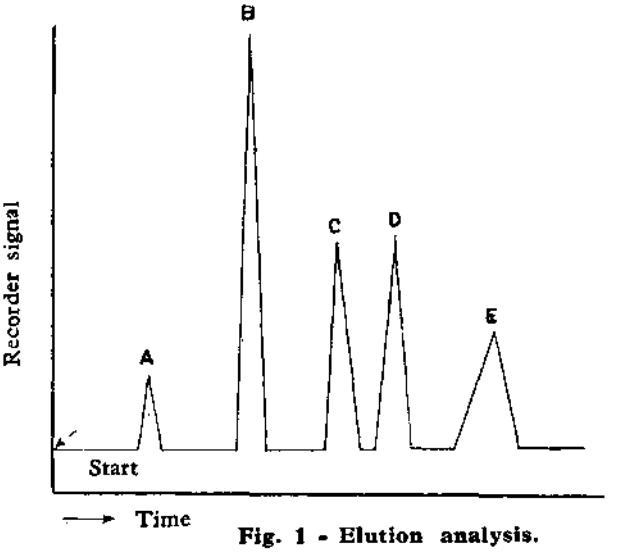

Fig. 1 - Elution analysis.

Elution analysis is usually the preferred method of development in gas chromatography. By this method, a small sample of the volatile mixture to be separated is introduced into the front end of the column. The column is maintained at a certain temperature and a constant current of a carrier gas is passed through the column. The carrier gas is the eluent, it transports the components of the mixture in the form of vapor or gas through the column where they are retained by the stationary phase in the column to a different extent, so that their effective speeds of transport also differ. The intensity of the force by which the stationary phase tends to hold each of the sample components is different. The nature of this force may be adsorption, solubility, chemical bonding or molecular filtration, etc. Because of the phase equilibrium differences, the sample components are separated from one another by distribution between the stationary and moving phase as they are moved down the length of a chromatographic column. Each component will move at the rate depending on its partition coefficient, K, where:

$$K = \frac{\text{amount of solute per unit volume of stationary phase}}{\text{amount of solute per unit volume of moving phase}}$$

Under favorable conditions, the individual components in the sample such as A, B, C, D, E, will have different partition coefficients and will be completely separated as shown in Figure 1.

The components emerge from the column at different times as individual bands separated by the zones of carrier gas. The composition of the effluent is sensed by a delicate detector at the end of the column. This detector is capable of indicating the presence of the components qualitatively and quantitatively with the order of emerging from the column.

The three main functions of the process are:

1. Effective separation of the sample into its components
2. Identification of these components (qualitative analysis)
3. Estimation of the amounts in which they are present (quantitative analysis).

When this method is used, the retention time or the retention volume of the component is used to identify it (qualitative analysis) (Figure 1). Retention time is the time from the start of the analysis until the component emerges from the column and the peak maximum occurs in the chromatogram. Retention volume is the volume of carrier gas measured at or corrected to column temperature

and column outlet pressure which passes through the column between the time that the sample is injected and the peak maximum occurs. The magnitude of the signals at the detector system which are transmitted to the recorder are proportional with the amount of the components in the sample, so that the peak height or the peak area is used as a quantitative measure of the component.

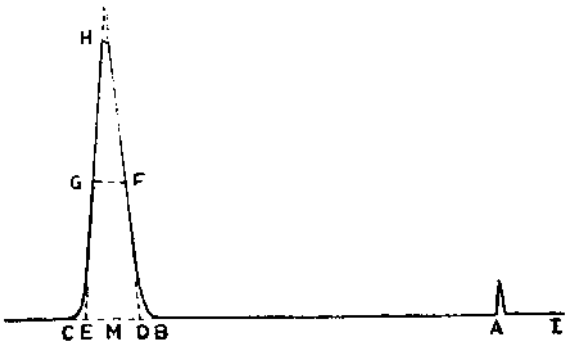

Fig. 2 - Two-component differential chromatogram.

A two-component differential chromatogram is shown in Figure 2 for convenience in the definition of the terms.

Where,

I = sample injection time or zero time

IA = time for non-adsorbed component to be eluted (the interval IA converted to a gas volume is the gas hold-up of the column)

IB = initial retention time for component no. 2

IC = final retention time

IM = retention time for the peak maximum of component no. 2. (This quantity is normally used in calculating and reporting retention times and retention volumes.)

With the measurement of retention time, column temperature, pressure at column inlet and column outlet and flow rate, it is possible to calculate the retention volume of a component. Retention time is considered as one of the most important values in recording chromatographic data.

AM = apparent retention time

FG = width at half of peak height

FG X HM = calculated area of a chromatographic peak

The uncorrected retention volume is given as follows :

$$V_R = F_c\, t_R$$

Where, VR = uncorrected retention volume

F_c = flow rate of carrier gas corrected to column temperature and outlet pressure

t_R = time elapsed between injection of sample and peak maximum

The compressibility of the carrier gas causes a variation in the linear velocity of that gas along the column length. This pressure gradient factor, f, can be calculated by the following formula :

$$f = \frac{3}{2} \times \frac{(P_i / P_o)^2 - 1}{(P_i / P_o)^3 - 1}$$

Where, f = pressure gradient factor

P_i = absolute pressure at column inlet

P_o = absolute pressure at column outlet

The corrected retention volume is given, by the following formula:

$$V°_R = f\ V_R = f\ F_c\ t_R$$

Where, V_oR= corrected retention volume

f = pressure gradient factor

If the retention time is measured from the non-adsorbed component peak to peak maximum of the component being considered (the quantity AM in the Fig. 2), this quantity is referred to as apparent retention time. The apparent retention volume is defined by :

$$(V^o_R)' = fF_c\ t$$

Where, $(V^o_R)'$ = apparent retention volume corrected for pressure drop of the column

F_c = flow rate of carrier gas corrected to column temperature and outlet pressure

f= correction factor for column pressure drop

t= apparent retention time

The partition coefficient, K, is related to the corrected retention volume by:

$$K = \frac{V^o_R - V^o_G}{V_L}$$

Where, V^o_R= corrected retention volume

V^o_G= total gas volume or gas hold-up of the column (corrected retention volume for a non-adsorbed gas)

V_L = volume of the liquid phase in the column at the temperature of the column

$$V^o_R - V^o_G = (V^o_R)'$$

Where, $(V°_R)'$ =apparent retention volume corrected for pressure drop of the column

Another method which has been employed generally for reporting gas chromatographic data is the use of relative retention volume tabulation or plots. According to that method, all retention volumes are reported relative to some compound which is selected as a standard. The major advantage of this method is that the effects of operating conditions and column dimensions are eliminated since these factors affect the standard compound and the sample component in the same way. In this case:

$$\frac{(V^o_R)'_s}{(V^o_R)'_n} = \frac{K_s}{K_n}$$

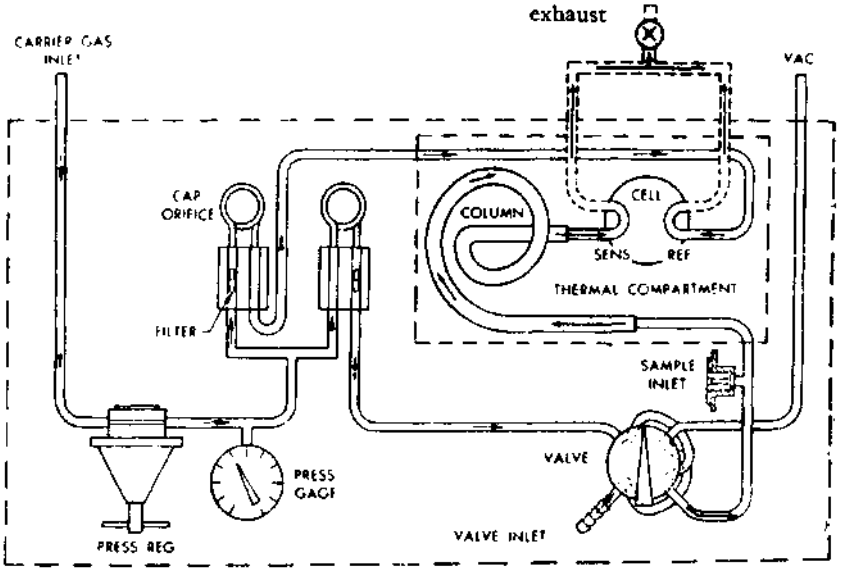

Fig. 3 - Flow diagram of Beckman GC-2 model Gas Chromatograph.

$(V^{\circ}_R)'s$ and $(V^{o}_R)'_n$ = apparent corrected retention volumes for standard compound and sample component of interest

K_s = partition coefficient of standard compound

K_n = partition coefficient of component of interest

or $$\frac{(V_R)'_s}{(V_R)'_n} = \frac{K_s}{K_n}$$

Where, $(VR)'_S$ and $(VR)'_n$ = apparent uncorrected retention volumes for the standard compound and sample component of interest

or $$\frac{t_s}{t_n} = \frac{K_s}{K_n}$$

Where, t_s and t_n = apparent retention times for standard compound and sample component of interest

The quantities in Fig. 2 are useful for comparing diagrams under equal operational conditions. Factors on which these values depend are the gas rate, the inlet and outlet pressures, the temperature, the nature and amount of stationary phase and the gas hold up of the column.

The essential elements of a Gas Chromatograph are carrier gas, carrier gas flow control system, sample inlet system, detector, temperature control system, and chromatographic column.

Figure 3 shows the flow diagram of a Beckman GC-2 Gas Chromatograph.

We will study essential elements of Gas Chromatography and the factors which affect the method in the following parts.

Carrier gas

Most of the gas chromatography instruments in use employ a thermal conductivity cell as a detector. This detector measures a difference in the thermal conductivity between pure carrier gas and carrier gas having sample components. Therefore, at equal amounts of sample, a signal of the greatest magnitude will be obtained when the difference in thermal conductivity between the carrier gas and sample components is at the maximum.

Thermal conductivity values of the gases are given in Table 1.

Table 1

Gas	*Temperature (°C)*	*Thermal conductivity** $\lambda \times 10^5$
H_2	0	39.60
H_2	100	49.94
He	0	33.60
He	100	39.85
Ne	0	10.87
CH_4	0	7.20
O_2	0	5.70
O_2	100	7.43
N_2	0	5.68
N_2	100	7.18
Air	0	5.57
Air	100	7.20
C_2H_6	0	4.31
C_2H_6	100	7.67
Ar	0	3.88
Ar	100	5.09
CO_2	0	3.39
CO_2	100	5.06
C_3H_8	0	3.58
n-C_4H_{10}	0	3.22
n-C_5H_{12}	0	3.12
iso C_5H_{12}	0	2.91
iso C_5H_{12}	100	5.10

* Thermal conductivity : cal/cm sec. °C.

After the examination of thermal conductivity values given in Table 1, it is known that thermal conductivity difference will be maximum when hydrogen is used as a carrier gas. Although hydrogen gives maximum sensitivity when a thermal conductivity cell is used as a detector, helium is usually preferred as a carrier gas. The use of hydrogen has some drawbacks. Organic compounds give catalytic reactions with hydrogen in the presence of platinum wire. These reactions cause upsetting of the signal by the heat effects involved. The use of helium avoids that drawback. Helium is not a potential explosion hazard as in the case with hydrogen. Nitrogen, argon, carbon dioxide, and air can also be used as carrier gases. These gases cause a significant decrease in sensitivity when a thermal conductivity detector is used. Sensitivity with helium is 2 to 3 times the sensitivity with nitrogen when the thermal conductivity detector is operated at equal currents.

Each column has an optimum flow rate of carrier gas which depends on the type of sample being run and the type, width and length of the column.

Some of the suitable methods which are used for measuring flow rates are moving soap bubble, differential pressure method and water displacement method. The sensitivity of flow control with changes in pressure regulation is largely controlled by a capillary orifice in Beckman Gas Chromatograph.

The following flow rates have been found suitable for 1/4 in (6.3 mm) diameter analytical columns :

30-80 ml/min for low boiling gases with partition column

40-100 ml/min for low boiling gases with adsorption column

50-200 ml/min for liquids with partition column

Sample inlet

The relatively small sample volumes required for an analysis with the gas chromatographic method may be introduced into the instrument by any of several different techniques. A gas sampling valve is used for introducing gas samples into the instrument in Beckman Gas Chromatograph. This valve permits the introduction of fixed volumes of samples into the instrument. The sampling volume of the valve may be filled by purging or by first evacuating and then filling to the desired pressure by use of conventional gas handling equipment.

Liquid samples are normally introduced into the instrument by a micro syringe through a rubber serum cap. A heated sample inlet is used and the sample is vaporized instantaneously.

The efficiency of separation in a gas chromatographic column improves as the size of the sample reduces. This fact makes possible using very small amounts of samples. With a normal analytical column of 4-8 mm I.D., a gas sample of 0.5 to 5 ml and a liquid sample of 0.02 to 0.002 ml is satisfactory. The size of the sample may be increased in proportion to the square root of the column length.

Detectors

The separation obtained with a chromatographic column is followed with a vapor detector. The gases flow from the column through detector cell to the exhaust. The output signal from the detector is transmitted to the recorder which plots chromatogram. Chromatogram consists of a series of peaks corresponding to the separated sample components (Fig. 1).

The characteristics which are desirable in a detector are as follows: stability, sensitivity, rapid, linear and repeatable response.

The different types of detectors which have been used in gas chromatography consist of automatic recording burette, gas density balance, infrared analyzer, hydrogen flame detector, surface potential detector, mass spectrometer, discharge detector, flame ionization detector, b-ray ionization detector and thermal conductivity cell.

We will explain here thermar conductivity cell which is the most widely used as detector in gas chromatograrphy.

This cell meets all the characteristics of an ideal detector very closely. Basically, the thermal conductivity cell consists of a filament held in the center of a metal block through which the gas passes. The filament is heated with constant electric current. The temperature rises to some constant value which depends on the current applied, the resistance of the filament, the temperature of the cell block, the nature of the gas and flow rate of the gas. If the cell block is held at some temperature below the temperature of the filament, heat will be conducted away from the filament to the cell block at a rate which depends on the thermal conductivity of the gas and the difference in temperature between the side walls of the cell block and the filament. Gas flowing through the detector cell passes over the filaments removing a quantity of heat which varies with the thermal conductivity of the gas and the rate of flow through the instrument. This removal of heat changes the temperature of the filaments. This change causes alteration of filament resistance. The four filaments in the detector cell (two reference, two sensing) are arranged in a «Wheatstone» bridge circuit. A change in voltage across the filaaments is developed with the change of the filaments resistance. This in turn results in a voltage differential across the bridge circuit. When only carrier gas flows through the system, the heat losses of the reference and sensing filaments are equal, so that the voltage developed across the filaments is equal and a zero signal is recorded. As the sample flows through the column, the components are

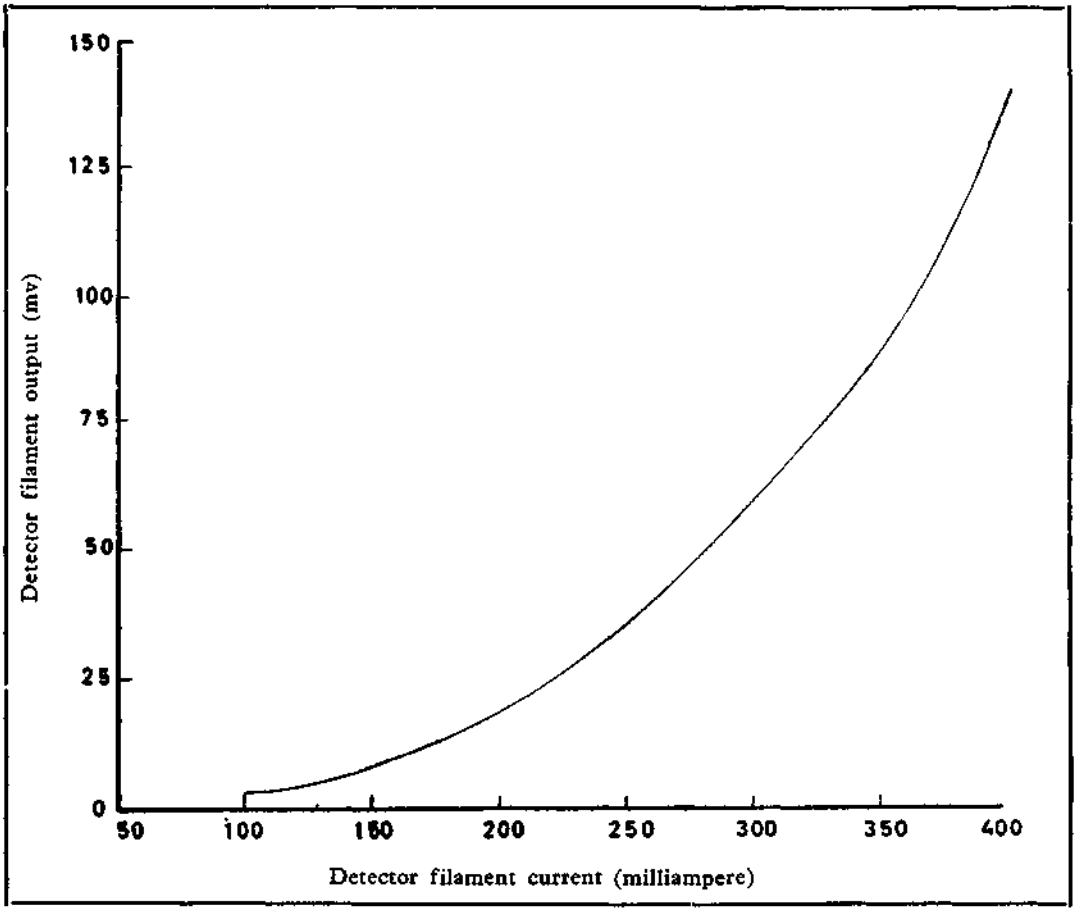

Fig. 4

separated from each other and they reach the detector cell at different times. In this case, the reference side will be filled with carrier gas and the sensing side will be filled with carrier gas having sample components (Fig. 3). Since the thermal conductivities of these components differ from that of the carrier gas, the heat loss from the filaments in the sensing side differs from the reference side. Equal current is applied to all filaments; therefore, the voltage developed on the sensing side differs from the voltage developed on the reference side resulting in a voltage imbalance in Wheatstone bridge. The actual magnitude of this voltage imbalance (signal) depends on the current applied, resistance of the filaments, temperature coefficient of the resistivity of the filaments, temperature of the cell block and difference in thermal conductivity between carrier gas and carrier gas having sample components.

Figure 4 shows the relationship between detector current and detector output.

The voltage imbalance in the detector cell varies with the quantity of the sample component passing through detector cell. Since the concentration of the sample components may vary over wide ranges, signals are attenuated by means of a sensitivity control which reduces the signal in steps up to a factor. The imbalance across the bridge circuit is transmitted through the attenuator control to the recorder and the recorder plows a curve showing the analysis of the sample qualitatively and quantitatively (Fig. 1). As the output signal produced by each component reaches the recorder, the pen plows a peak indicating relative quantity of the sample component passing through the detector cell. Recorder traces continue until all the sample components emerge from the column and only the carrier gas background line is traced.

Table 2 shows the recommended filament current values according to the type of the carrier gas and temperature.

Table 2

Carrier gas	*Temperature*	*Filament current values*	
		Normal	*Maximum*
Helium	160 °C and above	250 ma	350 ma
	Below 160 °C	250 ma	400 ma
Nitrogen or air	All temp.	150 ma	200 ma

Temperature range and control

An essential requirement in gas chromatography is that the components of the sample be moved through the column in the vapor state. Therefore, column temperature must be high enough to permit rapid vaporization of highest boiling point component into the carrier gas. If the column temperature is too low to permit a reasonable vapor pressure, the sample will move through the column

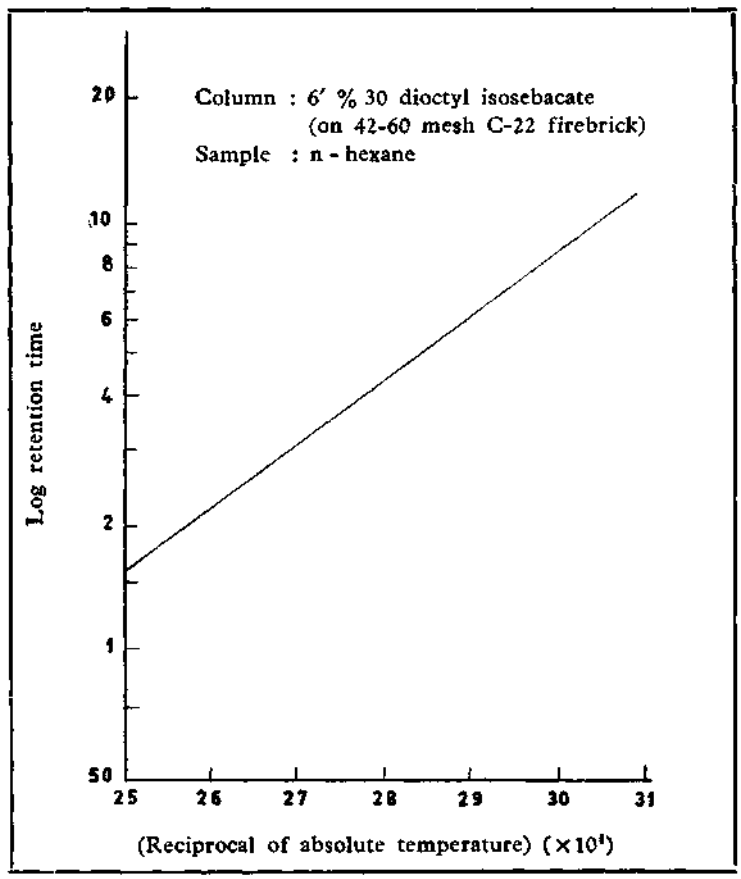

Fig. 5

too slowly resulting in a prolonged analysis time and very low sensitivity. If the column temperature is too high, the vapor pressure of the sample components will be too high, it will not be possible to obtain adequate resolution between the sample components. It must be possible to adjust the column temperature through a wide range. It is important to be able to control temperature precisely.

The retention time of a compound under fixed column temperature is the property by which a sample component is identified. The retention time of a compound decreases about 5 percent per 1 °C increase in temperature. The log of retention time is proportional to the reciprocal of the absolute temperature as shown in Figure 5.

The peak height will change with temperature since the retention time of the component is affected by temperature. If the detector is temperature-sensitive as in the case with thermal conductivity cell, the base line stability will also be affected by temperature changes. The change in the flow rate of carrier gas caused by a variable column temperature will also affect stability. In practise, it is required to control column temperature to better than ± 1° C and detector temperature to ± 0.1 °C if the detector is as temperature-sensitive as a thermal conductivity cell.

Operating temperature of the instrument is maintained by a dual element heater which is controlled and regulated by a precision electronic system. This feature permits precise control of the operating temperature.

Chromatographic column

Chromatographic column is the heart of the instrument. Because of the wide application of gas chromatography in the analysis of gas, vaporizable liquids and vaporizable solids, different columns are required in order to analyze different types of samples. It is possible to develop a satisfactory column or combination of columns to handle a particular sample by selecting column dimensions, column temperature, carrier gas flow control through the column, sample size, column filling and column arrangement.

Column efficiency is usually given in terms of number of theoretical plates because of similarity of a gas chromatographic column to a distillation column. The number of theoretical plates can be obtained by the following expression :

$$n = 16\left(\frac{d}{w}\right)^2$$

Where, n = number of theoretical plates of a column towards a particular compound

d = retention time of the same compound

w = peak width corresponding to the same compound

Once the number of theoretical plates, n, is known, the height equivalent to a theoretical plate, H, can be calculated by :

$$H = \frac{L}{n}$$

Where, n = number of theoretical plates

L = column length

At a constant carrier gas velocity through the column, retention volume will increase approximately linearly with column length. This means that the analysis time under fixed condition of carrier gas, flow rate and temperature will increase linearly with column length. However, the resolution between sample components does not increase linearly with column length. Therefore, the column length is increased preferably until analysis time prolongs in order to obtain adequate resolution and complete separation of the components.

The length of analytical columns may be between 1 and 50 m (3 and 150 ft). The internal diameter of analytical partition columns lies between 4 and 8 mm. The efficiency of columns having much larger diameters is lower per unit of length than that of columns within above range. However, large samples may be required for preparative work. In this case, if resolution is important and column efficiency must be maintained, it will be necessary to increase column diameter to handle large samples.

The basic difference between gas-liquid chromatography and gas-solid chromatography is column packing. In gas-liquid (partition) chromatography, the column contains an inert porous solid coated with a high-boiling organic liquid. In gas-solid (adsorption) chromatography, the column packing consists of an uncoated active solid.

Adsorption columns: The active solids used in gas-solid chromatography are usually materials with high surface area which separate the sample components by differences in adsorption. The useful adsorbents are molecular sieves, charcoal, alumina, silica gel and synthetic zeolites. The adsorbents should be properly activated and mesh size should be controlled. Once a sample component has been, adsorbed, the energy is needed to break the adsorption bond. For this reason, gas-solid chromatography may be applied to the analysis of very low-boiling sample components. In this case, the volatility of the component is high enough to reduce the strength of the adsorption bond. Generally, the samples analyzed by adsorption columns are the gases such as hydrogen, oxygen, nitrogen, neon, methane, ethane, carbon dioxide, argon, carbon monoxide, krypton, xenon, ethylene, propane and propylene.

Partition column : In partition chromatography, the column contains an inert porous solid coated with a high-boiling organic liquid. Partition column separates the sample components due to differences in volatility from solution. Since the energy required to remove a compound from solution is much lower than the energy required to break an adsorption bond, partition columns have a much wider range of application than adsorption columns. Here, we will explain shortly the solid supports used in partition chromatography.

Solid support. — One of the more important factors which affects column efficiency in gas-liquid chromatography is the solid support. The higher the surface area in the column, the greater the contact between the sample components and the liquid phase. Further, resistance to flow should also be considered. According to Keulemans, the ratio of column inlet pressure should not be greater than 2 if the column is to have maximum efficiency. Therefore, highly porous solids as solid support is preferred in partition columns. These are at a particle size which does not cause an unreasonable high pressure drop. Solid supports should not be soluble, should not react with or adsorp the sample components and should not change its characteristics at a temperature needed in operating gas chromatograpru It is possible to construct highly efficient columns with diatomaceous earth as solid support by selecting the best material and screening to a close mesh size classification. Celite 545, Johns-Manville C-22 firebrick and Chromosorb have proven to be the most satisfactory experimentally. The resolution or efficiency of a column is increased by the use of a high surface area, low pressure drop and a solid support with a narrow mesh size classification. In order to minimize the column length required and still obtain high efficiency, the mesh size classification of 42-60 mesh appears to be highly favorable.

Liquid phase. — The liquid chosen for coating the inert solid support must have a high boiling point and a low vapor pressure and it must permit adequate resolution of the sample components within a reasonable analysis time. Resolution requirements will be met when the sample components have sufficiently different partition coefficients. Stationary phase should be a liquid that is non-volatile at the column temperature of operation, so that it will not be eluted from the column with the sample components.

The thickness of the coating of liquid phase on the solid support is another factor which affects the efficiency and the resolution which can be obtained with a column. Ideally, it is desirable to have the greatest amount of liquid phase per

unit cross section of the column that can be coated over a given surface area at a thickness that permits the mass transfer rate to be held at a maximum. The ratio of stationary liquid to inert support may in practice vary between about 15/100 and 50/100 parts by weight. «Celite» and the firebrick fractions can take up the latter quantity without becoming sticky. If the proportion of liquid is large, diffusion phenomena in the solvent tend to impair separation at high rates of gas flow. At very low liquid ratios, the support may possess residual adsorptivity to cause tailing of elution peaks.

Viscosity of the liquid phase is also an important consideration in the choice of liquid phase. If the liquid phase is highly viscous, the mass transfer rate will be decreased, therefore the time required for moving the sample components in and out of liquid phase will be increased.

Distribution isotherms. — Separation in chromatographic processes is based on the distribution of the base material over two phases. Distribution or partition coefficient is defined as

$$K = \frac{\text{amount of solute per unit volume of stationary liquid phase}}{\text{amount of solute per unit volume of moving phase}}$$

The various peak shapes which may be encountered in gas chromatography with the corresponding distribution isotherms are shown in Figure 6.

According to Figure 6, case A, the distribution isotherm is linear with concentration and the corresponding peaks are symmetrical. In this case, we speak of «linear isotherms». In partition chromatography, the conditions are often such that we can assume the isotherms to be linear. Case B shows a «Langmuir» type isotherm indicating that the adsorptivity decreases with increasing sample size. This gives a peak with a sharp front and diffuse tail. This effect frequently occurs in gas-solid chromatography using adsorption columns. In case C, the distribution isotherms show an increasing adsorptivity or solubility with increasing sample size. The corresponding chromatographic peak has a diffuse front and a sharp tail. In gas-liquid chromatography, this case is usually caused by column overloading with too much sample.

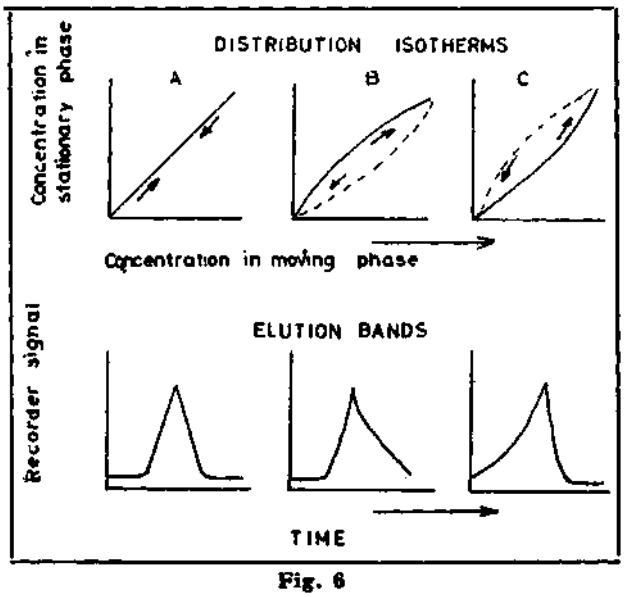

Fig. 6

In addition to the other requirements, the stationary phase should give linear isotherms with sample components.

Qualitative aspects of stationary liquid. — Molecules, either in a pure state or in solution are kept in the liquid state by cohesive forces and tend to escape from the liquid by thermal agitation. As soon as a molecule has acquired sufficient kinetic energy to overcome the forces of attraction

exerted by the surrounding molecules in the liquid state, it may escape into vapor. The forces of cohesion may be of various types. In the case of a solute that is kept in a liquid solution they are:

a) forces between permanent dipoles of solute and solvent (orientation forces),

b) forces between a permanent dipole, either of solute and solvent, and the induced dipole of the other (induction forces),

c) non-polar forces between solute and solvent molecules (dispersion forces).

The relative classification with compound type arranged in the order of increasing polarity or cohesive energy is indicated as follows:

1. Molecules without permanent dipoles or functional groups (saturated hydrocarbons, carbon tetrachloride, carbon sulfide, etc.).

2. Molecules with very small dipoles with active hydrogen atoms (aromatic and olefinic hydrocarbons, chloromethane, etc.).

3. Molecules with a permanent dipole with electronegative atoms but no active hydrogen (ketones, ethers, aldehydes, nitro compounds and nitriles without active hydrogen atoms).

4. Molecules with electronegative atoms with free pairs of electrons and active hydrogen atoms (phenols, primary and secondary amines, alcohols, fatty acids, etc.).

5. Molecules with a three dimensional network of hydrogen bonds (water, polyphenols, polyalcohols, di and tri carboxylic acids, etc.).

There are two general requirements with which the stationary liquid must comply in order to function properly. It must produce a differential partitioning for the component to be separated and it must have a sufficient solvent power for the vaporized component in question. If the absolute solvent power for a particular component is low, this component will pass rapidly through the column and the separation will be poor unless the component differs widely in solubility from neighboring constituents.

The second requirement demands a certain compatibility between the stationary phase and the components. A useful and practical rule for an efficient separation is that the components of the mixture and the stationary liquid should preferably show some resemblance. The groups with similar molecular types in the order of increasing polarity are shown above. For effecting separations according to boiling point in a homologous series, it is necessary to choose a non-polar solvent if the components are little or not polar. If the sample components have low polarity, they will be more soluble in a partition liquid which has a low polarity and they will be eluted from the partition column in the increasing order of their boiling points (as in the case of analysis of paraffinic hydrocarbons using a hexadecane partition column). An aromatic solvent such as benzyl diphenil for separating aromatics, a polar liquid such as polyethylen glycole for separating alcohols and amines may be used. When the sample components and the partition liquid are dissimilar in polarity, the solubility of the sample components in the partition liquid will be relatively low and the vapor pressures

will be higher than might be expected on the basis of boiling points. Benzyl ether which has a higher polarity than hexadecane gives faster elution times than hexadecane column in the analysis of hydrocarbons in natural gas. If it is desired to separate components of about equal boiling points but of different chemical nature, departures from the above rule of similarity are usually necessary. Partition liquids with relatively high polarity may be used in the separation of materials which have similar boiling points. Olefins and corresponding saturated hydrocarbons may be separated using a benzyl ether column. In this case, the olefins which have relatively higher polarity elute after the corresponding saturated hydrocarbons even though the boiling points are slightly lower. However, partition liquids with a high polarity are not always appropriate. If the sample components also have a high polarity, very strong internal forces may be set up which would make difficult to move forward the sample components through the column.

The wide range of factors which take part in the selection of a partitioning liquid makes it possible to develope proper columns for the separation of almost any combination of sample components. It is this flexibility and greater speed which gives gas chromatography its chief advantages over analytical distillation methods. The methods of obtaining resolution in gas chromatography are selection of proper liquid phase, operation of the column at favorable temperatures and carrier gas flow rates, increasing the total efficiency of the column by increasing the length or by control of the other factors discussed above. These methods make it possible to handle a large number of applications but there are other cases for which it is not possible to obtain adequate resolution with the above methods or the column efficiency may be so high, it causes excessively long elution times of the components. It may also be needed using together the columns having different characteristics to permit separation of various types of components in the sample. For all of these cases, it is possible to arrange the combination of two or more columns.

Advantages and limitation of gas-solid chromatography and gas-liquid chromatography

Except in the case of components of very low boiling point (e.g. hydrogen, nitrogen, oxygen, methane, carbon monoxide, etc.), elution peaks in gas-solid chromatography show a marked asymmetrical rise due to the fact that distribution isotherms are not linear.

Gas-liquid chromatography has the following favorable points as compared with gas-solid chromatography:

1. Gas-liquid chromatography is more advantageous than adsorption chromatography because the elution bands are narrow and almost symmetrical.

2. Gas-liquid chromatography allows high flow rates and it is rapid. The mass transfer rate from gas to liquid is higher than gas-solid chromatography.

3. There is a wide choice of stationary liquid in gas-liquid chromatography.

Gas-liquid chromatography also has its limitations. It is restricted to volatile substances. The vapor pressure of a component should exceed 1 mm mercury, otherwise its rate of transport through the column will be too low for practical purposes. The column may be operated at elevated temperatures to increase the

vapor pressure and rate of transport of components. A limit to this temperature is set by volatility and stability of the stationary liquid and the suitability of the detector temperature concerned. The upper limit imposed by the stationary liquid is about 300° C.

Gas-liquid chromatography is generally riot suitable for the analysis of low-molecular weight gases owing to the difficulty of finding a suitable solvent as stationary liquid. The light gases constitute one of the fields in which gas-solid chromatography has an advantage over gas-liquid chromatography.

Operational manual by gas chromatography

In performing analysis by a Beckman GC-2 Gas Chromatograph, carrier gas flow through the chromatographic column is regulated to an optimum rate. Temperature selector switch is set to the desired value and the instrument is allowed to reach temperature equilibrium. Thermal conductivity cell current is adjusted according to the temperature and the type of carrier gas (the values given in Table 2). Zero switch is adjusted so that recorder pen records zero line on the strip chart. Since the same carrier gas passes through both the reference and sensing sides of the thermal conductivity cell during that time, recorder will trace a line. The flow diagram of Beckman GC-2 Gas Chromatograph is shown in Figure 3.

A definite volume of gas sample is introduced into the instrument by using gas sampling valve. Purging method or vacuum method may be used to introduce gas samples. Liquid samples are injected by means of a micro syringe.

As may be seen in Figure 3, carrier gas flow is divided into two parts after passing pressure regulator. A flow of carrier gas, after being heated to the operation temperature of the instrument, flows through the reference side of the cell to exhaust. Another part passes through the sample inlet and includes the sample. Carrier gas transports the sample components in the form of gas or vapor through the column. The components are retained by the stationary phase at the different degrees; thus, their effective transportation rates differ. The time required for each component to pass through the column depends upon the equilibra between the sample components, carrier gas and column-filling material. Carrier gas having sample components flows from the column through the sensing side of the cell and is exhausted to atmosphere. The difference in thermal conductivity between the carrier gas in the reference side of the detector cell and the sample-carrier gas mixtures in the sensing side produces a voltage differential and is transmitted to the recorder. This voltage difference depends on the quantity of the sample components. In this case, recorder plots a curve giving separation of sample components, their qualitative and quantitative analysis (Fig. 1). The components are shown on the curve plotted by the recorder in the form of the peaks with the order of their exit from the column and their entrance to the cell.

Qualitative analysis

The rate at which a given compound will move through the column is an important characteristic which is used for the identification of the component. Under definite operational conditions, the retention time or retention volume is a characteristic value of a certain component. The actual retention time is a func-

tion of the column, compound, carrier gas velocity, column temperature and sample size. If unknown compounds are compared with known compounds of standards using the same column with a constant temperature and carrier gas flow rate, the convenient comparison is obtained on the basis of retention times. A direct comparison of retention times requires identical operating conditions. It is required to know that the sample contains some other components which would be eluted in the same time as a single peak with the particular column being used. If the same sample is run on a column of different characteristics, the degree of resolution and the order of elution will differ and more positive identification will be possible. Gas chromatography in combination with other types of instrumentation, such as mass spectrometer, infrared and ultraviolet, provides a wide possibility for the identification of the compounds. The sample can be separated into its components by gas chromatography and each conponent can be determined by the methods mentioned above.

Quantitative analysis

The primary application of gas chromatography as an analytical method is quantitative analysis of gases and liquids. Components in a sample are physically separated by gas chromatography and compared to corresponding components separated under identical operational conditions from a reference standard mixture of known composition. The chromatogram is interpreted by comparing the peak heights or peak areas with those obtained on the reference standards. Calibration data may be prepared on either peak area and peak height basis. The advantages or disadvantages of each of these techniques must be considered. Factors which must be considered in terms of effects on peak area and peak height include instrument temperature, flow rate and type of carrier gas, sample size, type and concentration of components and the degree of resolution between sample components.

Column temperature is a parameter of a gas chromatograph which affects peak area and peak height to a different degree. This effect is shown in Figure 7. A change in column temperature does not change the relative area sensitivity of the gas chromatogram. If a constant carrier gas flow rate is maintained as the temperature is changed, temperature has very little effect on individual component area sensitivity. On the other hand, both the relative peak height and individual component peak height sensitivity change with temperature. Therefore, it is necessary to calibrate at the same temperature at which samples are to be run if the peak height method is used for quantitative analysis.

Variations in filament current have the effect on both peak area and peak height. The relative sensitivity of the procedure does not change significantly with an increase in filament current as shown in Figure 8, but individual component sensitivity increases very sharply. Therefore, filament current must be kept con-

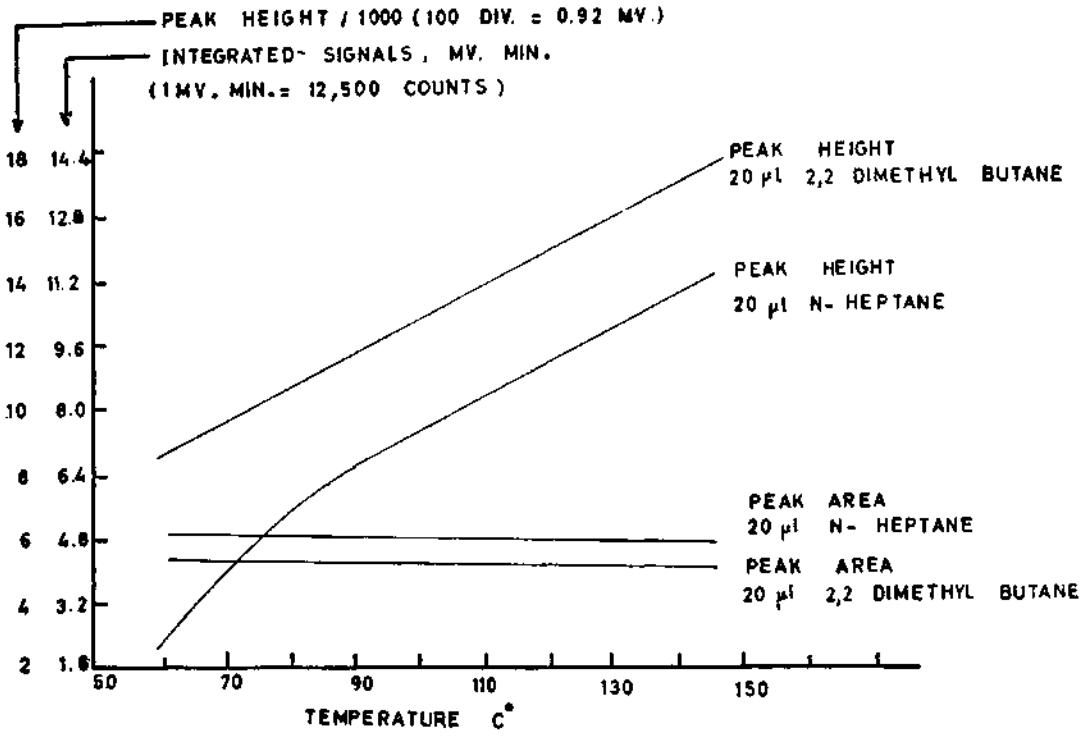

Fig. 7 - Variation of peak height and peak area with detector temperature.

stant during the analysis and calibration must be made at the same filament current which is applied when the samples are run.

Figure 8 shows that peak area increases linearly with sample size while peak height is not linear.

Other factors which change the relative and individual component peak height sensitivity are column length, particle size of the solid support and type and amount of partition liquid. These factors change flow rate and, in that case, affect individual component peak areas but not relative peak areas. Therefore, to obtain highly accurate and sensitive results by gas chromatography, calibration data must be prepared under identical operational conditions for each compound to be determined.

The quantitative interpretation of a differential gas chromatogram is based either on peak height or peak area.

Peak area calibration. — If the factors discussed above are considered, the area of a component peak can be expressed as follows :

$$A_1 = K_1' \left(\frac{k'TI^3}{F_c}\right) X_1$$

Where, A_1 = integrated signal or area for component I

K'_1 = sensitivity factor for component I

k' = instrumental constant (includes recorder sensitivity, filament resistance, cell geometry, bridge characteristics, etc.)

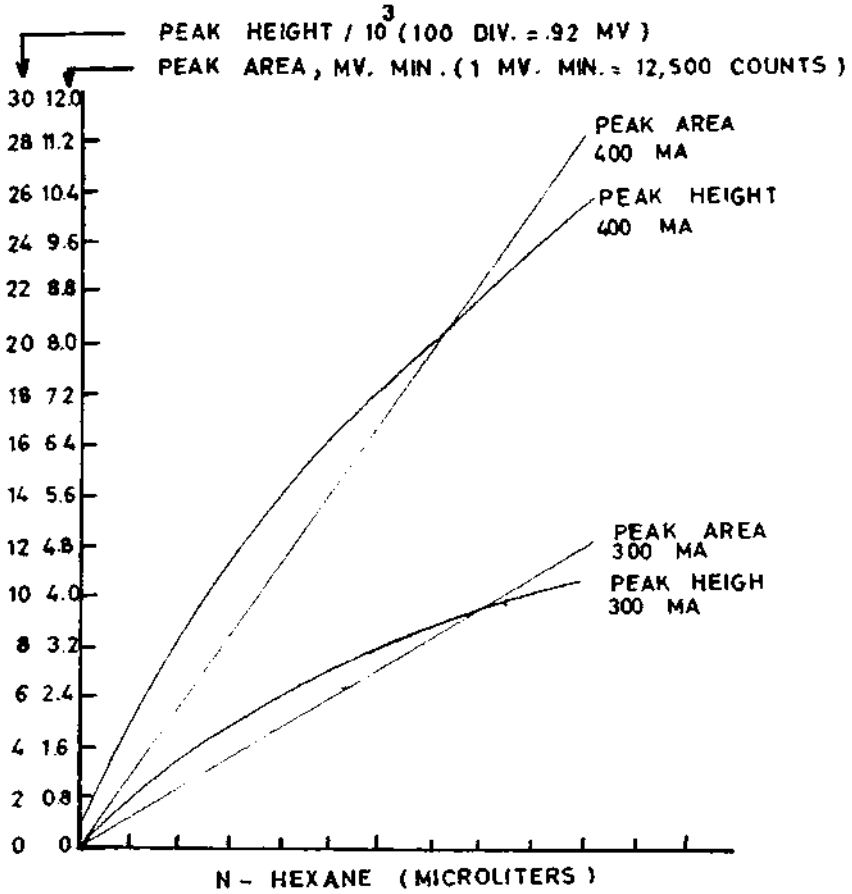

Fig. 8 - Variation of peak height and peak area with filament current and sample size.

F_c = flow rate of carrier gas

T = correction factor for temperature

I = filament current

X_1 = volume, weight or millimoles of component I

Under fixed operating conditions, the expression $\frac{k'TI^3}{F_c}$ is a constant and therefore, equation above reduces to:

$$A_1 = K'_1 CX_1 \quad \text{where } C = \frac{k'TI^3}{F_c}$$

Similarly, the equation for sample component no. 2 is

$$A_2 = K'_2 CX_2$$

Therefore, if two sample components are compared at equal amounts,

$$CX_1 = CX_2 \quad \text{and} \quad \frac{A_1}{K'_1} = \frac{A_2}{K'_2} \quad \text{or} \quad K'_2 = \frac{A_2 K'_1}{A_1}$$

Since only relative sensitivity factors are required for a quantitative analysis, K'1 is assigned a value of 1.0 and then K'_2 can be expressed as:

$$K'_2 = \frac{A_2}{A_1}$$

Method A (internal normalization): Let us first assume that the area under each peak is directly proportional to the amount of the component to which it belongs and is independent of its nature. In this case, we could calculate the composition by adding together all the peak areas and finding the proportion of each area to the total area. If hydrogen or helium is used as carrier gas and high accuracy is not required, this procedure may be adopted provided a small range of closely similar compounds are involved. In other cases, peak areas can not be used directly for calculating composition; they must be multiplied by factors depending on the components concerned, before they are added and proportioned. The factors must be determined by analysis of synthetic blends made up of the pure substances in question :

$$\frac{A_1}{K'_1} + \cdots \frac{A_6}{K'_6} = \text{C.T.A.}$$

Where,

$\frac{A_1}{K'_1}$ = measured area for component I over corresponding K' value on volume or weight basis

C.T.A. = sum of the calculated areas for individual components

The analysis for individual components is then obtained by:

$\frac{A_1/K'_1 \times 100}{\text{C.T.A.}}$ = percent (by volume or weight) of component I

When this method is used, it is not required to know the exact sample size, but the size of the sample should be kept within reasonable limits (approximately 0.001-0.03 ml for liquid samples) in order to preserve the linearity of the area calibration curves.

Method B : According to this technique, an approximate composition of the sample is first calculated by total peak area method without using calibration factors. Then, a synthetic mixture of this composition is prepared and analyzed under the same conditions. Peaks are compared with those obtained with the original sample.

$$V_n = \frac{V_n^c A_n}{A_n^c}$$

Where V_n = volume of sample component n

V_n^c = volume of compound n used for calibration giving an area signal of A_n^c

A_n^c = measured area signal of the compound used for calibration

A_n = measured area signal of component n

$$V_n = \frac{V_s^c A_n}{K'^v_n A_s^c}$$

Where, V_s^c = volume of standard compound s giving an area signal of A_s^c

A_s^c = measured area signal from V_s^c

K'^v_n = sensitivity factor of compound n relative to compound s at equal volumes

$\frac{V_n}{M.T.V.} \times 100$ = percent by volume of component n

$\frac{V_n}{C.T.V.} \times 100$ = percent by volume of component n

Where, M.T.V. = measured total volume

C.T.V. = calculated total volume of sample from sum of the individual component volumes

The equation above can also be used for this type of analysis if weight is substituted for volume. A normalized weight percent analysis is obtained if K values are substituted on equal weight basis.

When the equations in Method B are used, it is necessary to calibrate for each component under the same operating conditions at which the sample is run. The quantitative results obtained with the equation in Method B are very sensitive to changes in flow rates of carrier gas, filament current and temperature, etc. Therefore, if highest accuracy is required, calibration standards should be run at equal intervals.

The ratio of the peak area for each component used in calibration is plotted against the ratio of the amount actually present which may be expressed as volume percent or weight percent. This plot is frequently a straight line over the restricted range in question. Calibration curves are prepared using a fixed sample volume and the volume percent of the components is varied. Thus, the amount of any component is obtained from the value on calibration curve corresponding to measured peak area.

Peak heigt calibration. — Peak height calibration can also be used for quantitative analysis. Since the component signals vary with instrumental operating parameters, calibration data must be prepared under the same instrumental conditions at which the samples are to be run. Calibration data for peak height analysis may be prepared in several different ways. One of the methods is that the volume of pure component is plotted against the peak height signal. If it is desired, weight or pressure could be substituted for volume. According to another method, the peak height signal is plotted against volume percent or weight percent.

The methods for the peak height calculations can be expressed as follows :

Method A : Calculation of volume percent from millimeters pressure calibration curves

$$C_n = \frac{P_n}{P} \times 100$$

Where, C_n = volume percent of component n

P_n = partial pressure of component n (obtained by comparing the measured peak height of compound n with a calibration curve for compound n prepared with the same fixed volume but varying the pressures

P = total pressure of sample

This method is convenient in those cases where the components of the sample to be analyzed are gases and the corresponding pure standards are available for calibration.

Method B : The use of volume percent calibration curves

Calibration curves are prepared using fixed sample volume and the volume percent of the components is varied. Thus, the analysis for any component is obtained by comparing the measured peak height with the corresponding calibration curve.

Quantitative results can be obtained by substitution of weight per cent for volumes in methods described above.

— II —

EXPERIMENTAL STUDIES ON THE FLOW RATE EFFECTS OF CARRIER GAS

This section includes our experimental studies on the application of gas-liquid partition chromatography to qualitative and quantitative analysis of paraffinic hydrocarbon gases.

Before beginning the analysis of paraffinic hydrocarbon components we have studied determination of experimental optimum conditions emphasizing on the flow rate of carrier gas. We have studied the effects of flow rate in carrier gas on the retention time of the components, resolution of the peaks and relationship between flow rate of carrier gas and sensitivity of the results obtained.

We have used synthetic blends of pure «Philips» paraffinic hydrocarbons in the determination of optimum conditions of hydrocarbon analysis by Gas Chromatography.

The sensitivity of flow control with changes in pressure regulation is largely controlled by a capillary orifice in Beckman Gas Chromatograph. It is possible to vary the regulator pressure over a wide range (from 0 to 60 psi) to obtain a flow rate of 0 to 200 ml per minute of carrier gas. This relationship is shown graphically in Figure 9.

As may be seen in the figure, the pressures between 12-30 psi and flow rate of carrier gas are, to a very close approximation, linearly proportional. Therefore, we have measured and used pressure of carrier gas instead of flow rate in this range. The values of flow rates corresponding to the values of pressures applied are shown as follows :

12 psi = 20 ml/min, 18 psi = 37 ml/min, 23 psi = 53 ml/min.

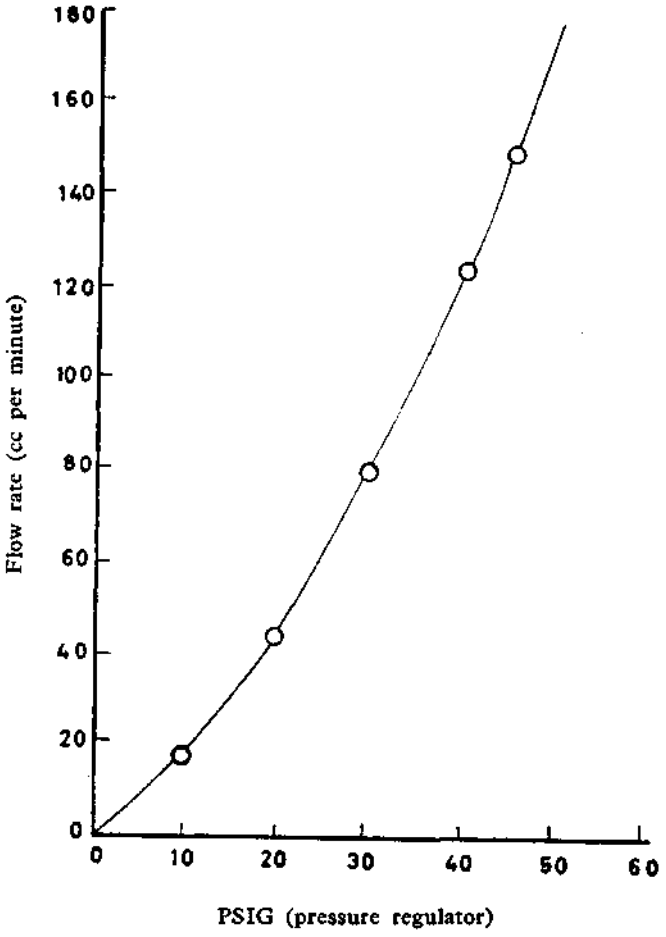

Fig. 9

The composition of synthetic hydrocarbon mixture prepared (no. 1) is as follows :

CH_4: 57.14%, C_2H_6: 27.86 %, C_3H_8: 10.00%, n-C_4H_{10}: 1.43%, iso-C_4H_{10}: 3.57 %

A 12-ft length benzyl ether partition column is used for the separation of no. 1 paraffinic hydrocarbon mixture in our experiments. This column contains 17.7 gr benzyl ether on 35.4 gr 42-60 mesh C-22 firebrick. Thermal compartment is maintained at 40°C as operation temperature. Filament current is selected as 150 ma. Nitrogen is used as carrier gas which transports the components of the mixture through the column. Purging method is applied to introduce gas mixture into gas chromatograph. (Operational manual about the analysis by Beckman Gas Chromatograph is explained in Section I.)

The thermal conductivity of methane component is higher than nitrogen. The thermal conductivities of ethane and higher paraffinic hydrocarbons in homologous series are lower when compared with nitrogen (Table 1). Therefore, negative deflection is recorded when nitrogen is used as carrier gas, this is eliminated by reversing polarity switch to negative at the beginning of the analysis. Polarity switch is turned on to positive between the peaks of methane and ethane.

By using attenuator control, it is possible to select a sensitivity value for each component. Recorder pen should record highest peak without exceeding chart range at this sensitivity value. Under our operational conditions described above, we have used the sensitivity value of 10 for methane and 1 for the other hydrocarbons. Corresponding sensitivity values of the components are indicated over peaks on the chromatograms. Peak areas or heights are multiplied by these values at the calculation of the results.

The effects of the variation in the carrier gas pressure on the retention times of the paraffinic hydrocarbons in the homologous series are studied in our work.

Therefore, gas mixture (no. 1) is analyzed at the conditions described above by using a 12-ft benzyl ether column at 40°C, at 150 ma of filament current, but varying the pressure of nitrogen used as carrier gas. The chromatograms obtained with the same sample at the pressures of 12 psi and 23 psi are given in Figures 10 and 11 respectively (12 psi in Fig. 10, 23 psi in Fig. 11). The retention times of the components obtained from the chromatograms at the carrier gas pressures of 12 psi, 18 psi and 23 psi are shown in Table 3.

Table 3

Components	*Retention times (seconds)*		
	Pressure of carrier gas (N_2)		
	12 psi	*18 psi*	*23 psi*
CH_4	189	125	97
C_2H_4	250	165	127
C_3H_8	401	265	205
n- C_4H_{10}	874	560	430
iso- C_4H_{10}	614	400	307

At a constant temperature, heavy molecules have less velocity than lighter molecules. As shown in Table 3, at a constant flow rate of carrier gas, velocities of paraffinic hydrocarbons in the homologous series decrease and their retention times increase as their molecular size grows.

According to the values in Table 3, which are obtained from our experiments the relation between retention times of the components and carrier gas pressures applied is shown on the curve in Figure 12.

As may be seen in Figure 12, the retention times of the components are inversely proportional to the flow rates of carrier gas. The relation between reciprocal of carrier gas pressures and the retention times is shown as a linear curve in Figure 12. (The values of gas pressure at the pressure regulator which are linearly proportional to the flow rates between 12-23 psi, as shown in Figure 9, are taken instead of flow rates of carrier gas.) The influence of factor f may be neglected since the ratio P_1 / P_o does not vary significantly with the same column in the range of pressure between 12 psi and 23 psi. As shown in the figure, the

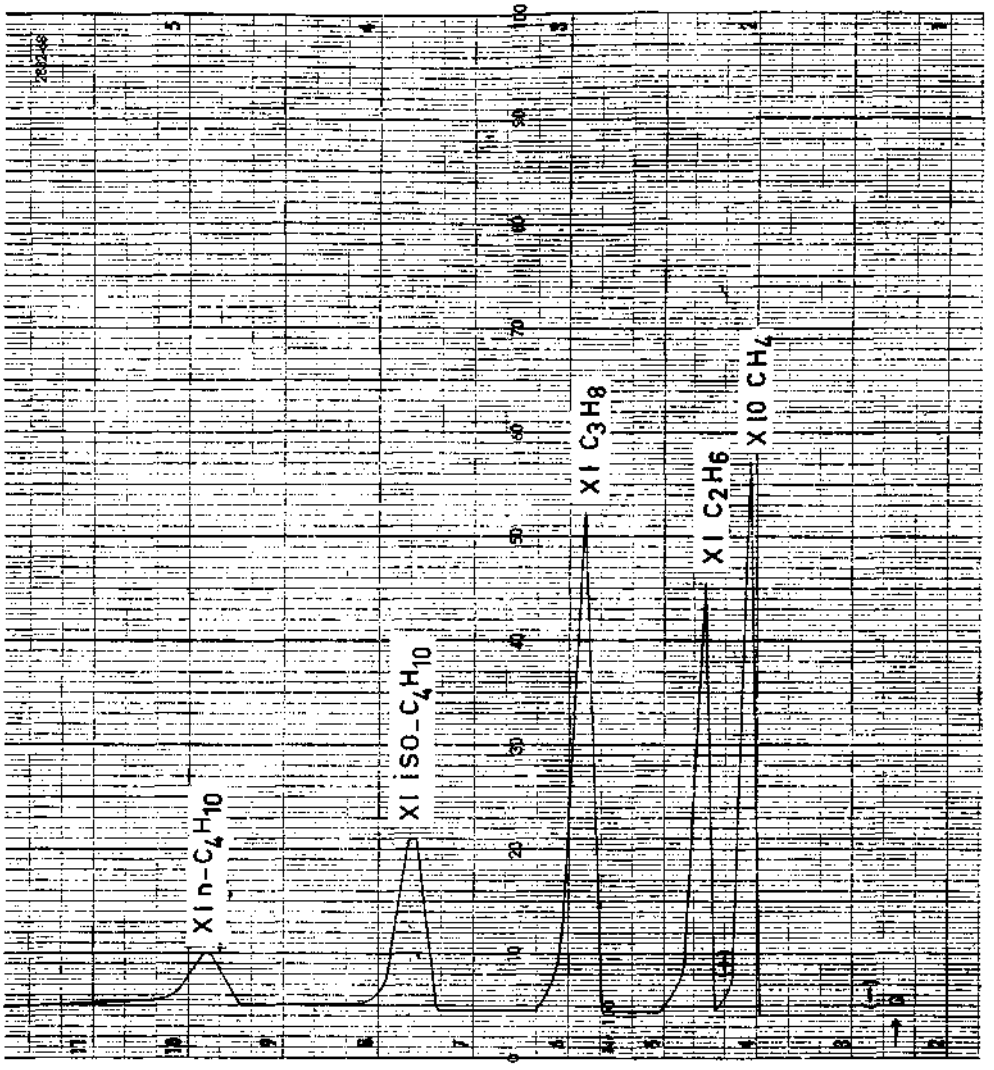

Fig. 10

retention times of the components decrease as the flow rates of carrier gas increase. Under definite operational conditions, retention volume or retention time is a characteristic of a certain component which is used for its identification. Therefore, flow rate must be kept constant at the same value during sample runs and calibration runs.

According to the values in Table 3, the retention time of iso butane is lower than normal butane although they have the same carbon number. The difference in the behaviors of two isomeric hydrocarbons is explained as follows:

One of the properties of atoms and molecules is to have relatively weak forces of attraction upon other atoms or molecules. These are called «van der Waals», cohesive or dispersion forces. These intermolecular cohesive forces which govern constitutive properties are expressed as the value of a in the van der Waals equation given in the following expression:

$$(1) \quad \left(P+\frac{a}{v^2}\right)(v-b) = RT$$

This force is universal and effective between non-polar molecules as well as between polar molecules.

According to the kinetic theory, experimental pressure of a gas is given in the following equation:

$$(2) \quad P = P_i - P'$$

Where, P = experimental pressure or impact pressure

Pi = kinetic pressure or internal pressure

P' = a factor for the correction of intermolecular forces

Intermolecular forces depend on the type of atoms and atomic arrangements in the molecular constitution. In addition to these attractive forces, there are

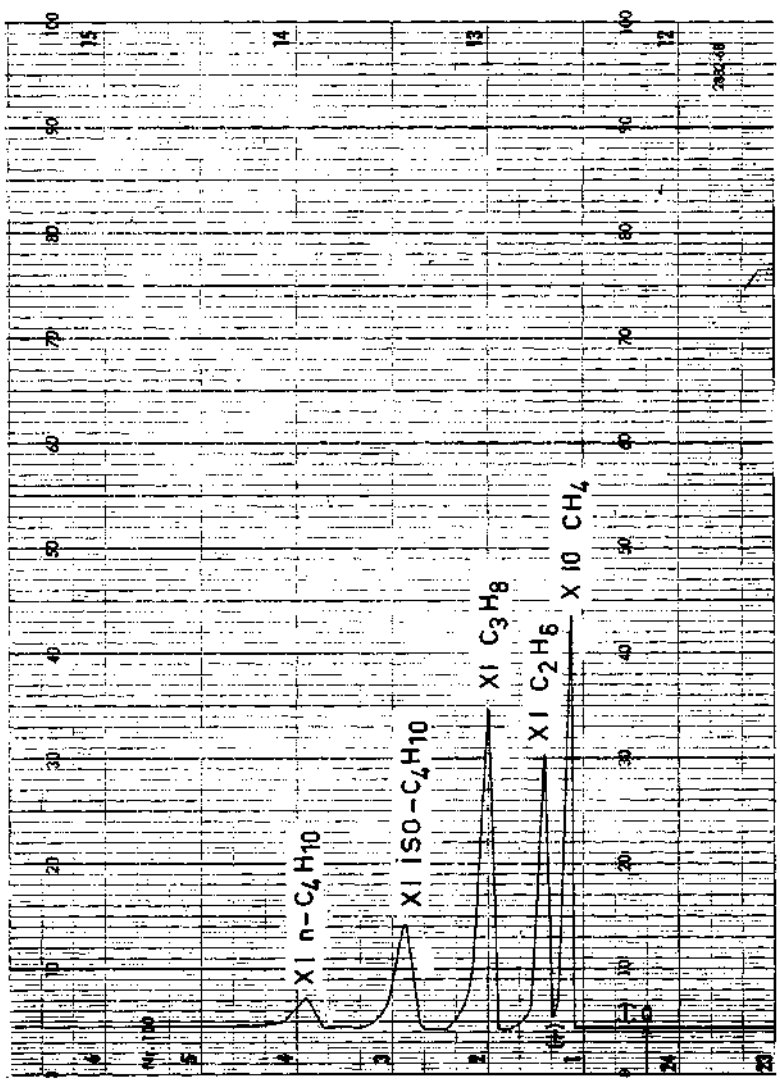

Fig. 11

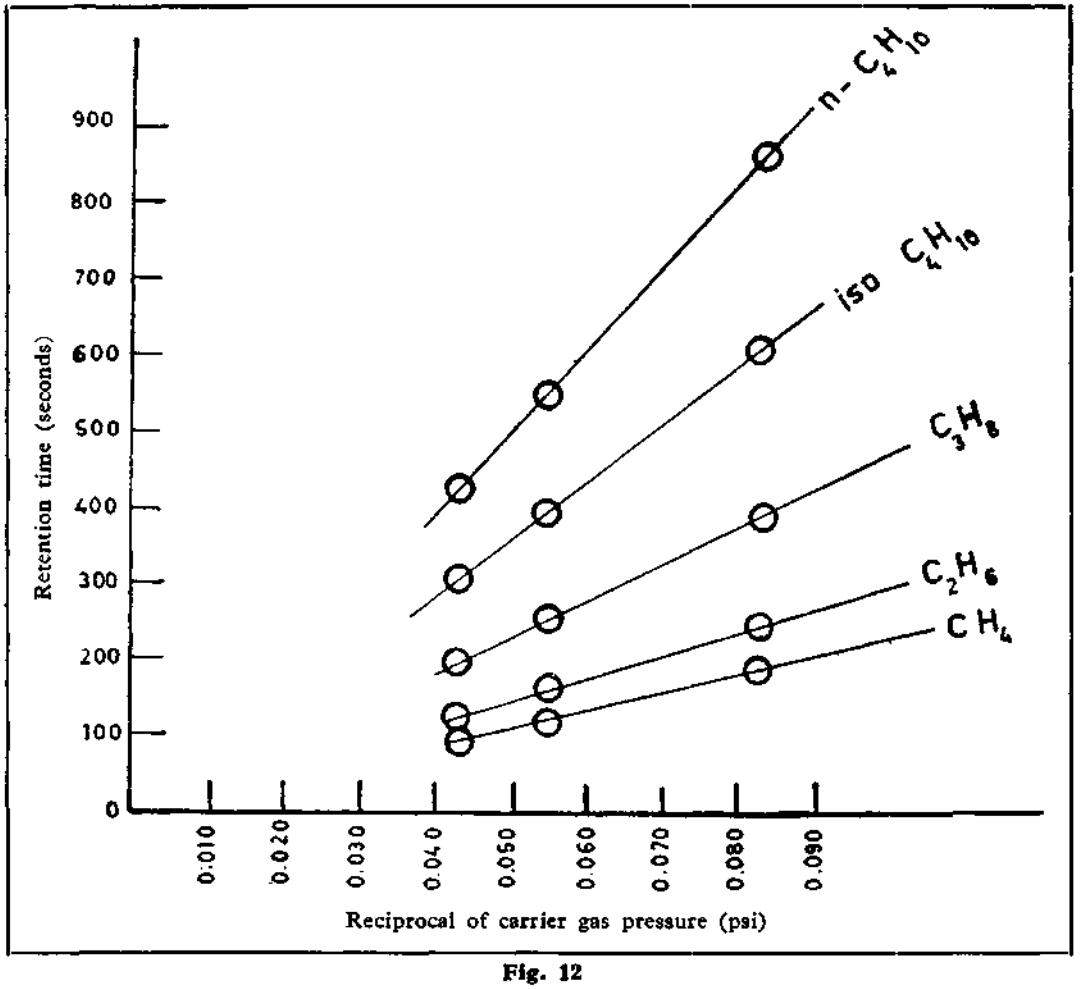

Fig. 12

repulsive forces effecting between all atoms and molecules at small distances. They set up rigid barriers to the closer approach of atoms or molecules to each other. These forces are termed as steric.

The constitution of normal chained hydrocarbons permits more attraction between hydrogen atoms than the constitution of branched chained hydrocarbons which are more spherical. Therefore, the forces of intermolecular attraction for normal hydrocarbons are greater.

The value of a in the equation of van der Waals above is a constant depending on the type of the gas. Intermolecular forces are expressed as the value of a in the equation. This value is 14.47* for n-butane and 12.87* for iso butane.

The difference in the intermoleeular forces of two isomeric hydrocarbons causes a difference in their vapour pressures as explained in equation (2) above. Therefore, the retention time of iso butane is lower than normal butane.

* $\frac{lt^2 \times at.}{(mole)^2}$

According to the values obtained from our experimental results in Table 3, the relation between log apparent retention times of normal paraffins (retention times corrected for gas hold-up capacity of the column) and their carbon numbes are plotted in Figure 13. According to the Figure 13, as the carbon numbers increase in the homologous series, retention times of the components also increase. As expected, paraffins emerge from the column in the order of their boiling points.

As shown in Figure 13, this relationship is linear under identical operational conditions for normal straight chain paraffinic hydrocarbon gases. The apparent retention times of iso butane do not agree with that linear relationship due to reasons explained above. When retention times are used instead of apparent retention times, instrumental conditions must be considered.

The relationship of the members in homologous series which is shown in Figure 13 constitutes a useful characteristic for gas chromatography. The advantage of homologous series plots in the identification of the components is that the homologous series plots can be interpolated or extrapolated. It will not be necessary to run more than two members in the homologous series to establish the slope of the curve.

The effects of the pressure or flow rate of carrier gas on the peak areas of the hydrocarbon components in the homologous series are studied and compared in our work. Gas mixture no. 1 is run by using a 12-ft benzyl ether column at 40° C, at the filament current of 150 ma and at the Values of carrier gas (nitrogen) pressures as 12 psi, 18 psi and 23 psi. The chromatograms at 12psi and 23 psi are given in Figure 10 and Figure 11 respectively. The values of peak areas which we have obtained from the chromatograms at the different carrier gas pressures are shown in Figure 14. The concentrations of the components are indicated on the corresponding curve in the figure. The curves in the figure are considered and studied individually due to differences in the concentrations of the components. Figure 14 shows the relationship between the peak areas of the individual components and the carrier gas pressures. According to the figure, as the pressure of carrier gas increases peak areas of the components decrease, because partial pressures of the components decrease due to dilution of the sample with greater volume of carrier gas.

This experimental work shows that individual component sensitivity expressed as the size of peak area varies inversely with flow rate of carrier gas. The curve plotted between reciprocal of carrier gas pressure or flow rate and peak area is linear. This relationship shows that the flow rate of carrier gas affects the quantitative results obtained. The flow rate of carrier gas must remain at the same value between calibration runs and sample runs.

According to Figure 14, ethane which is in the higher concentration than propane in the mixture has smaller peak area than the area of propane because the difference in the thermal conductivity between the carrier gas and the component affects the magnitude of the corresponding peak area. A thermal conductivity cell is used as detector in Beckman Gas Chromatograph. This detector measures a difference in the thermal conductivity between pure carrier gas and carrier gas having sample components. Therefore, at equivalent amounts of components, a signal of the greatest magnitude will be obtained when the difference in thermal conductivity between the carrier gas and sample components is at the maximum.

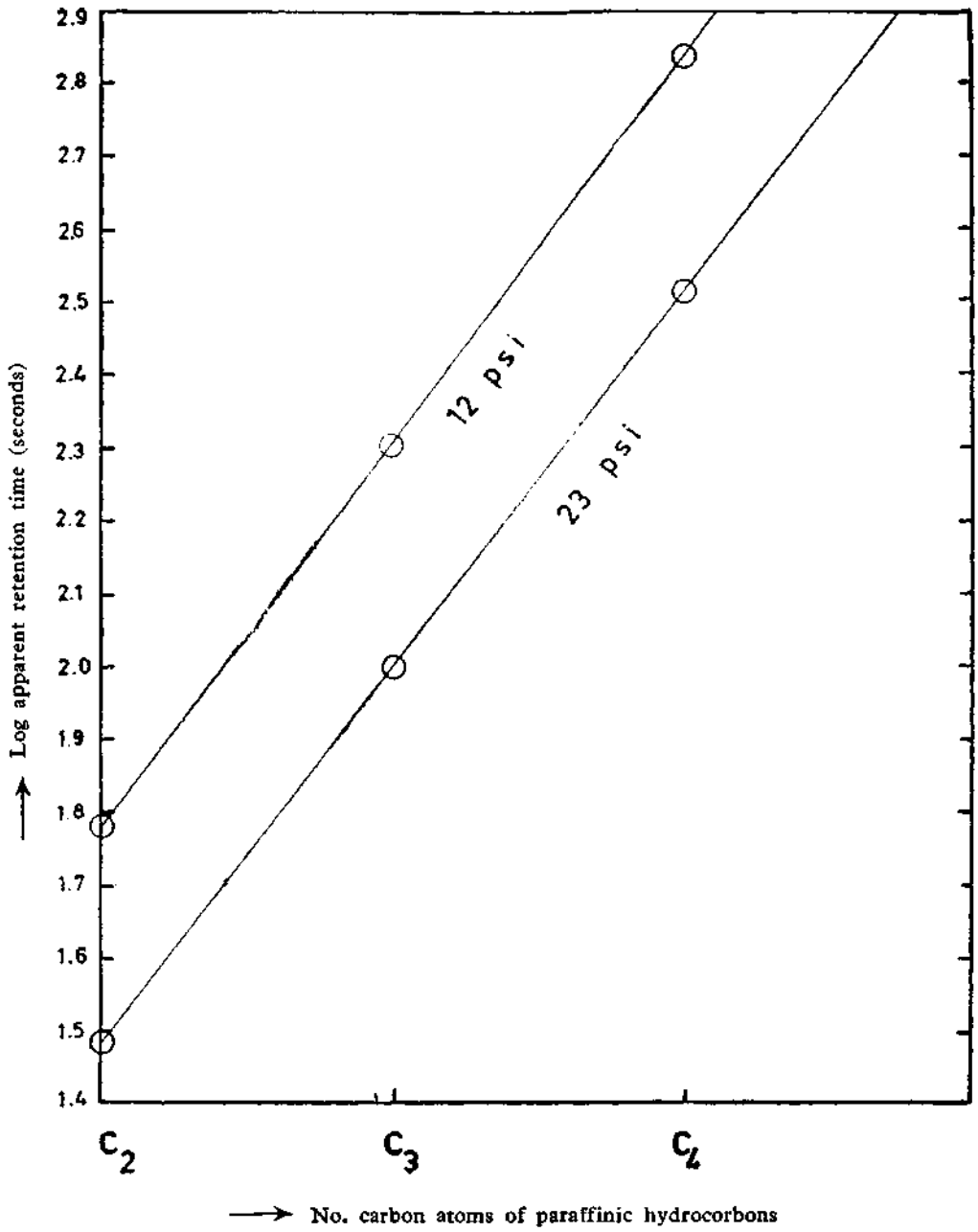

Fig. 13

Table 1 shows the thermal conductivity values of some gases. As shown in the table, the difference in thermal conductivity between nitrogen as carrier gas and ethane is smaller than the difference in thermal conductivity between nitrogen and propane. For that reason, the peak area of ethane is less than the peak area of propane although the concentration of ethane is greater (Fig. 10, 11 and 14).

Consequently, we can say that the difference in thermal conductivity between the carrier gas and the component consists of an important factor on the sensi-

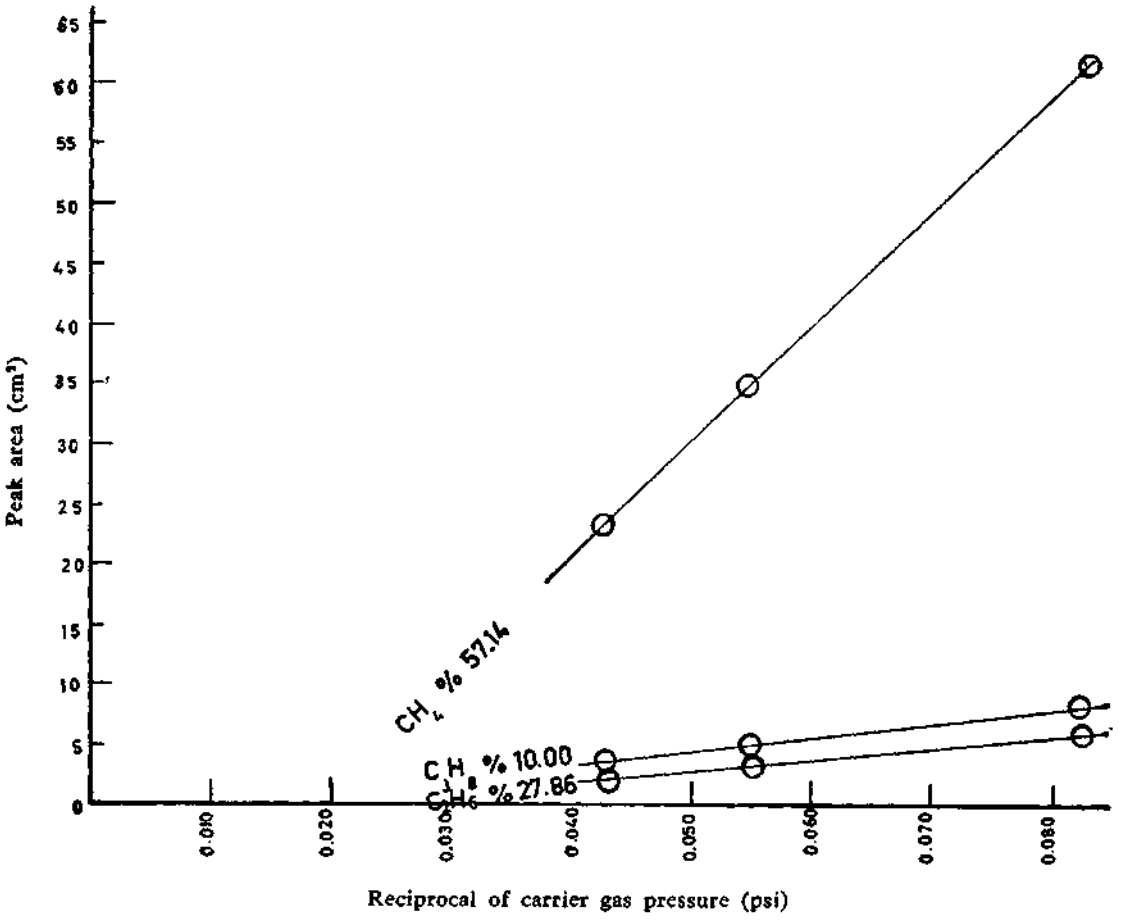

Fig. 14

tivity of the peak. This experimental work shows the importance of sensitivity factor for each individual component when nitrogen is used as carrier gas.

As may be seen on the chromatograms in Figures 10 and 11, peak width increases as the velocity of the hydrocarbon component decreases. As a component remains longer in the column, the signal taken as peak width gets greater. Peak width-peak height ratio increases as elution time is increased. Therefore, if a thermal conductivity cell is used as detector in gas chromatography method, calibration data must be prepared for each individual component to be determined.

We can summarize the results obtained from this comparative work in which we have studied the effects and optimum conditions of the flow rate of carrier gas in the analysis of paraffinic hydrocarbon gases in the following way :

The resolution between methane and ethane is better at 12 psi than the other values of carrier gas pressures and more time is available to turn polarity switch between the peaks of these components in this case. The sensitivity values expressed as peak height or area are also higher at 12 psi than the other values of carrier gas pressures (Fig. 10, 11 and 14).

Therefore, 12 psi (20 ml/min.) is determined as optimum inlet pressure or flow rate of carrier gas in the analysis of paraffinic hyrocarbon gases at the given operational conditions.

—III–

APPLICATION OF GAS CHROMATOGRAPHY METHOD TO HYDROCARBON ANALYSIS OF SOME NATURAL GASES IN TURKEY

The term «natural gas» is understood as the accumulation of gas, often in large quantities, which occurs underground in reservoirs of porous formations sealed by more impervious rocks. This gas may occur in such geological formations either with or without association with petroleum deposits.

Surface indications of petroleum are substances commonly associated with petroliferous deposits. Hydrocarbon gases have connection obviously with such deposits and they are regarded as direct indications. Recognition and discrimination of a true gas seepage from petroliferous beds is an important problem. Methane may be evolved in considerably large quantities by decaying vegetation, bacterial fermentation and decomposition of organic matters; in this case, this gas is not related to petroleum formations.

Natural gas assosiated with oil in the structure incorporates some of the hydrocarbon gases consisting of methane and higher homologues of paraffin series, such as ethane, propane, normal butane and iso butane, etc.

Gas Chromatography is a very convenient method for separation, identification and quantitative analysis of these hydrocarbon components and plays an important part in the identification of the surface indications of petroleum.

We used the gas mixtures of known concentrations as a reference for the calibration purposes in our work. These standard mixtures contain the hydrocarbon components in natural gases. According to the American Standard Testing Methods, the concentration of the component in the reference mixture should not differ by more than 10 per cent from the concentration of the corresponding component in the sample.

We prepared calibration curves for each individual component in the reference mixture showing the relationship between the concentration of the component and peak height or area. We applied identical operational conditions (same column, temperature, detector cell current, flow rate of carrier gas, etc.) on calibration runs and sample runs. We compared retention times of the sample components obtained from the chromatograms with the reference standards (qualitative analysis). We determined the concentrations of the sample components by interpreting the values of peak areas or heights obtained from the chromatograms on the calibration curves plotted as peak height or area against the concentrations of the reference components (quantitative analysis).

In the following parts, some examples are given about the application of our analysis on the hydrocarbon components of some natural gases in Turkey by gas chromatography and operational conditions are explained.

The occurrence of natural gas around the village of Dodurga in Ulus county, in the province of Zonguldak, is investigated by the Mineral Research and Exploration Institute and a report was-given about the occurrence by Geologist Erdoğan Demirtaşlı. (Report no. 3221, dated March 10, 1963. The location of

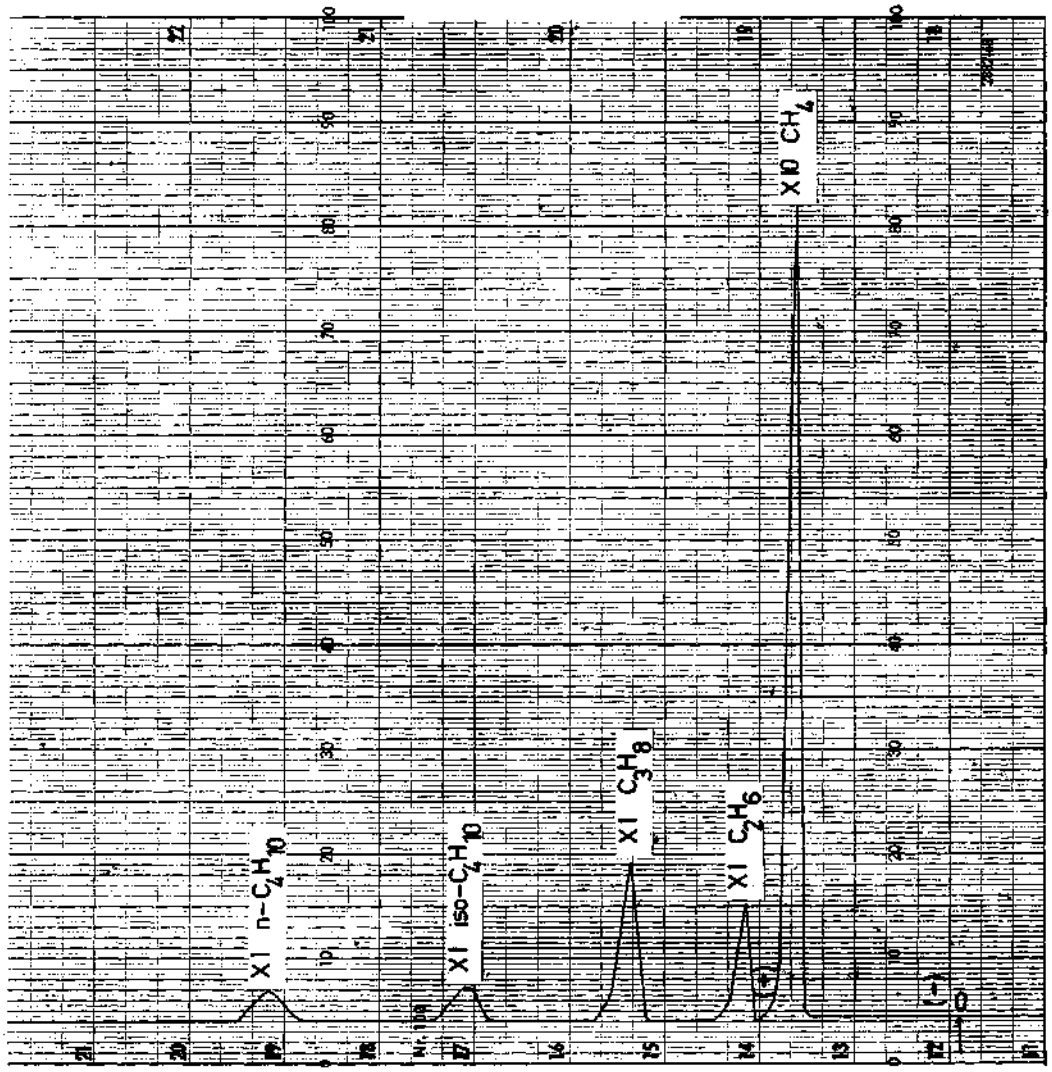

Fig. 15 - Chromatogram of the natural gas from Dodurga, Ulus.

the seepage near to the quarter of Aslancı is indicated on the map sketch no. 15683.)

The chromatogram of the analysis of the gas from Dodurga, Ulus, which we have made by Gas Chromatography is given in Figure 15.

Purging method is applied to introduce the sample into the instrument for the analysis. A benzyl ether column, 12-ft length, 1/4-in diameter, is used for the separation of paraffinic hydrocarbon gases. This column contains 17.4 gr benzyl ether on 35.4 gr 42-60-mesh-sized C-22 firebrick. Nitrogen is used as carrier gas. Carrier gas pressure in the value of 12 psi is applied for the transportation of the components through the column. Temperature is selected as 40° C and filament current is applied as 150 ma at the thermal conductivity cell detector.

Comparing the chromatograms obtained with the sample and calibration standards at the identical operational conditions, interpretation is made qualitatively and quantitatively.

The analysis of natural gas from Dodurga, Ulus is given as follows:

CH_4: 89.3%, C_2H_6: 6.3%, C_3H_8: 2.7%, n-C_4H_{10}: 0.8%, iso C_4H_{10}: 0.5%, $C0_2$: 0.4%.

The gas contains methane and higher homologous series of paraffinic hydrocarbons. The existence of the higher members of paraffin series in the natural gas indicates that this gas may be related to petroliferous deposits and it is significant from that point of view. This matter also agrees with the geological possibilities explained in the report.

By Gas Chromatography Method, we analyzed the gas sample from the well of «Bakuk-l», at Bakuk Mountain around Nusaybin, drilled by Pan Oil Company.

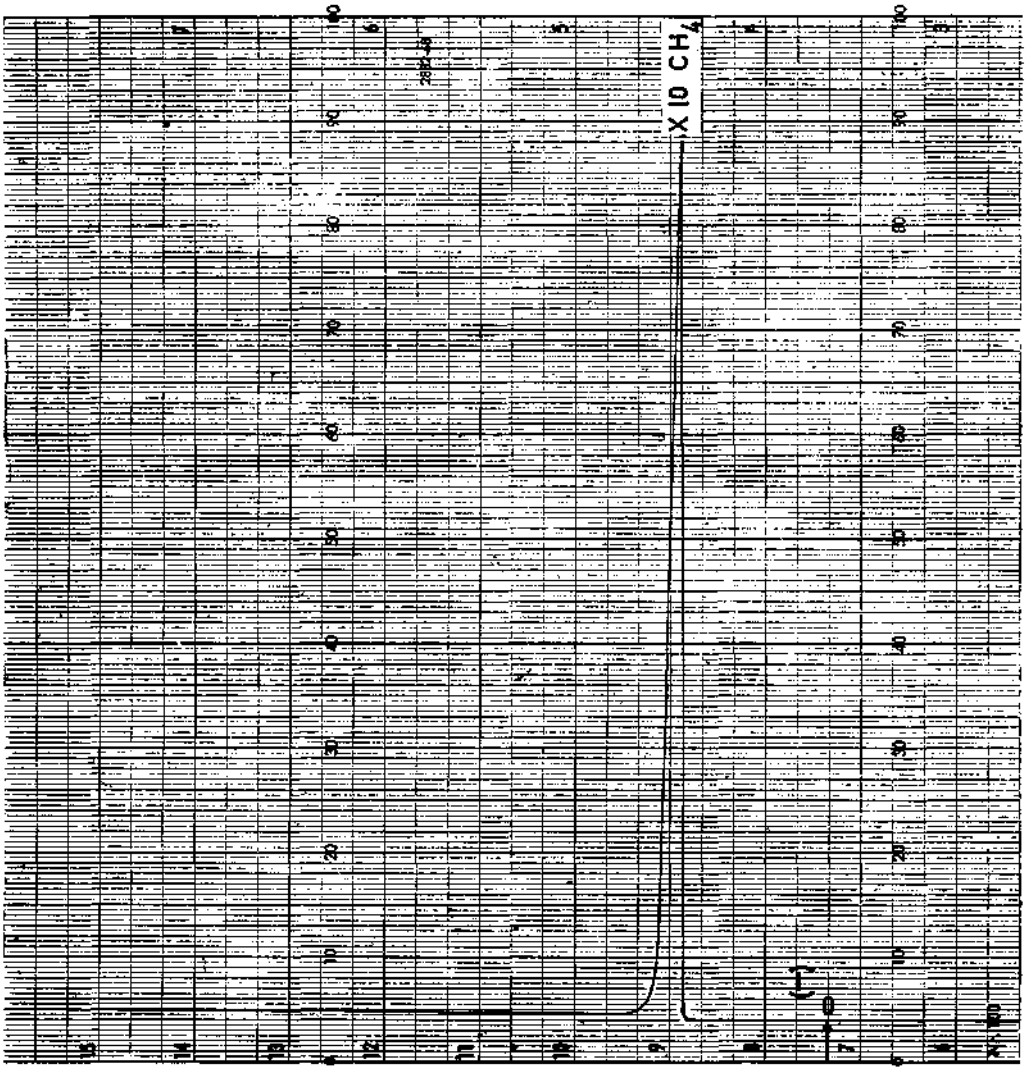

Fig. 16 - Chromatogram of the gas from the well «Bakûk-1».

Operational conditions: 12 ft X 1/4 in benzyl ether column (17.7 gr benzyl ether on 35.4 gr 42-60 mesh-sized C-22 firebrick), 12 psi of nitrogen as carrier gas, 40° C temperature, 150 ma filament current.

The chromatogram of the analysis is shown in Figure 16. As shown on the chromatogram, higher hydrocarbons of the paraffin series are not available in the gas. The gas contains mainly methane. Its composition consists of 95.5 % methane and 4.5 % nitrogen.

The gas sample from the well «Çelikli-4» of Turkish Petroleum Corporation is analyzed by gas chromatography method.

Operational conditions: 12 ft X 1/4 in benzyl ether column, 12 psi of carrier gas pressure (nitrogen as carrier gas), 40° C temperature, 150 ma filament current.

The gas contains 9.7 % carbon dioxide which is determined by Orsat method. Carbon dioxide is absorbed before introducing the sample into the gas chromatograph so that it will not be eluted with ethane in the same time as a single peak with benzyl ether column.

The results of the gas analysis from «Çelikli-4» are given as follows :

CH_4: 66.5%, C_2H_6:8.1%, C_3H_8: 4.7%, n-C_4H_{10}: 1.4%,
iso C_4H_{10}: 0.6%, $C0_2$: 9.7%, O_2: 1.1%, N_2: 9.7%

The results of the hydrocarbon analysis are obtained from the chromatogram* shown in Figure 17. The gas contains normal pentane and iso pentane in trace amount.

The results of the gas analysis from «Çelikli-4» on the air-free basis are as follows :

CH_4: 70.4%, C_2H_6: 8.6%, C_8H_8: 5.0%, n-C_4H_{10}: 1.4%,
iso C_4H_{10}: 0.7%, CO_2: 10.2%, N_2: 3.7%

The existence of higher homologous of paraffinic series hydrocarbons in the gases from the well «Çelikli-4» shows the relationship of these gases to petroleum.

Consequently, we can say that Gas Chromatography Method which has proven its favorable advantage in the identification of petroleum gases plays an important part in the exploration of petroleum and natural gases.

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* The chart speed of the recorder is 0.5 in per minute in the chromatograms.

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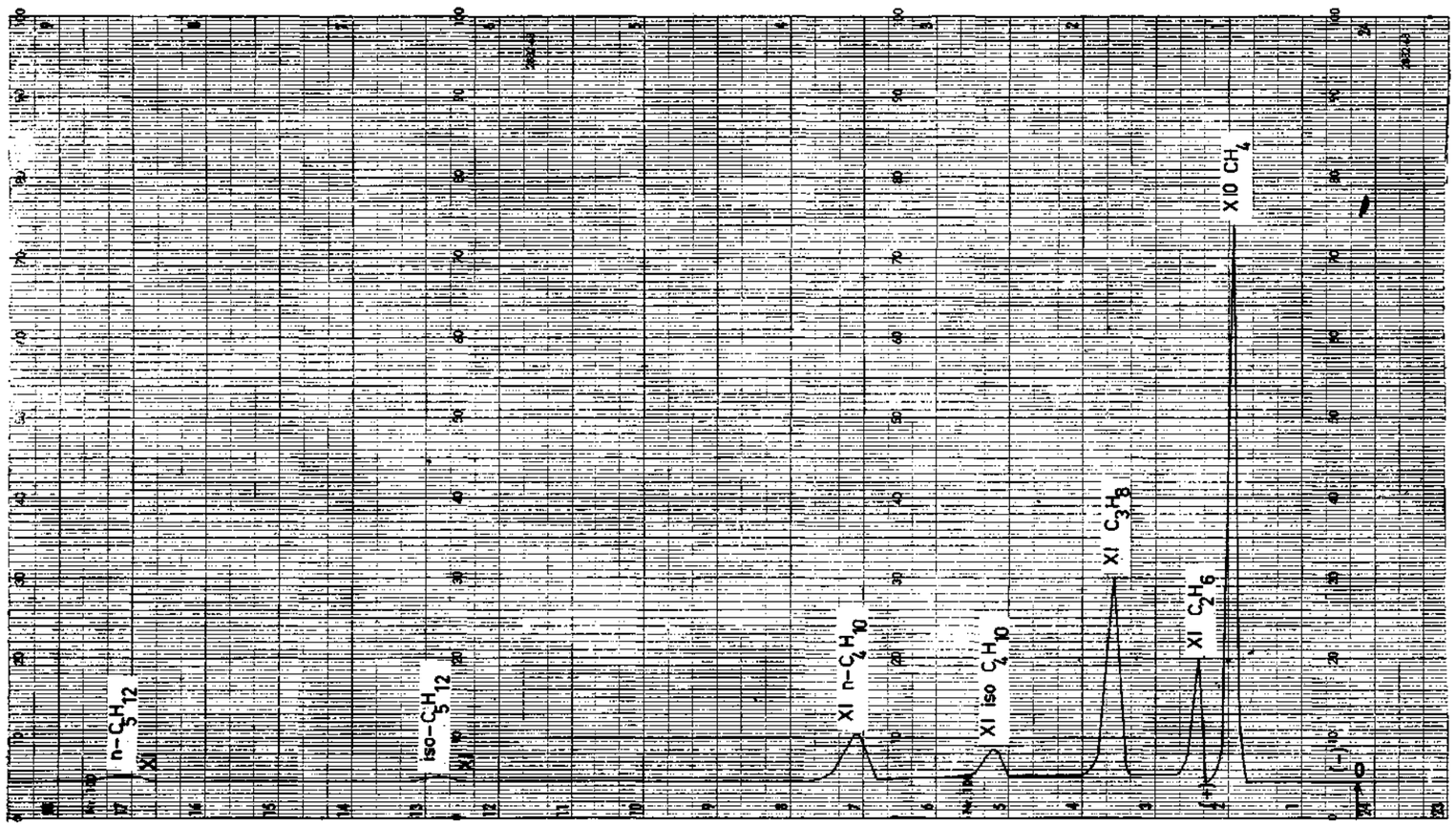

Fig. 17 - Chromatogram of the gas from the well «Çelikli no. 4».

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