INVESTIGATION OF GROUP SEPARATION OF n-PARAFFINS IN GARZAN CRUDE OIL BY POLARIC SOLVENT EXTRACTION

Submitted to the faculty of Engineering
of the Middle East Technical University
in partial fulfilment of the requirements
for the degree of Master of Science in
Chemical Engineering.

by
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January, 1971

Approved by:.ORIGINAL.SIGNATURE,
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ACKNOWLEDGEMENT

I consider myself being indebted and wish to express my gratitude to my advisor Prof. Dr. Ing. E. Weingaertner for his worthy supervision and timely advice, without which this research would have never reached the completion.

I am grateful, to Türkiye Petrolleri A.O. Batman refinery for providing Garzan Crude Oil, and to Messrs. Farbwerke Hoechst, Frankfurt-Main, Germany, for providing the Gas Chromatograph, for the investigation.

My deep thanks also go to all those who have helped me during the completion of this research work.

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At.No.	Autonation Number of G.C.
BP	Boiling Point, ^{o}C
BP_c	Boiling Point Calculated, ^{o}C
D-C-At-	Series of Samples Prepared by Treating of Origional Crude Oil with Acetone
D-C-H-	Series of Samples Taken From the Origional Crude Oil and Treated with n-Hexane for the Removal of Asphaltenes.
D-R-C-	Series of Samples of Reduced or Deasphalted Crude Oil.
D-R-C-At-	Series of Samples Prepared by Treating the Reduced Crude Oil with Acetone
F	In Sample Denotation it Represents the Filtrate Layer from the Corresponding Sample.
i	Iso
m	Meta
Me	Methyl
Med.	Medium
Naph.	Naphtalene
n	Normal
o	Ortho
p	Para
PT	Peak Temperature
R	In sample Denotation it Represents the Residue Layer from the Corresponding Sample.
rpm	Revolutions per minute.
RT	Retention Time (min)
Sp	Speed

tert.	Tertiary
tr.	Trans.

In the Sample Denotation:

The First Number is the Number of the sample in its series.

The second and the following Numbers except the last one represent the ratio of the corresponding compounds in the samples, taking the crude oil in unit volume.

The last Number indicates whether the same sample is prepared in small or larger quantities.

In the Notation of chromatograms the Last Number represents the number of run of the same sample through G.C.

5. SUMMARY

In the present work, it was aimed to see to which extent group seperation would be possible by direct application of a polaric solvent, such as acetone on the crude oil itself.

Measured wolumes of dewatered pure acetone were mixed with deasphalted Garzan Crude Oil with different n-hexane contents and with the Origional Garzan Grude Oil. In some of these samples which contain non-hexane, and which contain very little amount of n-hexane, paraffinic, waxy type precipitates formed. These were desirable with regard to the aim of the work. Hence, two of these samples, having the ratios of origional crude oil to acetone 1:1 and 1:4, and two samples prepared in the same rations but in larger quantities were investigated in detail.

Gas chromatographic analyses were carried out, of the origional reduced oil, of the acetone extract and the residue from the acetone treatment for both contacting rations. These chromatograms were evaluated both qualitatively and quantitatively.

Enrichment of n-paraffins up to n-C_{13} was observed in the acetone extract of the 1:1 volume ratio experiment and a respective enrichment of n-paraffins higher than n-C_{13} in the residue part of the extraction. The quantitative results are presented in Table:7, and in Figure: 16 in Section 9.4. 1-2.

In the experiment using 1:4 ratio only a very slight enrichment of the higher n-paraffins was observed while simultaneously the limit of separation was found transferred to the higher molecular side lying approximately at n-C_{23}. The respective quantitative results are presented in Table :8, and in Figure: 17, in Section 9. 4. 1-2.

It was observed that a market separation or enrichment respectively of n-paraffins can only be expected when rather low ratios of crude oil to acetone were being employed, thereby making the use of the limited solubility of n-paraffins.

Enrichment of the compounds other than n-paraffins which were in larger quantities was observed in the acetone extract of the 1:1 volume ratio sample. The quantitative results are presented in Table: 9, In Section: 9. 4.3.

6. INTRODUCTION

6.1. AIM OF THE PRESENT WORK:

Ever since the crude oils of different types have been mined and processed, the intial step has always been carried out in the form of a fractional distillation, which is in principal a separation according to increasing ranges of boiling points, irrespective of hydrocarbon groups according to structural differences.

This is to say that in almost every boiling point fraction representatives of four major groups; n-paraffins, i-paraffins, naphtenes and aromatics are found side by side due to closely boiling points. Within such types of separation no separation according to groups of different structures can directly be achieved.

On the other hand it would be most valuable, -and demand for its is increasing, - if a straight forward separation into substances of the same chemical structure could be found and tried.

Processes which are aimed at this achievement are existing and are successfully carried out in practice. For instance, removal of higher normal paraffins (waxes) by precipitation with liquified propane, removal of aromatics by liquid-liquid extraction with diethylene glycol, sulfolane, liquified SO_2, removal of low boiling normal paraffins by molecular sieve treatment, recovery of medium size n-paraffins by urea treatment and precipitation of asphaltenes by n-hexane or n-heptane, to mention some of these processes.

However these treatments have so far been successfully and in a large scale employed on crude oil fractions only, not directly on crude oil itself.

With a view point in mind on a possible future development in basic refinery technique, a more general investigation, of which this study from a certain part, has been established in order to find out, whether and to which extent, ways and means would be possible in achieving group separation effects by direct application on the crude oil itself, using respective methods.

Hence, the work of O.Ansen (1) in 1968 has dealt with the possibilty of identification and recovery of n-paraffins by the Urea Method. The work of T.Gür (6) in 1967-68 was concerned with identification and recovery of aromatics by using di-ethylene glycol extraction. The work of O.Baynus (3) 1969 has dealt with identification and enrichment of preferentially of i-paraffins and naphtenes using the molecular sieve technique. All these works have shown that group separation would basically be possible and could be employed with a great degree of success and under economically feasible conditions.

The principal approach in these studies could be seen in the use of either non polaric solvents or employing clathrate forming substances like urea and molecular sieves. It is however a well known fact that treatments with polaric solvents or mixtures of polaric, non-polaric solvents may result in selective separation of components belonging to different groups. Many of the earlier liquid-liquid extraction processes in Crude Oil refining operations make use of the selective solubility of certain components in polaric solvents, like treatment with phenol, with furfural, with higher alcohols, ketones , esters and liquified SO_2. Also in the work of O.Ansen (1) acetone was used in the early purification step for the supposed removal of asphaltic and resinous matter for the only reason to apply gas chromatiography in the investigation. While this treatment it was also observed that some parts of n-paraffins specially on the higher boiling side were precipitated, hence being removed and seperated. Such preferential precipitation could be safely traced to the influence of acetone. Having in mind to apply in general in the course of this study the action of polaric solvents and precipitants and having observed such preferential precipitation within the earlier investigations, it was considered of importance to try and investigate in such treatments applying separation by substances having polaric forces.

Such work using Garzan Crude Oil as the raw material and acetone as a highly polaric solvent has been carried out in the present study mainly with the aim to see to which extent group separation would be possible. Such investigation would be possible with the expectation of some tangible result by the use of the highly efficient analytical method of Gas Chromatography only. In this connection the results of the study chould be considered as the very first result of such kind of investigation.

6.2. INDUSTRIAL EXTRACTION PROCESSES OF CRUDE OIL FRACTIONS:

So far liquid-liquid or solid-liquid extraction processes are technically employed only with crude oil fractions for different purposes, but not yet directly on crude oils. Such solvent treating or extraction processes which have been successfully employed in a large scale on crude oil fractions in the refineries could be summarised as follows:

1. Edeleanu Process (13) is applicable to light distillates such as heavy naphta, kerosene and diesel fuel for the separation of aromatics and unsaturated hydrocarbons from the paraffins and naphtenes by employing liguified SO_2 at 14°F.

2. The Liquified Propane Process (16) is employed for dewaxing of lube oil-fractions. The precipitating action of lower n-paraffins on crude oils of asphaltic types makes it rather difficult to mix paraffinic type crude oils with other types for transportation and storage purposes.

3. The Udex Process (13) is used for the recovery of benzene, toluene and xylenes from catalytic reformates by solvent extraction with di-ethylene glycol.

4. The Molecular Sieves Process (13), which utilizes crystalline zeolites synthetically produced and having special adsorption properties for n-paraffins, is used commercially in performing the separations of n-hydrocarbons from branched chain or cyclic hydrocarbons. Its

usage is limited to n-paraffins up to n-C_{10}.

5. The Urea Dewaxing Process (13) is used in industrial extraction technique for the recovery of higher molecular linear aliphatic hydrocarbons from Diesel Oil and Gas Oil. The linear saturated hydrocarbons can form adducts with urea which are being easily separated and decomposed successively in hot water.

6. The Furfural and the Phenol Processes (14) are used for the production of High Viscosity Index lubricating oils for removal of higher aromatic compounds.

6.3. THEORY OF EXTRACTION:

Extraction is a physical separation process that is governed by the distribution law, which states that the ratio of the concentrations of a component distributed between two mutually insoluble phases is a constant. (11)

$$\frac{C_1}{C_2} = K \qquad (1)$$

where C_1 = concentration of solute in solvent phase, percent by weight.

C_2 = Concentration of solute in second liquid phase, percent by weight.

K = a constant depends only on temperature.

The solvent rich solution is called the "extract" solution, and the oil or component rich solution is the "raffinate" solution.

In the theory of extraction if w represents the stock in weight, S the amount of pure solvent, x the amount of component to be extracted per weight of stock and y the amount of component per weight of solvent; (13)

$$W\ (x_1 - x_2) = S\ (y_1 - y_2)$$

$$\frac{W}{S} = \frac{y_1 - y_2}{x_1 - x_2} \qquad (2)$$

The subscript 1 refers to the incoming liquids and 2 to the outgoing liquids in continous operations.

The combination of the Equations 1 and 2 would result (13)

$$y = \frac{x}{K + xK - x} \qquad (3)$$

Equation 2 represents the operating curve while Equation 3 represents the equilibrium curve, both of which could serve for extraction calculations.

6.4. SOLUTIONS AND POLARITY OF COMPONENTS:

Although the theory of miscibility of two substances has not been established in full detail, it has been experienced that the solubilities of the components were strongly dependent of the chemical structures of the solvent and the solute, their conc., and of the temperature at which the mixing process was taking place. Further investigations have resulted that the polarity of the molecular structure has a great influence on the solubilities of certain components. This has been postulated, - with a few exceptions, - that polaric solutes were more soluble in polaric solvents while the non-polaric solutes were more soluble in non-polaric solvents.

In certain organic compounds net forces arise from non-symmetrical charge distributions in the molecular structures. These molecules in which the positive and negative centers of charge do not coincide are called polar molecules, and any bond in which the sharing between two kernels is unequal is a polar bond. The molar polarization can be calculated by using the Mosatti-Clausius Equation: (7)

$$P = \frac{D-1}{D+2} \cdot \frac{M}{\rho} = 3/4\pi N\alpha \qquad (4)$$

where P = Molar polarization

D = Dielectric constant

M = Molecular weight

ρ = Density

N = Avogadro Number

α = Polarizability

The dielectric constant is determined by means of a condenser while the polarizability is calculated by using the Vapor Temperature of Refractive Methods. (7)

Among the hydrocarbons and their derivatives, after the nitrites and nitro compounds acetone has the second highest dipole moment (μ) 2.70 Deby units or 2.70×10^{18} e.s. cm., and acetone is available in sufficient amounts as a solvent for this extraction process. In Table 13, in Appendix A, the Values of the Dipole Moments of hydrocarbons and hydrocarbon groups are listed.

7. GAS CHROMATOGRAPHY FOR THE ANALYSIS OF CRUDE OIL AND CRUDE OIL FRACTIONS:

7.1. HISTORY AND PRINCIPALS OF G.C. ANALYSIS

The analytical methods; specific gravity determination, characterization factor, aniline point method, ring analysis method of Waterman and the infra red analysis could only give information to ascertain the base or type of a crude oil but they do not provide the opportunity to analze the mixture into its single constituents.

On the other hand, Gas Chromatography is principally used as an analytical technique for the separation, identification and quantitative determination of volatile compounds having boiling points up to about 350 or even 400°C.

Although the separation methods which use the principals of chromatography have been know since the beginning of 16th century, the greatest development in chromatography has come in 1940.

In 1812 Dittel (10) a surgeon employed the principal of gas liquid chromatography in the purification of alcohol by employing a sponge soaked in oil as the stationary phase.

At the beginning of 19th century Runge (10) showed the possibility of separating coloring matters on paper.

In 1906 Tswett (10) separated a samll amount of plant pigments through a chalk column by washing with light petroleum.

In 1941 Martin and Synge (10) developed paper chromatography.

In 1950 James and Martin (10) carried out the experiments in adsorption chromatography.

Since than gas chromatography becomes a sensitive rapid and automatically performed analytical method in the qualitative and quantitative determinations of even extremely small smount of samples.

All the chromatographic separations involve the transport of a sample of a mixture through a column or a physical equivalent of a column. The mixture may be a liquid or a gas. The column contains a substance - the stationary phase - which may consist either of a solid adsorbing agent or of a liquid partitioning agent.

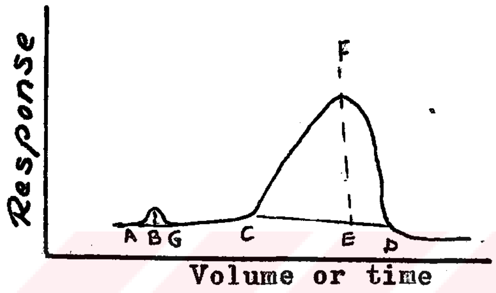
Gas - solid and gas - liquid chromatography, which are included inthe general concept gas chromatography, are requiring an inert mobile gas as a carrier gas of the mixture to be analysed (= carrier or effluent gas).

Depending on the volatilities and the affinities, the substances are retained to a greater or lesser degree by the stationary phase, and the separation is accomplished.

The theory of separation in the gas chromatography can be explained by the Elution Development. A sample of a simple mixture of A and B is introduced to a column of solid adsorbent. B is more powerfully adsorbed by the adsorber. Then a slow current of fluid (the eluent) that is not adsorbed is introduced to wash down the components selectively. A and B travel down the column at different speeds in accordance with the strenght of adsorption of the components. The band of the solution of A is ahead of that of B and is separated from it by a zone of pure eluent.

In case of more complex mixtures the separation technique is the same and the separated fractions emerge at the end of the column along with the carrier gas. The substances in the flowing carrier gas stream are then detected by messuring a chemical or physical property.

A simple elution diagram of a chromatogram is in such a form:



BE is retention time referred to peak hight. Or BE is retention volume referred to peak hight which is BE. This volume required to elute a particular peak (V_R) can easily be calculated from the rate of flow of the carrier gas, which should be kept constant, the elapsed time and the recorder reading. V_R^o, the corrected retention volume due to the pressure gradient is calculated: (2)

$$V_R^o = \frac{3\left(\frac{P_1}{P_o}\right)^2 - 1}{2\left(\frac{P_1}{P_o}\right)^3 - 1} \cdot \frac{V_R}{\text{g. liquid phase.}} \qquad (5)$$

P_1 = Pressure at start of the column.

P_o = Pressure at the end of the column.

Number of theoretical plates to achieve this separation (H) is calculated; (2)

$$H = 16 \left(\frac{AE}{CD}\right)^2 \qquad (6)$$

This helps to appraise the separating power of a column (Ref: 2)

7.2. ADVANTAGES AND DIS-ADVANTAGES OF GAS CHROMATOGRAPHY:

7.2.1. Advantages:

1. Speed: The entire analysis is completed within 20-30 minutes. The use of carrier gas as the moving phase has the advantage of rapid equilibrium between the moving and stationary phases and allows high carrier gas velocities to be employed.

2. Resolution: In some compounds the boiling point difference is negligible. The separation of these compounds by other techniques is extemly difficult or impossible; Gas chromatography can separate compounds with almost identical boiling points. By using selective solvents G.C, provides resolution which is impossible by distillation or other techniques.

3. Qualitative Analysis: The retention time (RT), the retention volume (V_Ro) and retention indeces (1) are characteristic properties of the compounds. By chosing the proper liquid phase and controlling the flow rate and temperature these can be reproduced to within 1 % and used to identify each peak.

4. Quantitative Analysis: The area of each peak, which is produced on the chromatogram, is proportional to that

substance's concentration in weight per centages, and this can be used to determine the exact concentration of each component.

7.2.2. Disadvantages:

It is restricted to volatile substances. The vapor pressure of a component sahould exceed, at least 1 mm Hg., at the temperature of the column, otherwise its rate of transport will be too low for particular purposes. To increase the vapor pressure and rate of transport of components, the column may be operated at an elavated temperature. There is a limit to this temperature due to the stability and volatility of the stationary phase and also the suitability of the detector for high temperature.

7.3. Programmed Temperature Gas Chromatography:

The isothermal operation has two disadvantages:

1. Early peaks are sharp and closely spaced while late peaks are low, broad and widely spaced.

2. High boiling compounds are undetected. A linear programmed temperature operation avoids these defects and it also increases the speed and flexibility. To approach temperature equilibrium at high heating and rapid cooling rates the column and the heater should have low heat capacity.

With increasing column temperature the carrier gas flow rate at constant pressure decreases. To eliminate this a differential flow controller is used.

A programmed temperature gas chromatography apparatus is composed of four sections:

1. Equipment for providing a controlled flow of carrier gas: For quantitative analysis the flow of the carrier gas must be constant, so that all components recorded on the time axis may be sensed on the same volumetric basis. The flow of gas at certain temperature is controlled by providing pressure regulators at both or only one end of the column. The flow rate can be measured by means of a rotameter, an orifice meter or a soap film meter.

Carrier gas might be one of these N_2, CO_2, H_2, or He. The gas free from moisture is provided in high pressure cylinders through reducing valves.

2. The column and the thermostat: The column may have any lenght from a few feet to 60 feet is made of 1/4" I.D., Copper tubing. Metal tube is better than glass in heat transfer and constancy of temperature.

The support employed is 30/50 or 50/80 mesh screen fraction of ground fire brick which has been freed from dust. This support is made a slurry with the caculated amount of stationary liquid dissolved in a suitable solvent. After it is dried, it is filled in the tube and the packed column is coiled in 6-8 inches, diameter.

For quantitative analysis close temperature regulation is necessary if the height of the peak is used as the parameter for calibration. Various thermostats are used for adjusting the column temperature. The chromatographic column is located in a vartical tube, down or up which air is drown at about 50 ft/sec by a high speed radial fan.

The linear programmed temperature thermostat is an electrical resistant heater having the rates from 0.5 to 30°C/min., in the temperature range of 22-400°C.

3. Introduction of the Sample: For liquid samples the most convenient method of introducing the sample is by micro-syrings. Another method is crushing a sealed ampoule in a chamber in the carrier gas supply. For gaseous samples the usual technique is the displacement of a known volume from a calibrated chamber by the carrier gas.

4. Katharometers are the most commonly used detectors, and it is regarded as the standard against the other detectors. In theory, thermal detection systems are based on the principals that each gas has its own individual thermal energy transfer characteristic and metal filament thermisters have fixed resistance temperature relationships. The Katharometer is simply a Wheatstone bridge with two equal resistances and while the third resistance is inserted through a pure carrier gas channel, the fourth resistance is placed in the channel through which the gas mixture from the column passes. The difference in thermal conductivities of the two gas streams results an out-of-balance potential which can be amplified and recorded on a chart. Other detectors are flame ionization detector, the argon - ray and the gas discharge tube.

7.3.1. Qualitative Gas Chromatographic Analysis of Crude Oil:

Garzan Crude Oil is paraffinic in base, so in chromatograms n-paraffins are remarkable by their large peaks of systematic appearance and order. Hence, the n-paraffinic peaks can conveniently be used as a guiding principle and as a criterion for the estimation and identification of other hydrocarbons. It is however, necessary to identify the correct n-C number of the first n-paraffin on the chromatogram. Such estimation is facilitated by the case of n-C_6 for precipitation of asphaltenes in surplus. Although most of the n-C_6 is being removed afterwards by fractional distillation, sufficient quantity is left to indicate the n-C_6 peak in prominence to the other ones, thereby setting a clear indication for the number sequence of the higher n-hydrocarbons.

In case of any uncertainty a check could be and has been carried out by injection of pure n-paraffins together with the sample, into the column.

The substances other than n-paraffins were identified by a calculus method based on the equation. (3)

$$(RT) = Ax(BP)^m \qquad (7)$$

$$\log(RT) = \log A + m \log (BP) \qquad (8)$$

This equation is applied between two n-paraffins of increasing carbon numbers i.e., the constants A and m are calculated for each intersection between two neighbouring n-paraffins. All the peaks of hydrocarbons falling between the two limits indicated by the n-paraffins are then identified by using their (RT) values in the above equation while calculating the respective (BP) values. The calculated (BP) values are compared to known (BP) values of hydrocarbons in literature (14). These values falling next to the known (BP) values are likely to represent the hydrocarbons searched for.

These calculations can be carried out by using a F Fortran lV computer programme which is presented in Appendix B.

7.3.2. Quantitative Gas Chromatographic Analysis of Crude Oil.

The area of each peak, which is produced on the chromatogram, is proportional to that substance's concentration in weight percentages, and this can be used to determine the exact concentration of each peak.

In this work the planimetric method was used to determine the relative amounts of the ingredients in Garzan Crude Oil. The planimeter is an instrument which measures area of a curve by tracing the perimeter manually. It is in accuracy ± 0.02.

For other qualitative and quantitative methods for evaluation of gas chromatograms consult Appendix: C.

8. EXPERIMENTAL PROCEDURE:

8.1. Dewatering of Garzan Crude Oil:

Garzan Crude Oil whose properties are presented in Table 14, in Appendix A, was kept in a separatory funnel over night, for the separation of water. As there was no visible water separated it was then treated with $CaCl_2$ for the removal of any remaining moisture content.

8.2. Deasphalting of Crude Oil with n-Hexane:

The asphaltenes must be removed to prevent the clogging of the tube of the Gas Chromatograph which would be used in the later course of the experiments. In order to remove the asphaltenes measured volumes of dewatered crude oil was mixed with n-hexane in the volumetric ratio of Garzan Crude Oil to n-hexane 1:4. The composition of the n-hexane used in this study was analyzed by gas chromatography. The chromatogram is shown in Figure No.1 on the following page. The results of the qualitative and quantitative analysis are shown in the following Table No: 1. The technical n-C_6 contains appreciable amounts of close boiling isomers.

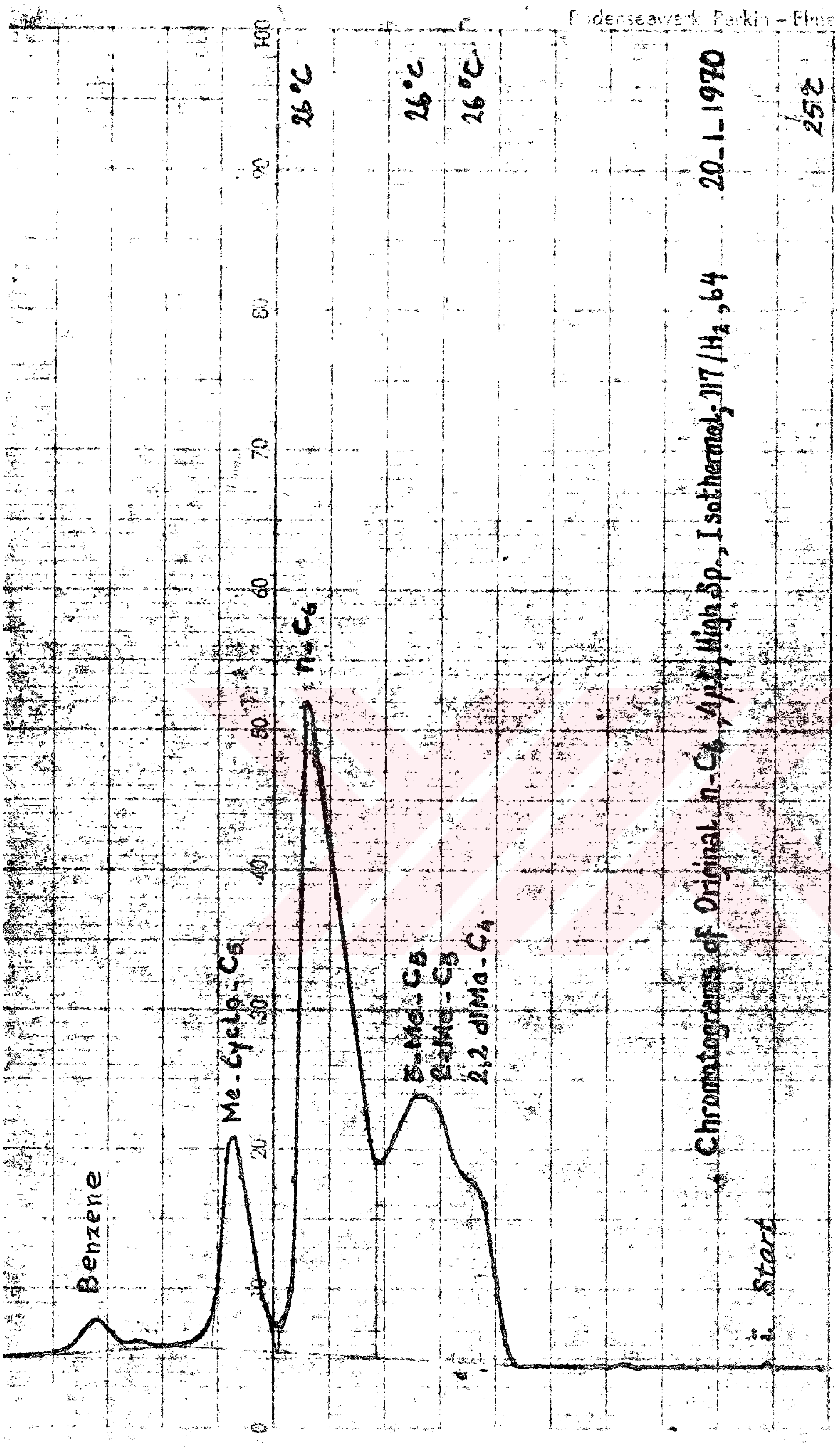


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Figure 1. Chromatogram of original n-C_6 used.

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It is well known that propane, n-pentane, n-hexane when used in large quantities are precipitating asphaltenes in crude oils. The quantitiy of the precipitate of asphaltenes increases by the decrease in the molecular weight of the precipitant. In this respect liquified n-propane was expected to be the efficient precipitant, but it is highly volatile and it is very difficult to handle liquified propane. On the other hand, n-pentane would have been the most suitable one; due to its low boiling point removal of n-pentane would have been easy without interfering the composition of the crude oil. However it was not available in large quantities and, hence, n-hexane- n-C_6, which was available in plenty, had been used for the purpose. Its precipitation power is practically not very different than that of n-pentane, and, its boiling point, 68°C, is still sufficiently low not to interfere the composition of the lower boiling components of the crude oil significantly. n-Heptane was also available, but it was difficult to separate from the crude oil without significant changes in the composition due to its high boiling point, 78 °C .

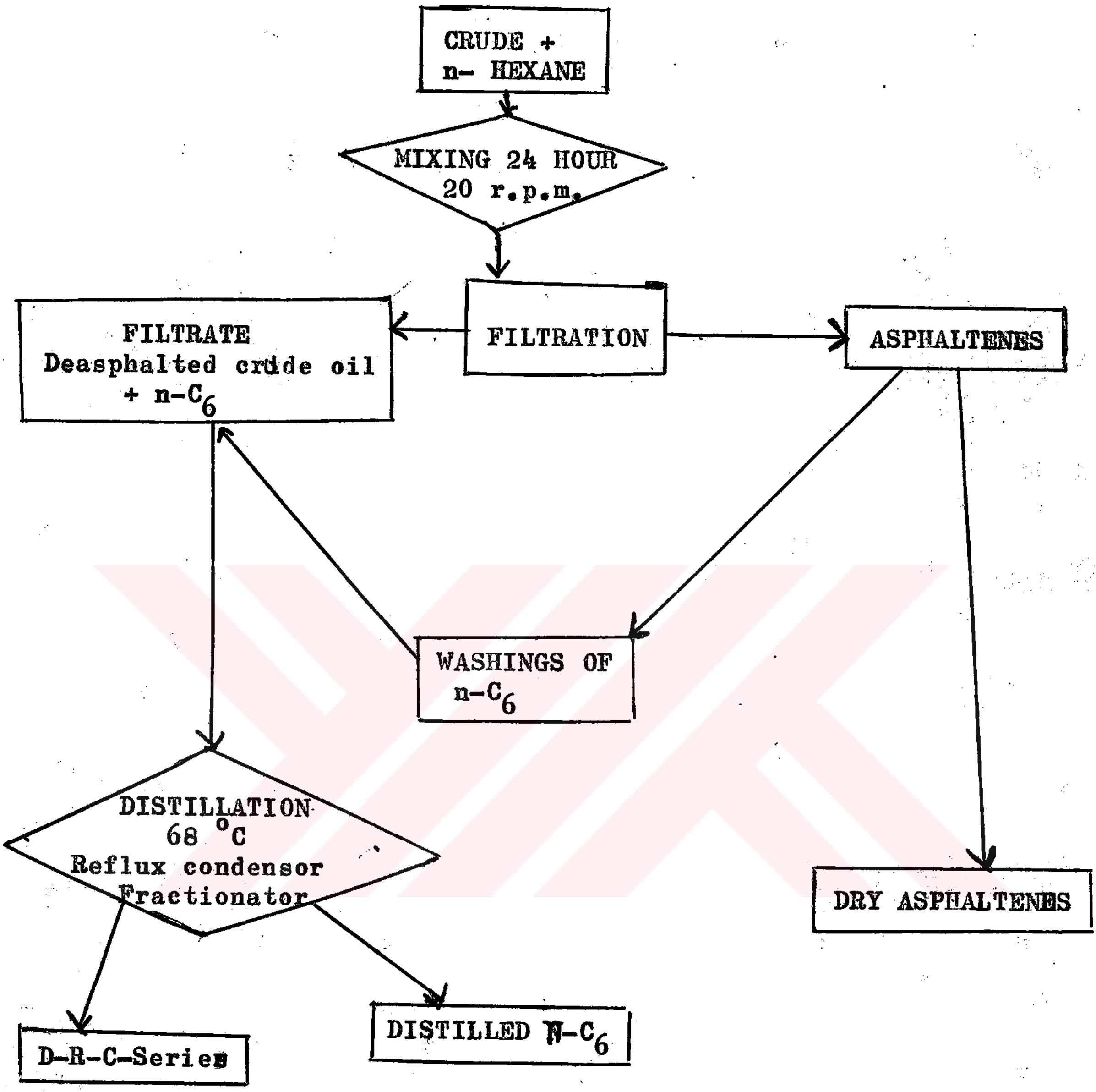
The mixtures of Crude Oil plus n-hexane were left a stand for settling. Then the top layers were filtered through an ordinary filter paper, a small residue remained on the filter paper. The main residues which remained in the settling flasks were washed with fresh n-hexane until they became completely free from oil and after a short settling time, the n-hexane, used for washing, was as well filtered through the same filter paper.

wereby the precipitate which had accumulated on the filter paper was also washed. Finally the total precipitate from the flasks was taken onto the filter paper and washed completely dry until the filtrate became colorless. The filtration was carried out through a closed system to avoid the evaporation of n-hexane.

The dry asphaltenes, after being held in a drying oven at about 100°C for one hour, was weighed to determine the asphaltenes content. See Table No: 10 in Appendix A.

FIGURE - 2

BLOCK DIAGRAM OF EXPERIMENTAL PROCEDURE OF PREPARATION OF REDUCED CRUDE OIL.



8.3. Removal of Surplus n-Hexane From Deasphalted Crude Oil.

The additional amount of $n\text{-}C_6$ for washing had increased the volumetric ratio of reduced crude oil to $n\text{-}C_6$ to 1:22.6. In order to prepare different ratios of reduced crude oil to $n\text{-}C_6$, batch-wise distillations to different extents were carried out.

Measured volumes of samples of the reduced crude oil ratio of 1:22.6 were taken into a two liter distillation flask with a thermometer attached, to measure and observe the temperature of the liquid, which was heated by a mantle. A short fractionation column of 14 cm height, internal diameter of 5 cm., filled with Berl Saddles, and isolated by glass wool was attached to the distillation flask. At the end of the column a thermometer was placed to determine the temperature of the vapors before condensation. The vapors were cooled by a Liebig Cooler, the distillates were measured in a calibrated receiver. The temperature of the liquid was raised by 5 °C/min., and the distillation was performed at a liquid temperature of 68°C, which correspondend to a vapor temperature of 62°C. Under these conditions only $n\text{-}C_6$ and a few negligible volatile hydrocarbons were distilled while the distillation rate of 40 drops of distillate per minute was maintained. The apparatus is shown in Fig. 3 on the following page.

This procedure was used to obtain six samples having different ratios of reduced crude oil to n-hexane. The naming and compositions of these samples are presented

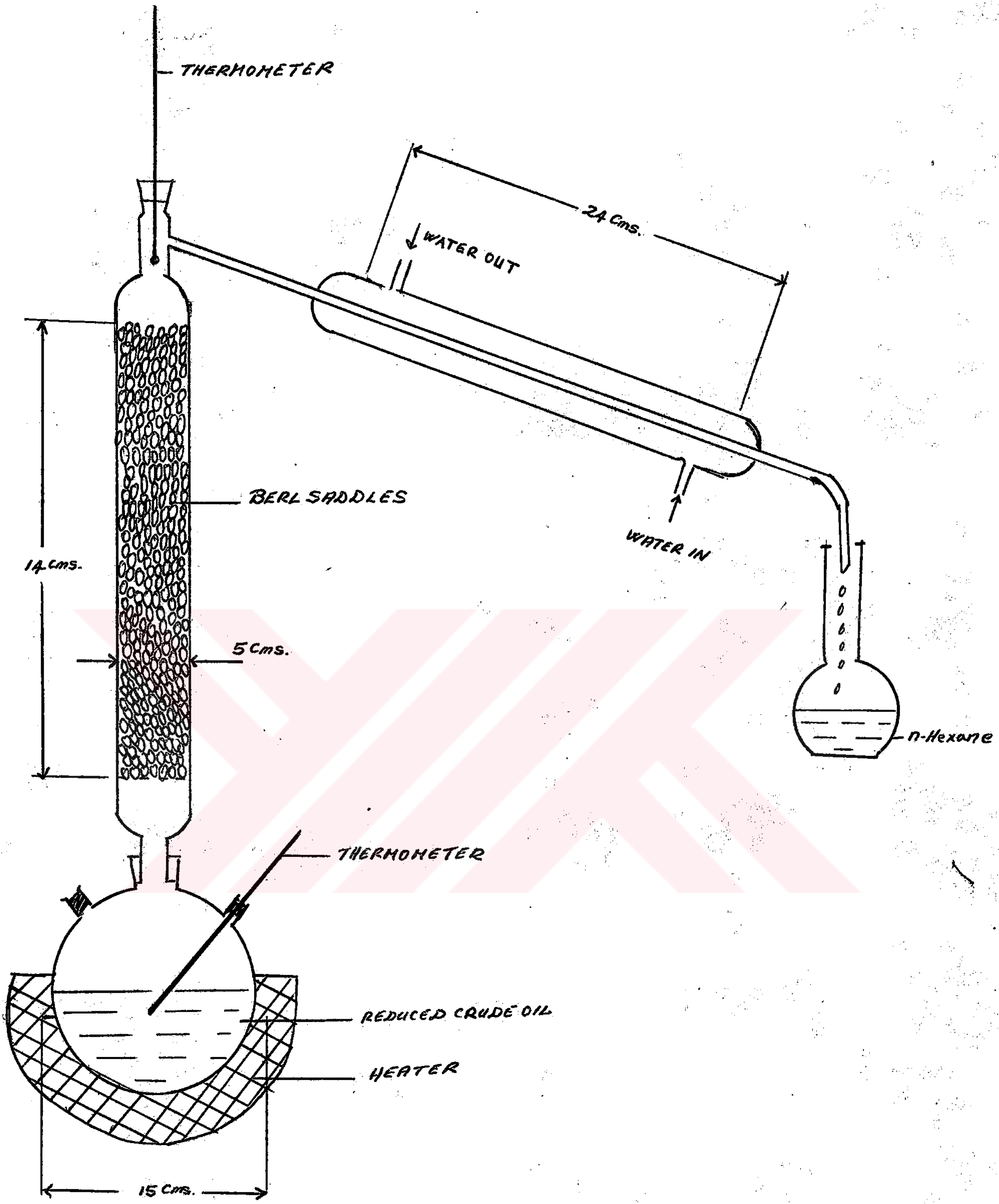


FIG. 3. SET - UP FOR THE DISTILLATION OF n-HEXANE FROM THE REDUCED CRUDE OIL

in the following Table. 3.

TABLE . 3. NAMES AND COMPOSITIONS OF SAMPLES OF REDUCED CRUDE OIL.

Notation of Samples	Amount taken from the Origional Sample to Distill Excess n-C_6 (ml.)	Oil without Asphaltenes in the samples, ml.	n-C_6 Distilled off ml.	n-C_6 Remain in the Samples, ml.	Reduced Crude Oi Ratio to n-C_6
D-R-C-1-1-22.6-1	Main Sample				
D-R-C-2-1-7-1	1300	56.4.	850	393.6.	1:7
D-R-C-3-1-4-1	1300	56.4	1015	228.6	1:4
D-R-C-4-1-0.935-1	500	21.2	459	19.8	1:0.93
D-R-C-5-1-0.685-1	1300	56.4	1205	38.6	1:0.68
D-R-C-6-1-0.650-1	500	21.2	465	13.8	1:0650

One of these samples having the ratio of reduced crude oil to n-C_6 to 1:0.935 and the distilled n-hexane were analyzed by gas chromatography. The chromatograms of the reduced crude oil Figure 8 and Figure 9 are presented in Section 9.3.

The chromatogram of the distilled n-hexane is presented on next page Fig: 4 and the compounds present in the distillate and their composition are given in the following Table 4.

Tables 1 and 4 are compared in Section 9.1.

TABLE 4. QUALITATIVE AND QUANTITATIVE ANALYSIS OF THE DISTILLED n-HEXANE

Name of Compounds	Relative Quantities	Weight Percents
2,2-DiMe-C_4	0.22	8.94
2-Me-C_5	0.72	29.26
3-Me-C_5		
n-C_6	1.22	49.61
Me-Cyclo-C_5	0.25	10.16
Benzene	0.05	2.03
Total	2.46	100.00

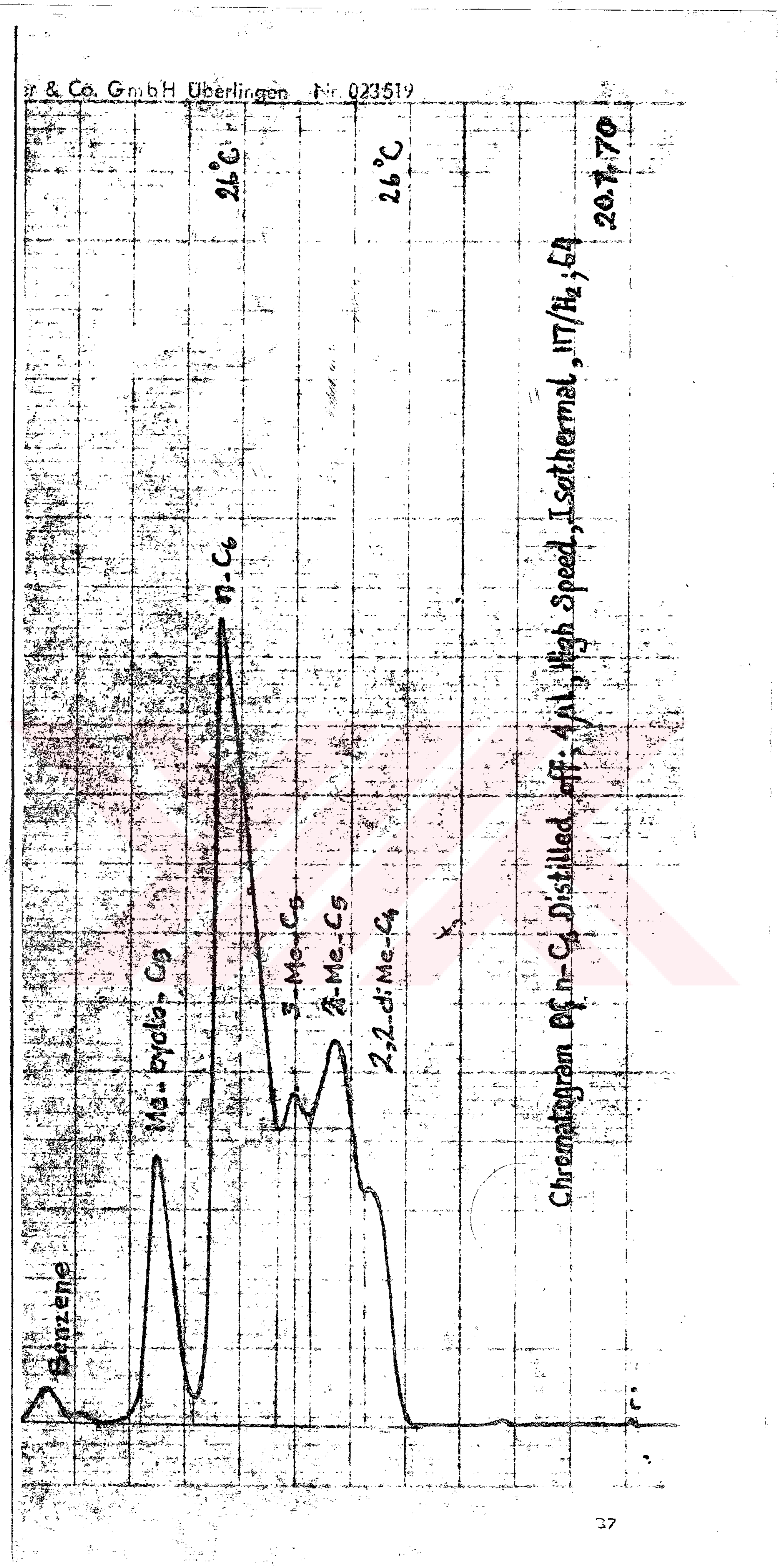


Figure 4. Chromatogram of distilled n-C_6

8.4. Preparation of Three Component Mixtures of Crude Oil, n-Hexane, Acetone.

Measured volumes of dewatered acetone (by $CaCl_2$ treatment) were mixed with different volumes of reduced crude oil samples and origional crude oil. Altogether twenty one of such mixtures have been prepared; of those fifteen were prepared from reduced crude oil with different n-C_6 content, and, six were prepared from origional crude oil. Details about these samples are given in Table: 5 on next page.

Their composition was estimated after the samples had been kept standing for one month in order to be sure of having reached a steady state. They are represented in the triangular Gibb's Diagram of Figure 7 in Section 9.2.

The representation of different mixtures in the triangular diagram, of Figure 7, shows only mixtures having no or little n-C_6 content produce a rather solid precipitate. With increasing amount of n-C_6 no more a solid precipitate is obtained but two nonmiscible liquids have formed. As the precipitates, obtained by addition of acetone to origional crude oil seemed to be paraffinic or waxy, these preparations appeared to be the most desirable with regard to the aim of the study. See also Section 9.2. Hence out of 21 samples only two were taken for a detailed investigation, which had the crude oil to acetone ratios of 1:1 and 1:4.

Further treatments of these samples are shown in

Table 5. SAMPLES PREPARED FOR TRIANGULAR DIAGRAM REPRESENTATION

Naming of Samples	Red Crude Oil taken from Sample	R.C.O* taken (ml)	Acetone added (ml)	FRACTIONS Reduced Crude n-C_6; Acetone	Oil
D-R-C-At-1-1-22.6-23.6-1	D-R-C-1-1-22.6-1	50	50	2.12;47.88;50.00	
D-R-C-At-2-1-7-8-1	D-R-C-2-1-7-1	25	25	6.24;43.76;50.00	
D-R-C-At-3-1-7-39.6-1		5	25	2.10;14.60;83.40	
D-R-C-At-4-1-4-5-1	D-R-C-3-1-4-1	25	25	10.00;40.00;50.00	
D-R-C-At-5-1-4-12.5-1		10	25	5.70;22.80;71.50	
D-R-C-at-6-1-4-25.3-1		5	25	3.30;13.30;83.40	
D-R-C-At-7-1-0.935-0.65-1	D-R-C-4-1-0.935-1	15	5	38.50;36.50;25.00	
D-R-C-At-8-1-0.935-1.29-1		12	8	31.00;29.00;40.00	
D-R-C-At-9-1-0.935-1.71-1		9	8	27.40;25.60;47.00	
D-R-C-At-10-1-0.685-1.69-1	D-R-C-5-1-0,685-1	25	25	29.60;20.40;50.00	
D-R-C-At-11-1-0.685-4.25-1		10	25	16.80;11.70;71.50	
D-R-C-At-12-1-0.685-8.42-1		5	25	9.90;6.76; 83.40	
D-R-C-At-13-1-0.685-5.6-1		15	5	4.46;30.40;25.00	
D-R-C-At-14-1-o.650-0.824-1	D-R-C-6-1-0.650-1	10	5	40.40;26.30;33.30	
D-R-C-At-15-1-0.650-2.48-1		10	15	24.20;1580;60.00	
S A M P L E S	Original Crude Oil	O.C.O (ml)	Acetone added (ml)	Crude Oil/Acetone	
D-C-At-16-1-1-1	Original Crude Oil	5	5	50.00 ; 50.00	l
D-C-At-17-1-4-1		5	20	20.00 ; 80.00	p
D-C-At-18-1-0.578-1		10	5	63.30 ; 36.60	m
D-C-At-19-1-0.21-1		10	2	83.30 ; 16.70	m
D-C-At-20-1-0.4-1		10	4	71.40 ; 28.60	m
D-C-At-21-1-0.754-1		5	3.8	57.00 ; 43.00	l

m: complete miscibility

p: precipitate formed

l: nonmiscible two liquid layers

*: Reduced crude oil

Figures 5, 6 in this Section and described below:

As there was not a clear separation between the two layers of sample having the ratio 1:1, centrifugation for the sufficiently satisfactory separation of the two layers ~~for~~ was required as an initial step. The upper liquid layer was taken out by means of a pipette. The remaining thick bottom layer was then treated with n-C_6 for the removal of asphaltenes. Then asphaltenes were washed with excess n-C_6 as described in Section 8.2.

The sample of ratio 1:4, showed a better separation; thus the upper layer was separated by decantation through a filter paper, and the precipitate was washed with acetone. The washings were kept separate. The residue was deasphalted by n-C_6 treatment as described in Section 8.2.

The filtrate and the residue dissolved in n-C_6 from sample of ratio 1:1 were analysed by gas chromatography. The chromatogram of the filtrate Figure 10, and, that of the residue Figure 11 were qualitatively evaluated. They showed an obvious enrichment of lower n-paraffins in the filtrate and of higher n-paraffins in the residue. These chromatograms were presented in Section 9.3.

The sample of ratio 1:4 was containing very little amount of origional crude oil when compared with the volume of acetone added, thus the filtrate layer and the residue (soluble in n-C_6) layer were too diluted with acetone and n-C_6 to be analysed by gaz chromatography. The investigation for this ratio was left to the larger sample as decribed in section 8.5. The washings of the residue of above sample were also not investigated because they were in negligible amounts.

FIGURE 5

BLOCK DIAGRAM OF PREPARATION OF SAMPLES CRUDE OIL TO ACETONE RATIO 1:1

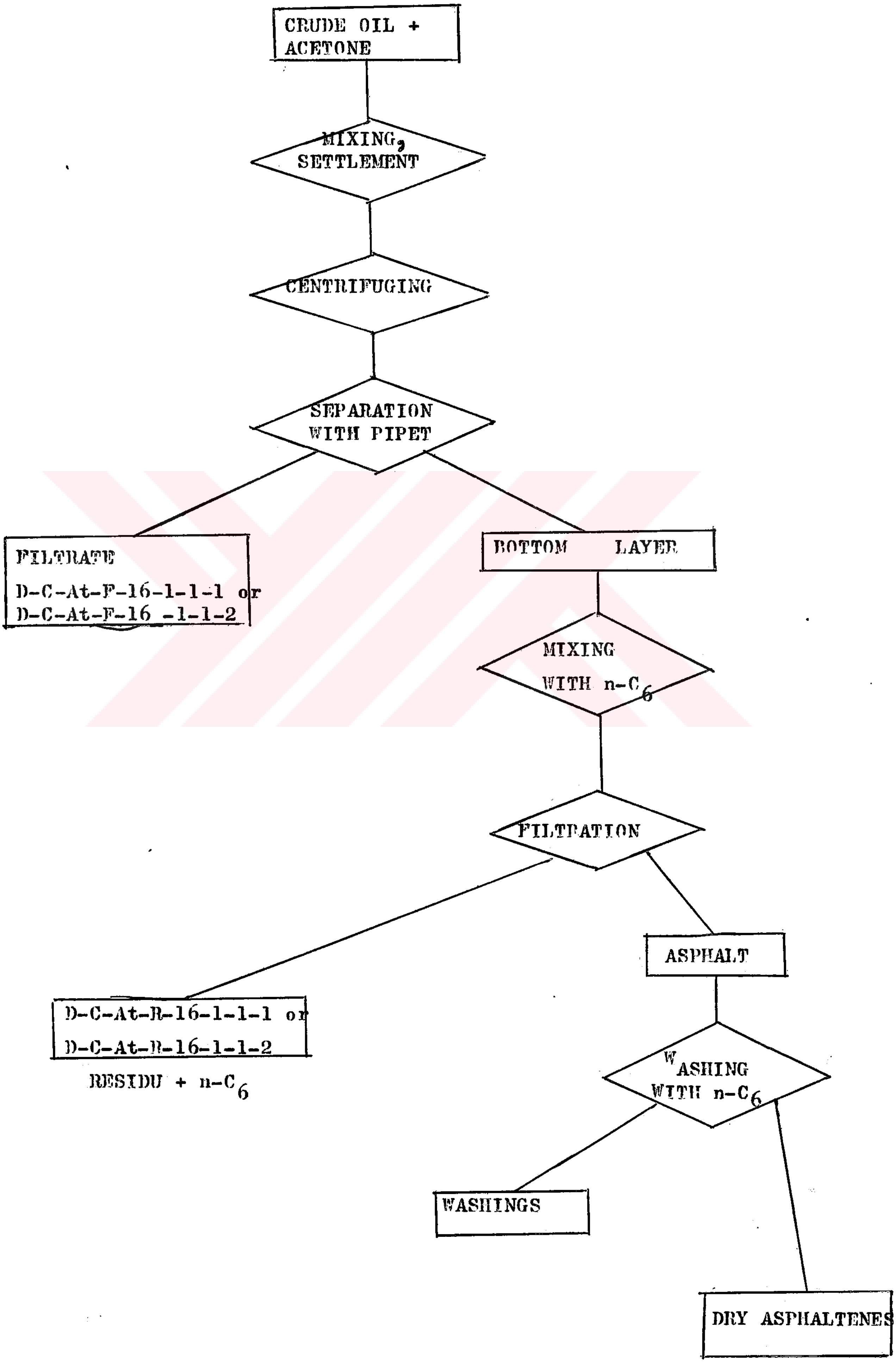
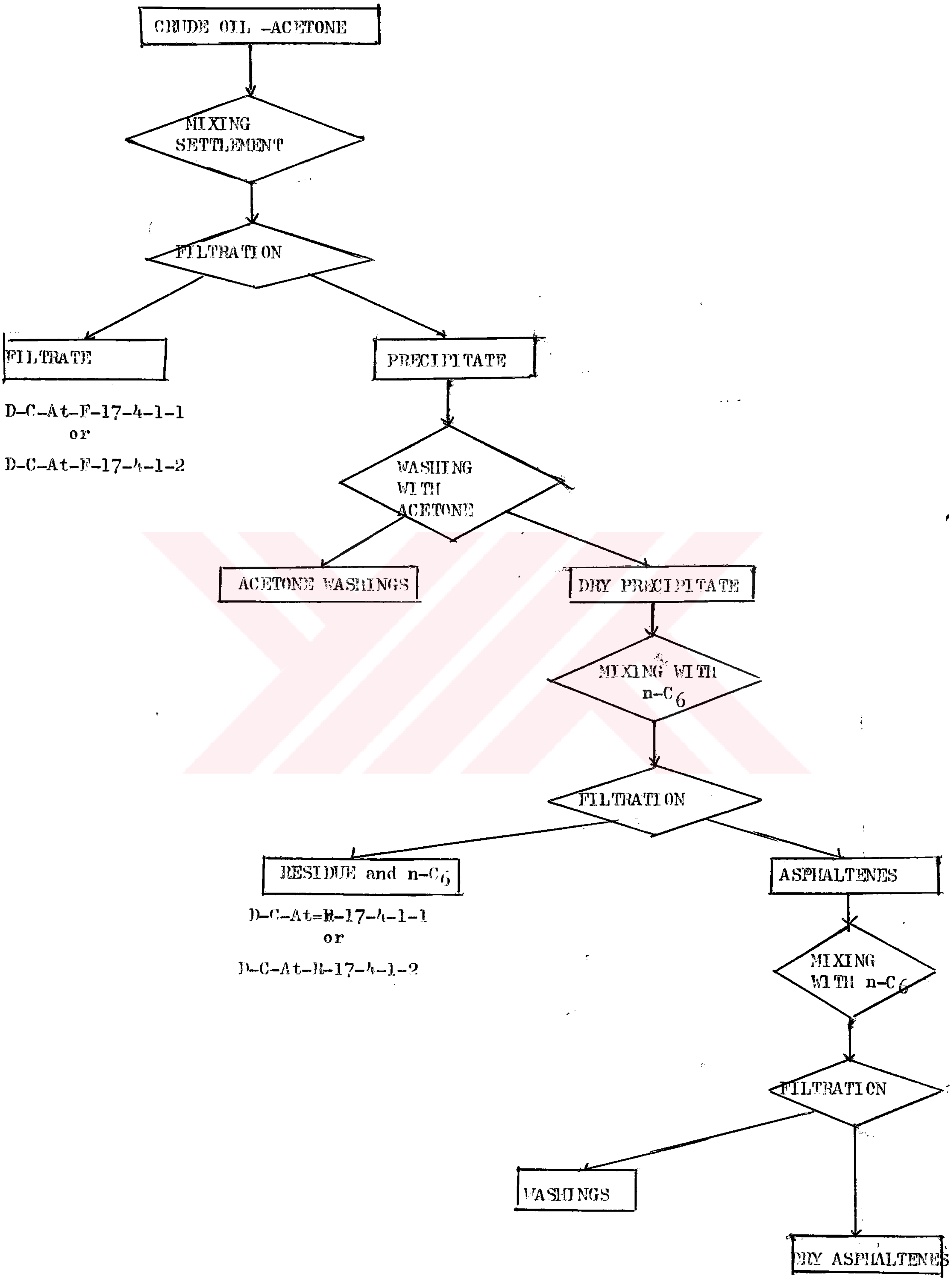


FIGURE -6

BLOCK DIAGRAM OF PREPARATION OF SAMPLES', CRUDE OIL TO ACETONE RATIO 1 : 4



8.5. Treatment of Garzan Crude Oil-Acetone Mixtures for Quantitative Separation Investigation:

A more precise quantitative investigation of the enrichment and separation of n-paraffins could be accomplished by preparing the two samples, of ratios of crude oil to acetone, 1:1 and 1:4 respectively, in larger quantities. The mixtures were separated into the filtrate (acetone rich) and residue (soluble in n-C_6) layers by following the same procedure as has just been described in section 8.4 and presented in Figures 5 and 6 on previous pages. Each respective part was accurately weighed. The fraction of crude oil soluble in acetone and the remaining fraction dissolved in n-C_6 were taken as Yield Factors. See Table: 10, in Appendix A.

The filtrate and residue layers of both samples were analyzed by gas chromatography and the corresponding chromatograms Figures 12, 13, 14, and 15 are presented in Section 9.3. The results of qualitative evaluation of the respective chromatograms are presnted in Table 6, in the same Section, while the quantitative determainations of n-paraffins are prsented in Tables 7 and 8 in Section 9.4.1.

The amount of hydrocarbons which were in the washings were considered to be negligible when compared with the amount of residue layer. Hence they were not taken into further considerations. See Table: 10 in Appendix A.

9. RESULTS AND DISCUSSION

9.1. Separation of Asphaltenes:

In such an investigation, the first step was the separation of asphaltenes, to avoid the clogging of the tubes of gas chromatography. In the earlier work (1), it had already been determined that the lowest aimed ratio of crude oil to n-hexane should be 1:4. This ratio was employed in this investigation. Comparison of Tables 1 and 4 in Section 8.2-3; the analysis of origional n-hexane and that of the distilled n-hexane shows that the treatment of tthe crude oil with n-hexane was not resulting a significant change in the origional composition of the crude oil. Asphaltenes content was pound to be 13.3.wt.%

9.2. Triangular Diagram Representation of Crude Oil, n-Hexane and Acetone Mixtures:

In this Gibbs' Diagram Figure 7 on next page, it was observed that the area of producing a solid precipitate was very small and limited within the region of low n-hexane content. With increasing the content of n-C_6 no more precipitate obtained, but rather two non miscible liquids, in the area on the Triangular diagram, shown by dotted lines. Beyond this region with ever increasing n-C_6 content only a uniform liquid was obtained without any separation any more. Although the precipitate after acetone tratment appeared to be mainly paraffinic, still some other components, most probably resine, were co-precipitated for which to rather nasty nature of the precipitate could be accounted.

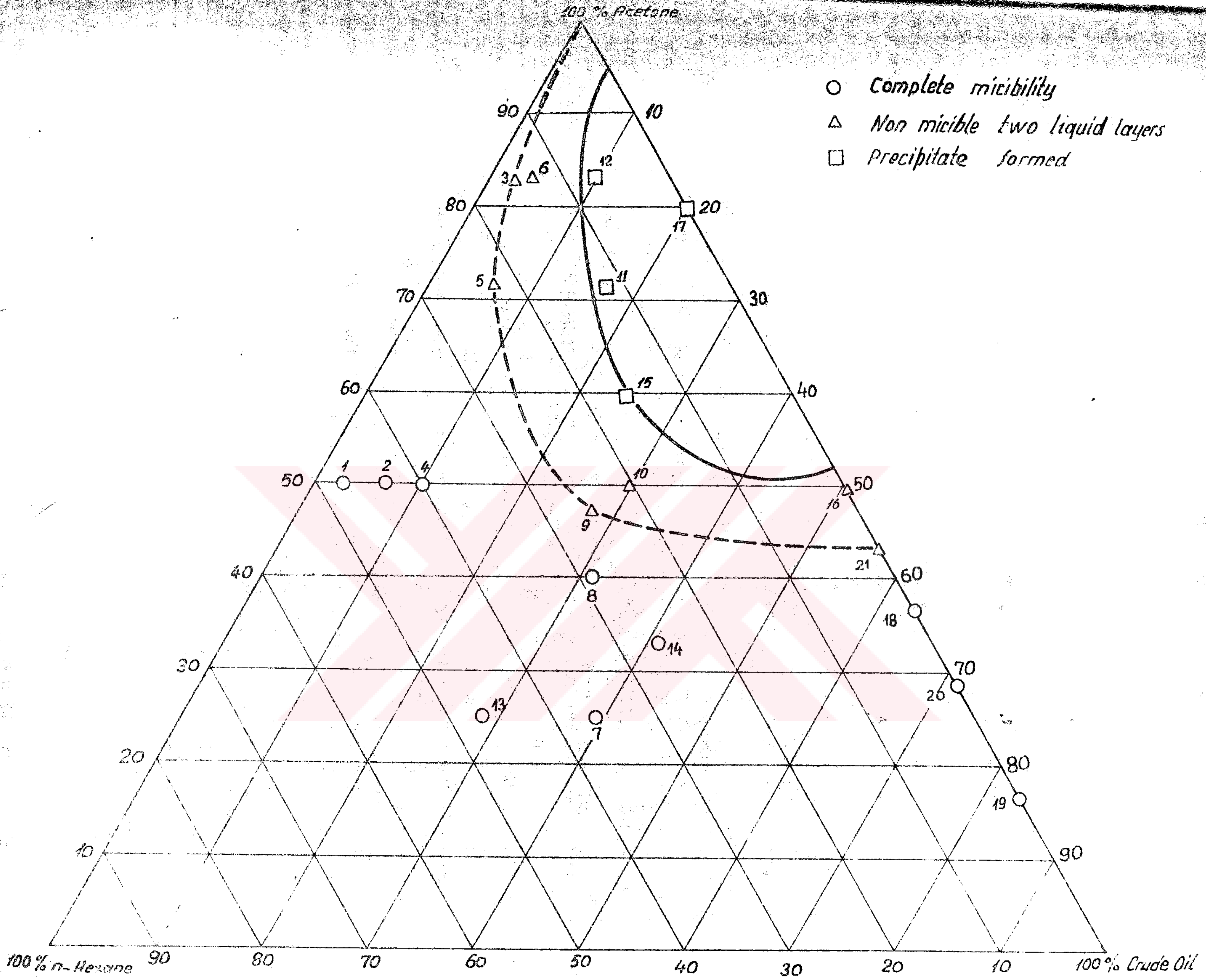


FIG. 7 Gibb's Triangular Representation Diagram.

9.3. Results of Qualitative Analysis of Origional Reduced Crude Oil, and Qualitative Comparison of the Peaks of n-Paraffins on the Chromatograms of the Crude Oil Fractions:

For the identification of hydrocarbons in reduced crude oil a proper chromatogram is required. In the first chromatogram, Figured 8, there is some uncertainty within the range of peaks 5 to 10 due to frequent change in attenuation. The second chromatogram of reduced crude oil, Fig 9, represents a proper composition and it is taken as base for the calculation and identification.

The peaks which appear on the chromatograms of the filtrates and residues of the acetone treated crude oil are identical with these on Figure 9, but besides the normal paraffins they are not all used for identification. Some of the peaks of the low boiling components have changed retention times, due to the surplus of n-C_6 and acetone.

As a result, by using Equation 8, and taking the results of Figure 9 into consideration, 132 hydrocarbons, 24 of which are n-paraffins, could be identified. Almost all of them are in agreement with earlier investigations. The list of the identified hydrocarbons is given in Table 6, on the following pages.

Comparison of Figures 10 and 11, which are the chromatograms of the filtrate and the residue of the acetone treated crude oil in 1:1 ratio, shows an enrichment of lower n-paraffins in the filtrate, while an enrichment of higher n-paraffins is found in the residue. This is also found when comparing chromatograms of, Figures 12 and 13, of the filtrate and the residue of the larger sample in ratio 1:1. It is, however no more so well marked in Figures 14 and 15 of the filtrate and residue of the larger sample in ratio 1:4. This result seems to be due to the excess amount of acetone used in this case, and the limited solubility of n-paraffins in acetone.

All the chromatograms are presented at the end of this section.

After having observed this differentiation rather qualitatively, these chromatograms, together with the yield factors in Table 10, in Appendix A, were evaluated quantitatively.

TABLE 6.

Presentation of the Identified Components in Reduced Garzan Crude Oil.

g.hyd.: guiding hydrocarbon ; m.l : most likely ; l ; likely

No.	No of Peaks	HYDROCARBONS	B.P, °C	B.Pc, °C	Conclusion
1	3	n-C_6	68.740	68.740	g.hyd.
2	4	Me-cyclo-C_5	71.812	75.49	m.l.
3	5	2,2-di-Me-C_5	79.197	78.19	l.
4	5a	Benzene	80.15	79.65	l.
5	6	2,4-di-Me-C_5	80.51	83.91	l.
6	6	Cyclo-C_6	80.738	83.91	l.
7	6	2,2,3-tri-Me-C_4	80.882	83.91	l.
8	6a	3-3-di-Me-C_5	86.064	86.97	m.l.
9	7	2,3-di-Me-C_5	89.784	89.69	m.l.
10	8	3-Ethyl-C_5	93.475	92.94	l.
11	9	n-C_7	98.427	98.427	g.hyd.
12	10/11	Ethyl-cyclo-C_5	103.466	104.09	l.
13	10/11	1,1,3-tri-Me-cyclo-C_5	106.84	107.440	l.

No.	No. of peaks	HYDROCARBONS	B.P, ^{o}C	B.Pc, ^{o}C	conclusion
14	12	2,2-di-Me-C_6	106.84	107.440	l.
15	13	Toluene	110.62	110.719	m.l.
16	14	2,3,4-tri-Me-C_5	113.467	112.976	l.
17	15	1,cis-2,tr.-4-tri-Me-cyclo-C_5	116.731	116.910	m.l.
18.	16	3-Me-3-Ethyl-C_5	118.259	118.396	m.l.
19.	16	3-Ethyl-C_6	118.534	118.396	l.
20	17	1-Me-1-Ethyl-cyclo-C_5	121.522	122.022	l.
21	17	2,2,4,4-tetra-Me-C_5	122.284	122.022	m.l.
22	18	n-C_8	125.665	125.665	g.hyd.
23	18a	2,3,5-tri-Me-C_6	131.34	131.61	l.
24	18a	Ethyl-cyclo-C_6	131.83	131.61	m.l.
25	19/20	2,2,3,3-tetra-Me-C_5	133.016	133.132	m.l.
26	19/20	2,4-di-Me-C_7	133.5	133.132	l.
27	21	1,1,3-tri-Me-cyclo-C_6	137.138	137.155	l.
28	21	3,3-di-Me-C_7	137.3	137.155	m.l.
29	22	m-Xylene	139.09	139.798	l.
30	22	cis,1,3,5-tri-Me-cyclo-C_6	140.05	139.798	l.
31	23	4-Me-C_8	142.48	142.544	m.l.
32	23	1-i-propyl-2-Me-cyclo-C_5	142.5	142.544	m.l.
33	23	3-Ethyl-C_7	143.0	142.544	l.

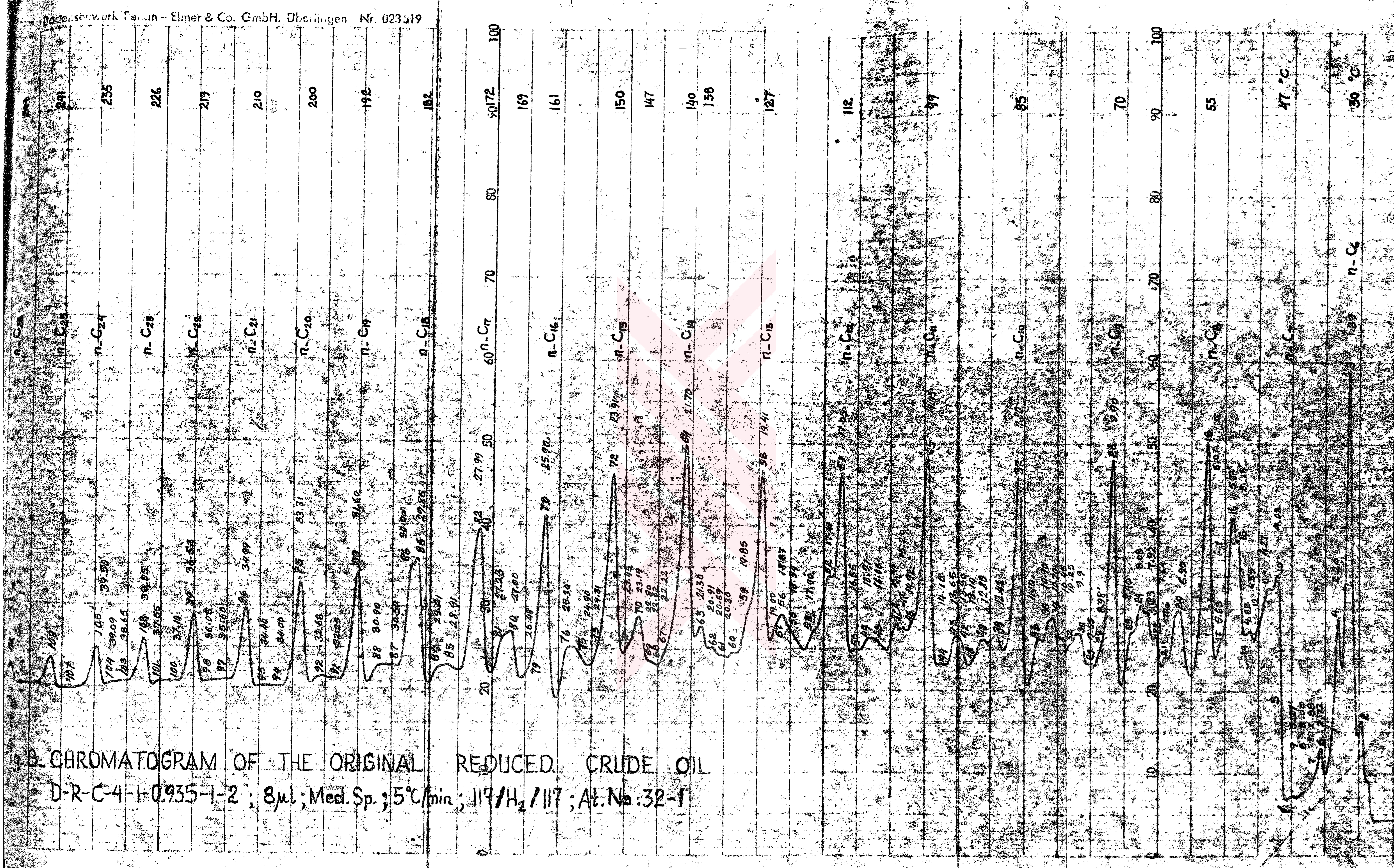
No.	No. of peaks	HYDROCARBONS	B.P, °C	B.Pc, °C	Conclusion
34	24	2-Me-C_8	143.26	143.797	l.
35	24	3-Me-C_8	144.18	143.797	l.
36	25	3-3-di-Ethyl-C_5	146.168	146.079	m.l.
37	26	n-C_9	150.81	150.81	g.hyd.
38	27	i-Propyl-cyclo-C_6	154.5	154.21	m.l.
39	29	n-Butyl-cyclo-C_5	156.56	156.797	m.l.
40	29	n-Propyl-cyclo-C_6	156.724	156.797	m.l.
41	30	2,2,3,4,4-penta-Me-C_5	159.29	159.336	l.
42	30	n-Propyl-Benz.	159.31	159.336	m.l.
43	32	4,5-di-Me-C_8	162	161.910	l.
44	32	3-4-di-Ethyl-C_6	162	161.910	l.
45	32	4-n-Propyl-C_7	162	161.910	l.
46	33	3-Me-3-Ethyl-C_7	163.8	163.595	l.
47	34	4-Me-C_9	165.7	166.001	l.
48	34	2-Me-3-Ethyl-C_7	166	166.001	l.
49	34	3,4-di-Me-C_8	166	166.001	l.
50	34	2,2,3,3,4-penta-Me-C_5	166.1	166.001	m.l.
51	35	2,Me-C_9	166.8	167.12	l.
52	35	d-l-i-Propyl-3-Me-cyclo-C_5	167	167.12	l.
53	35	3-Ethyl-4-Me-C_7	167	167.12	l.

No.	No.of peaks	HYDROCARBONS	B.P.°C	B.Pc.°C	Conclusio
54	35	4-Ethyl-3-Me-C_7	167	167.12	1.
55	35	4-Ethyl-4-Me-C_7	167	167.12	1.
56	36	tert.-Butyl-Benz.	169.1	169.33	m.1.
57	36	1,2,4-tri-Me-Benz.	169.4	169.33	m.1.
58	37	n-C_{10}	174.123	174.123	g.hyd.
59	38	1-Me-2n-Propyl-cyclo-C_6	175.5-6.	175.753	1.
60	39	n-Pentyl-cyclo-C_5	180	179.721	m.1.
61	40	1-Me-3-n-Propyl-Benz.	181.8	182.453	1.
62.	40	n-Butyl-Benz.	183.27	182.453	1.
63	41	1-Me-2-n-Propyl-Benz.	184.8	184.818	m.1.
64	42	3-Me-2-Phenyl-C_4	188	188.029	m.1.
65	43	1-3-di-Me-4-Ethyl-Benz.	188.4	188.902	1.
66	43	3-tert.-Butyl-1-Me-Benz.	189.3	188.902	1.
67	44	4-tert.-Butyl-1-Me-Benz.	192.8	192.817	m.1.
68	44	i-amyl-cyclo-C_6	193	192.817	1.
69	44	1-Ethyl-2-i-Propyl-Benz.	193	192.817	1.
70	44	2-Phenyl-C_5	193	192.817	1.
71	45	n-C_{11}	195.89	195.89	g.hyd.
72	46	1-3-di-Me-4-i-Propyl-Benz.	199.1	199.353	m.1.
73	46	3-Me-Indene	199.2-200	199.353	m.1.

No.	no. of peaks	HYDROCARBONS	B.P, °C	B.Pc, °C	Conclusion
74	47	1,2-di-Me-4-i-Propyl-Benz.	201.8	201.772	m.l.
75	48	2,5-di-Ethyl-1-Me-Benz.	207.1	207.433	l.
76	48	Tetralene	207.6	207.433	l.
77	48	1,3-di-Ethyl-2-Propyl-Benz.	207.6	207.433	l.
78	48a	1,2-di-Me-4-n-Propyl-Benz.	208.9	209.292	l.
79	48a	1,3-di-Me-5-n-Propyl-Benz.	209	209.292	l.
80	48a	2-Me-3-Propyl-Benz.	209	209.292	l.
81	50	3-Ethyl-4-i-Propyl-1-Me-Benz.	213	213.205	l.
82	50	5-Ethyl-1,2,4-tri-Me-Benz.	213	213.205	l.
83	50	6-Ethyl-1,2,4-tri-Me-Benz.	213	213.205	l.
84	50	1,10-di-Me-tr.-deca-hydro-napht	213	213.205	l.
85	51	n-C_{12}	216.278	216.278	g.hyd.
86	52	1-Me-1,2,3,4-tetra-hydro-napht	219	219.325	m.l.
87	53	1-Me-3-n-Pentyl-Benz.	223	222.908	m.l.
88	54	3-Me-3-Phenyl-C_6	226	226.209	l.
89	54	n-Hexyl-Benz.	226.1	226.209	m.l.
90	54	3-Phenyl-C_7	227	226.209	l.
91	55	2,6-di-i-Propyl-1-Me-Benz.	228	228.364	l.
92	55	5-n-Propyl-1-2-4-tri-Me-Benz.	228	228.364	l.
93	56	2,2-di-Me-1,2,3,4-tetra-hydro-napht.	230	230.188	l.

No.	No. of peaks	HYDROCARBONS	B.P, °C	B.Pc, °C	Conclusion
94	58	n-C_{13}	235.44	235.44	g.hyd.
95	59	1,4-di-sec.-Butyl-Benz.	239	238.99	l.
96	59	1,5-di-Me-1,2,3,4-tetra-hydro-napht	239	238.99	l.
97	59	3-Ethyl-3-Phenyl-C_6	239	238.99	l.
98	60	5-Ethyl-2,2,3,4-tetra-hydro napht	242	242.038	m.l.
99	61	a-Me-Naphtalene	244.8	245.174	l.
100	64	n-C_{14}	253.57	253.57	g.hyd.
101	67	B-Ethyl-Napht	257.9	258.01	l.
102	68/69	2-7-di-Me-Napht	262	262.260	l.
103	68/69	n-nonyl-cyclo-C_5	262	262.260	l.
104	70	2,3-di-Me-Napht,	265-6	264.748	l.
105	72	n-C_{15}	270.63	270.63	g.hyd.
106.	73	2-n-Propyl-Napht	273.5	273.981	l.
107	74	1-n-Propyl-Napht.	277	274.714	l.
108	75	Acenaphtheno	278	278.850	l.
109	75	n-decyl-cyclo-C_5	279.3	278.850	l.
110	76	n-nonyl-cyclo-C_6	282	281.267	l.
111	76	1-i-Propyl-7-Me-Napht.	282	281.267	l.
112	76	n-nonyl-Benz.	282	281.267	l.
113	78	n-C_{16}	286.793	286.793	g.hyd.

no.	No. of peaks	HYDROCARBONS	B.P, °C	B.Pc, °C	Conclusion
114	79	1-n-Butyl-Napht.	289.34	290.898	1.
115	80	Flourene	293.5	294.666	1.
116	81	n-undecyl-cyclo-C_5	296	296.307	1.
117	82	n-C_{17}	301.82	301.82	g.hyd.
118	83	2-n-Pentyl-Napht.	310	309.392	1.
119	84	2-Me-C_{17}	311	311.365	1.
120	85	n-C_{18}	316.12	316.12	g.hyd.
121	87	1-n-Hexyl-Napht.	322	322.298	1.
122	88	2-n-Hexyl-Napht.	324	325.405	1.
123	89	n-C_{19}	329.7	329.7	g.hyd.
124	91	Phenyl-Napht.	336.5	335.548	1.
125	93	n-C_{20}	342.7	342.7.	g.hyd.
126	96	n-C_{21}	356.5	356.5	g.hyd.
127	97	1,1-di-Naphtyl-Me	360 >	361.404	1.
128	99	n-C_{22}	368.8	368.8	g.hyd.
129	102	n-C_{23}	380.2	380.2	g.hyd.
130m	103	Pyrene	385	384.312	1.
131	104	1-decyl-Napht.	387	387.598	1.
132	105	n-C_{24}	391.3	391.3	g.hyd.



4.B. CHROMATOGRAM OF THE ORIGINAL REDUCED CRUDE OIL

D-R-C-4-1-0.935-1-2 ; 8μl ; Med. Sp. ; 5°C/min ; 117/H$_2$/117 ; At. No: 32-1

-55- -55

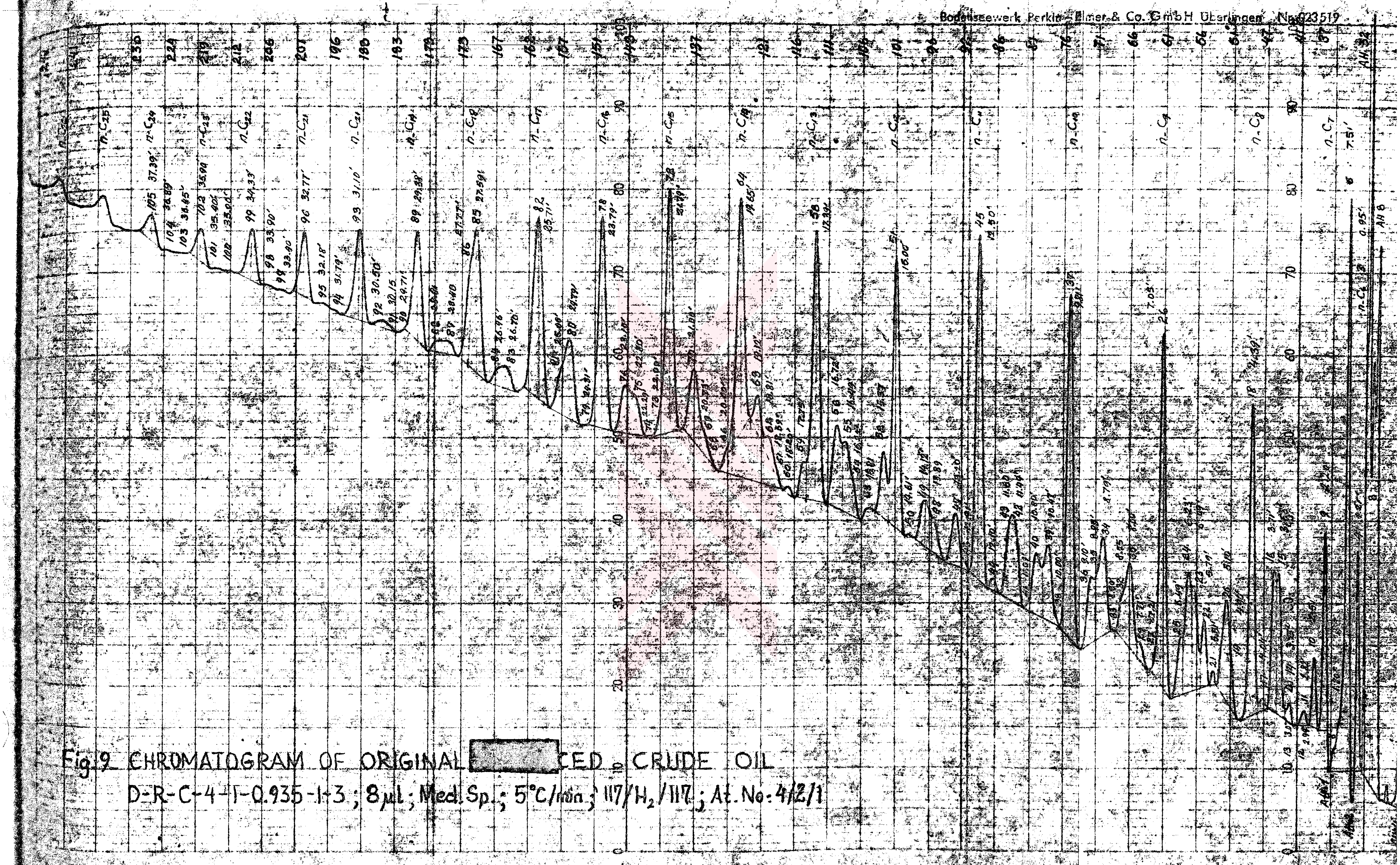


Fig. 9 CHROMATOGRAM OF ORIGINAL [redacted] CED CRUDE OIL
D-R-C-4-1-0.935-1-3; 8 μl; Med. Sp.; 5°C/min.; 117/H_2/117; At. No: 4/2/1

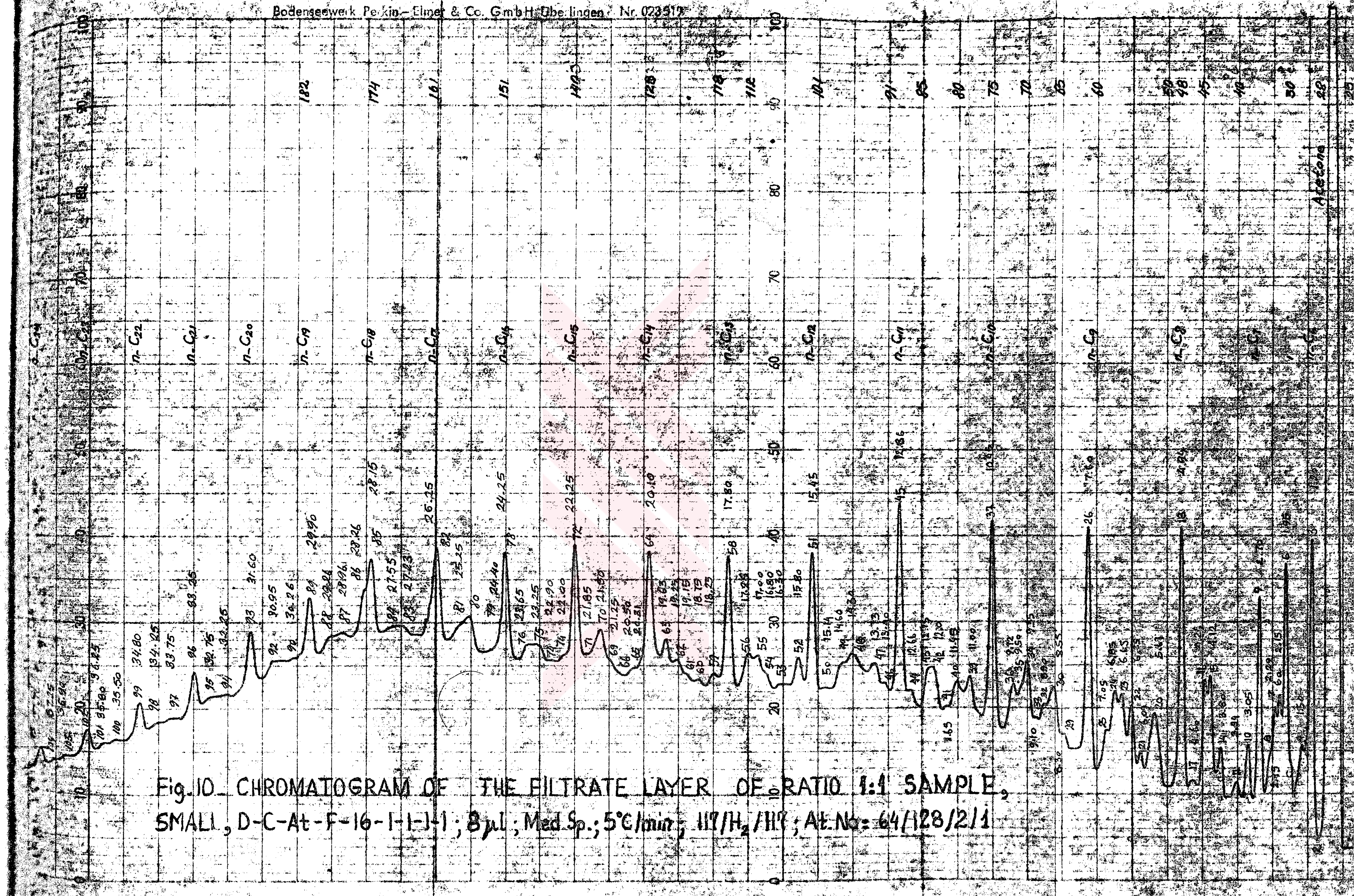


Fig. 10 CHROMATOGRAM OF THE FILTRATE LAYER OF RATIO 1:1 SAMPLE, SMALL, D-C-At-F-16-1-1-1-1; 8 µl; Med. Sp.; 5°C/min; 117/H_2/117; At. No: 64/128/2/1

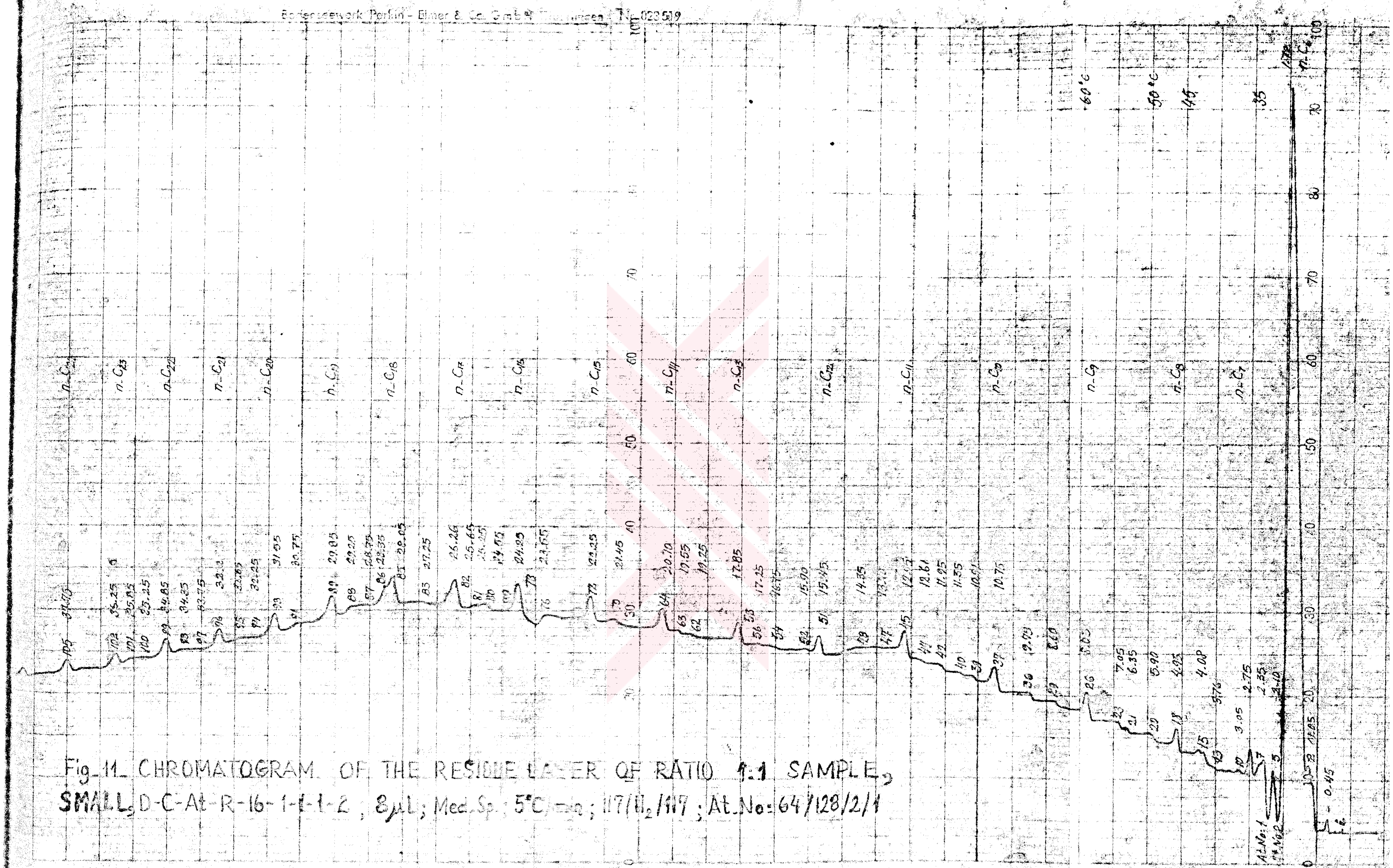


Fig-11. CHROMATOGRAM OF THE RESIDUE LAYER OF RATIO 1:1 SAMPLE, SMALL, D-C-At-R-16-1-1-1-2, 8µL; Med. Sp.: 5°C/min; 117/H₂/117; At. No: 64/128/2/1

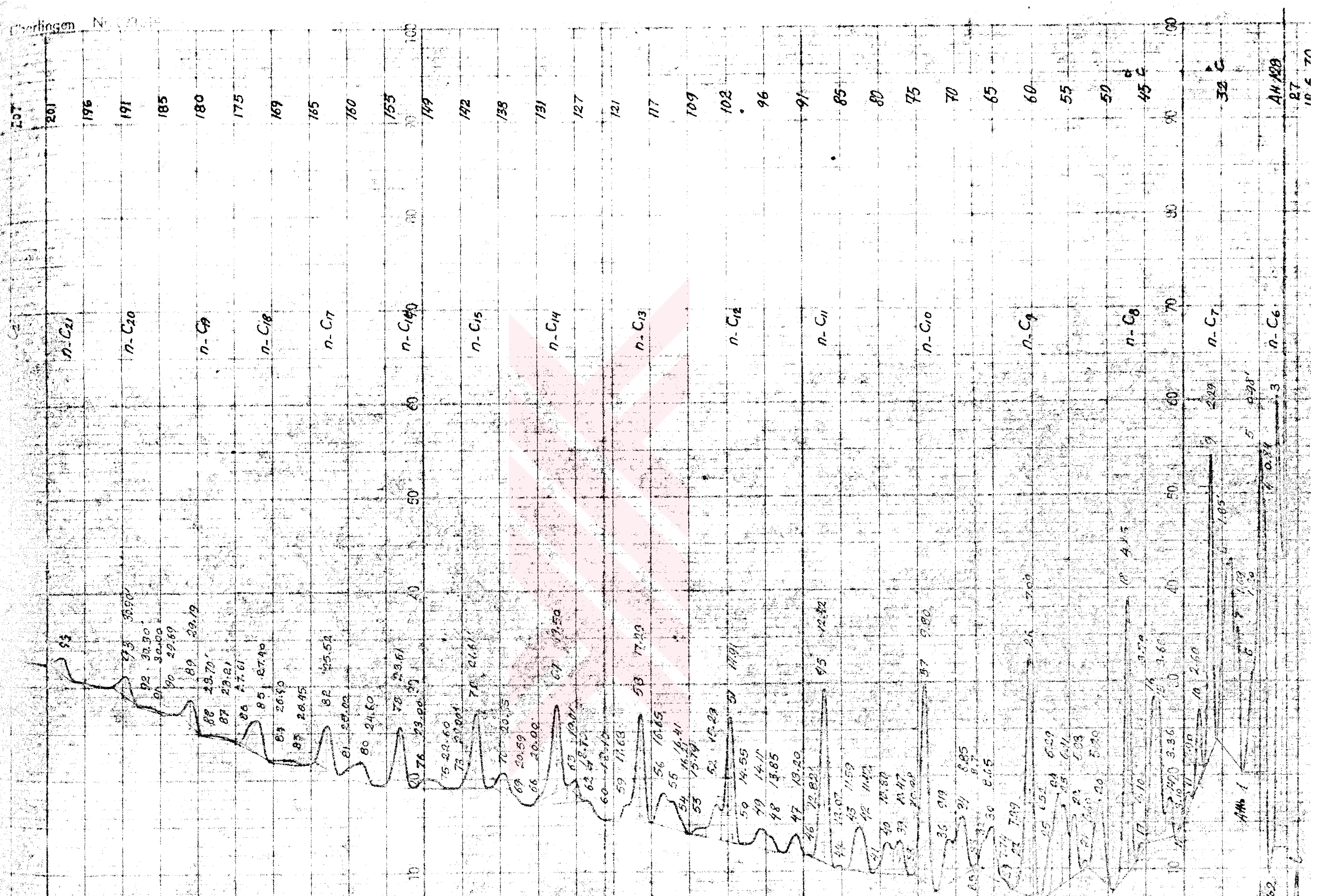


Fig. 12. CHROMATOGRAM OF FILTRATE LAYER OF RATIO 1:1 SAMPLE, LARGER, D C-At-F-16-1-1-2-2; 8 μl; Med. Sp; 5°C/min; 117/H₂/117; At. No: 4/129/2/1

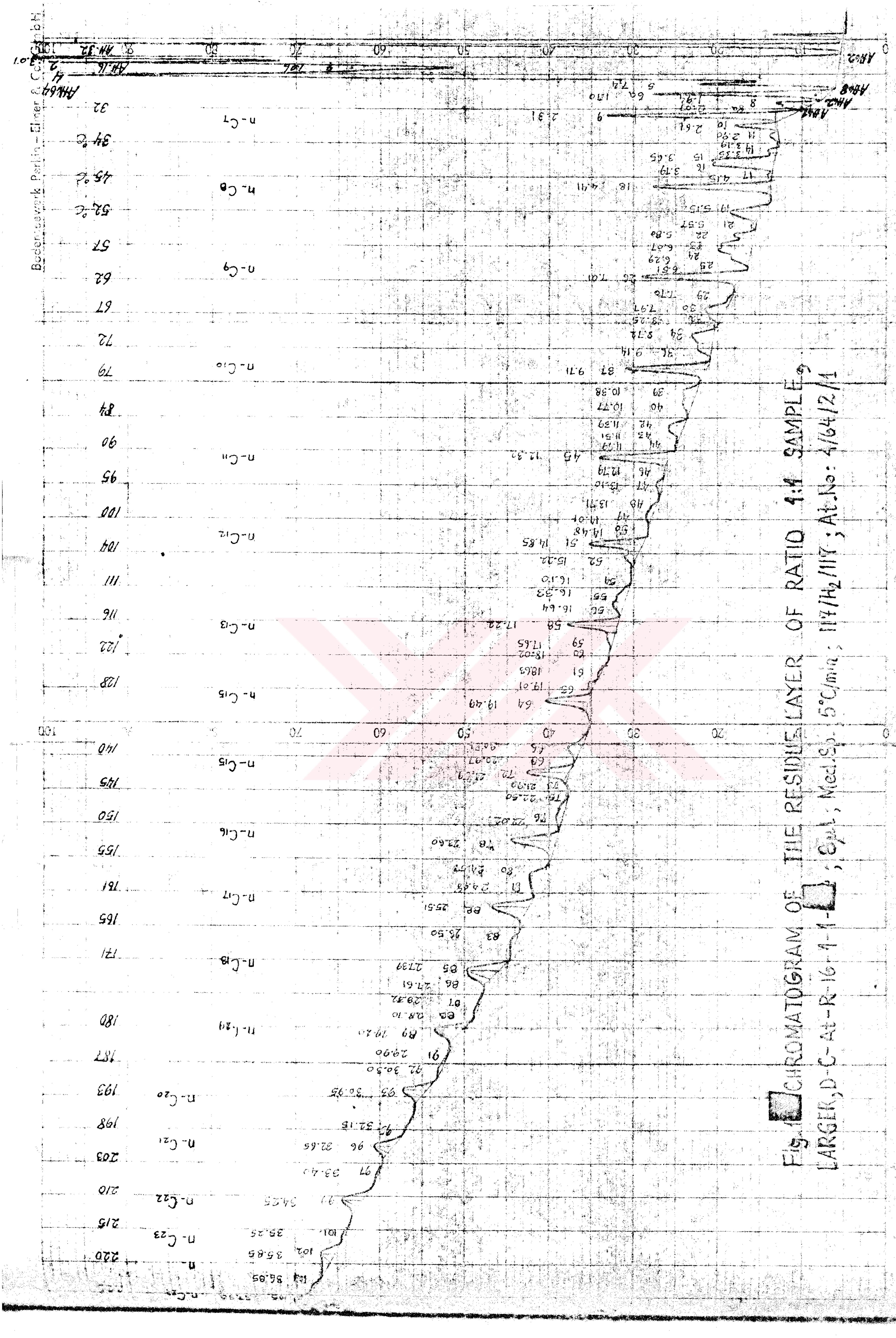


Fig. [redacted] CHROMATOGRAM OF THE RESIDUE LAYER OF RATIO 1:1 SAMPLE 9

LARGER, D-C-At-R-16-1-1-[redacted]; 8μL; Med.Sp.; 5°C/min; 117/H_2/117; At.No: 4/64/12/1

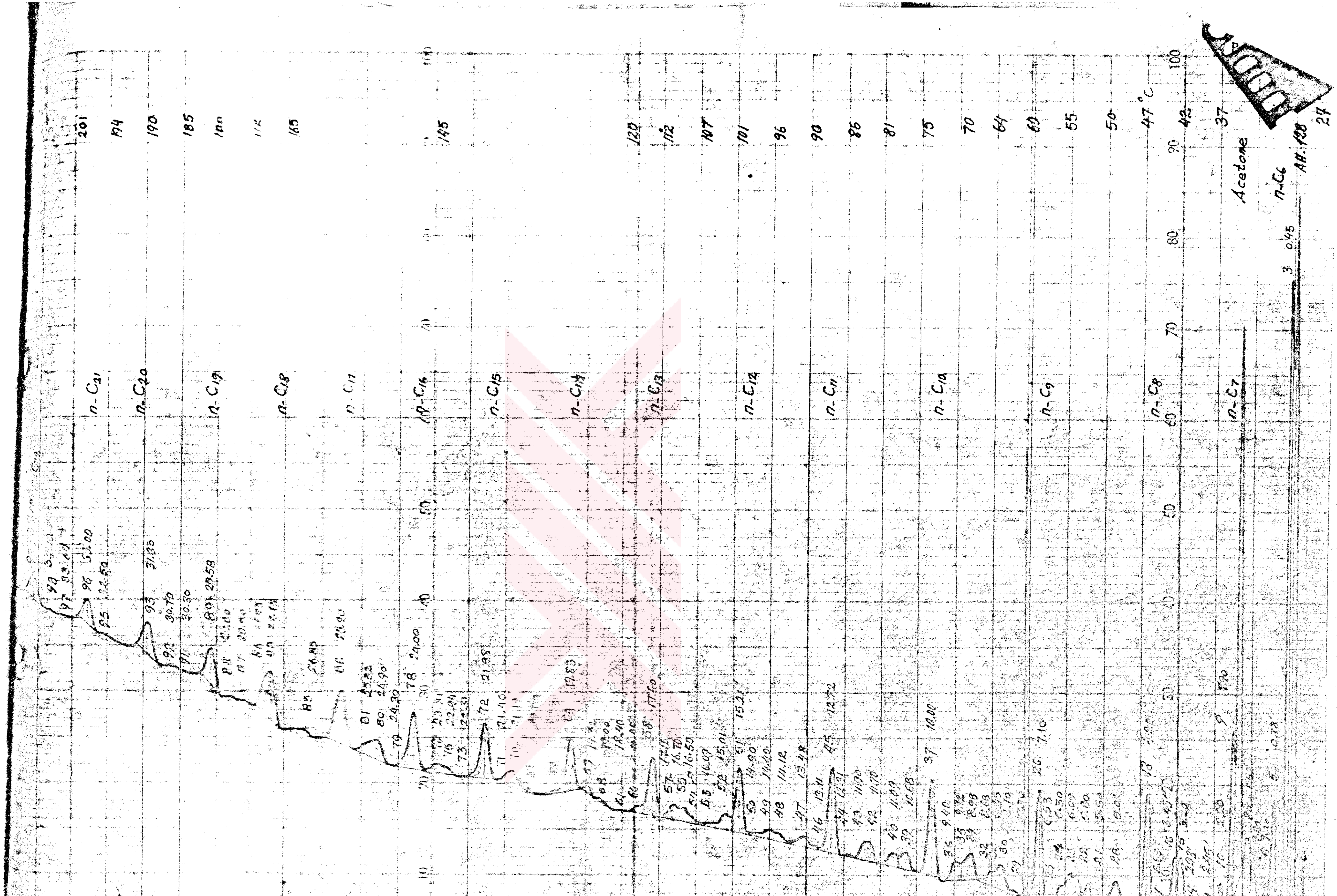


Fig.14 - CHROMATOGRAM OF FILTRATE OF RATIO 1:4 SAMPLE, LARGER,D-C-AL-F-17-1-4-2-1; 8µl; [illegible] 6p; 5°/min; [illegible]

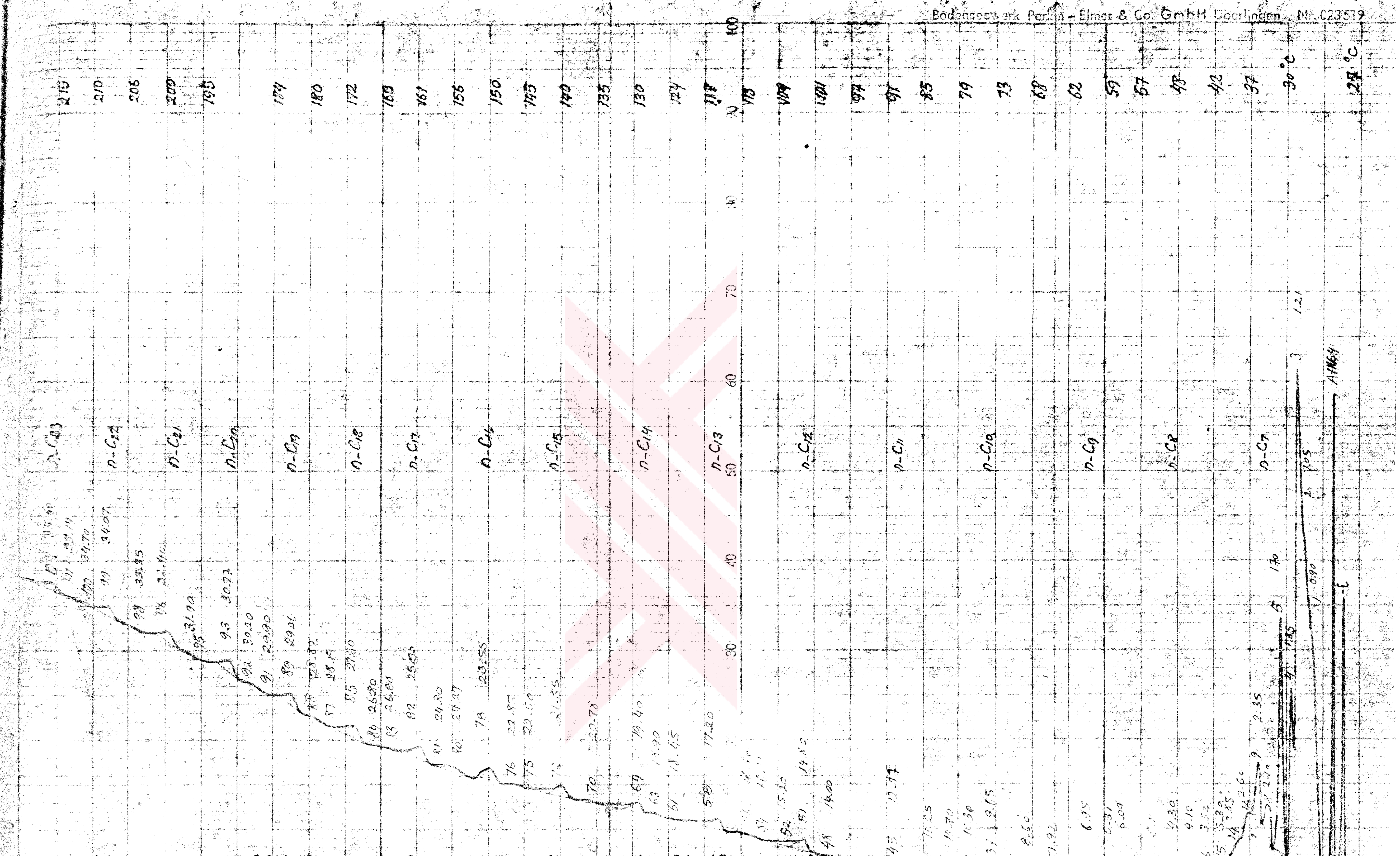


Fig. 15. CHROMATOGRAM OF RESIDUE OF RATIO 1:4 SAMPLE,
LARGER D-C-AL-R-17-1-4-2-1½; 8 µL; Med. Sp.: 5°C/min; 117/11; 117; At. No: 4/10/2/11

9.4. Results of Quantitative Analysis

9.4.1. Distribution of n-paraffins in Reduced Garzan Crude Oil:

Determination of peak areas on chromatograms, Figures 9,12,13,14 and 15, was made by planimetric measurements. From the measured relative values the weight percentages of n-paraffins and their absolute quantities, in the origional reduced crude oil and in the filtrate and residue layers of acetone treated samples, were calculated. The results are presented in Tables 7 and 8 on following pages. The quantities of n-paraffins in each sample, in terms of Mols are presented in Table 11, in the Appendix A.

The distibution curves of n-paraffins in the crude oil, showed a distinct pattern having two maxima, the first one at n-C_{10} and the second one at n-C_{14} and perhaps the trace of the third one at n-C_{17}. This finding was in agreement with the distribution of n-paraffins in Garzan Crude Oil found by O.Ansen (1) and T.Gür (6). This distribution pattern appeared due to the genesis of Garzan Crude Oil, in whish the break down of fatty acids had taken place. The fatty acids might have been present earlier and they broke down in an unknown way, hence, resulting this Dual-Maximum distribution. See Figures : 16 and 17 on the following pages.

This typical distribution stayed almost preserved in the filtrate fractions of the acetone treatment while the first maximum was much increased and the second one was much decreased. In the residue fractions, from the origional redistribution the first maximum has completely disappeared.

TABLE 7. QUANTITATIVE DETERMINATIONS OF n-PARAFFINS IN THE ORIGINAL REDUCED CRUDE OIL AND IN THE FILTRATE AND RESIDUE LAYERS OF SAMPLE; RATIO OF CRUDE OIL TO ACETONE: 1:1

n-PARAFFINS	B.P. (°C)	RELATIVE VALUES			WEIGHT PERCENTS			Wt. % x YIELD FACTORS		SUM OF ACTUAL Wt. in FILTRATE AND RESIDUE	Wt. % SEPARATION OF EACH n-PARAFFIN		Wt. % INCREASE in FILTRATE
		in ORIGINAL	in FILTRATE	in RESIDUE	in ORIGINAL	in FILTRATE	in RESIDUE	ABSOLUTE Wt. in FILTRATE (.544)	ABSOLUTE Wt. in RESIDUE (.456)		in FILTRATE	in RESIDUE	
n-C_7	98.43	0.40	0.24	0.10	3.50	4.30	3.28	2.34	1.50	3.84	61.0	39.0	+ 22.0
n-C_8	125.66	0.52	0.32	0.12	4.55	5.75	3.94	3.13	1.79	4.92	63.6	36.4	+ 27.2
n-C_9	150.81	0.52	0.35	0.11	4.89	6.29	3.61	3.42	1.65	5.07	67.5	32.5	+ 35.0
n-C_{10}	174.12	0.59	0.34	0.11	5.16	6.11	3.61	3.32	1.65	4.97	66.6	33.4	+ 33.2
n-C_{11}	195.89	0.52	0.28	0.12	4.55	5.03	3.94	2.74	1.80	4.54	60.4	39.6	+ 20.8
n-C_{12}	216.28	0.42	0.20	0.10	3.67	3.59	3.28	1.96	1.46	3.42	57.4	42.6	+ 14.8
n-C_{13}	235.44	0.45	0.19	0.12	3.93	3.48	3.94	1.89	1.79	3.68	51.5	48.5	+ 3.0
n-C_{14}	253.57	0.51	0.22	0.16	4.46	3.95	5.24	2.15	2.39	4.54	47.4	52.6	- 5.8
n-C_{15}	270.34	0.48	0.20	0.14	4.20	3.58	4.60	1.95	2.09	4.04	48.3	51.7	- 3.4
n-C_{16}	286.79	0.45	0.18	0.13	3.93	3.23	4.26	1.76	1.95	3.71	47.5	52.5	- 5.0
n-C_{17}	301.82	0.42	0.16	0.13	3.67	2.92	4.26	1.58	1.95	3.53	44.8	55.2	- 10.4
n-C_{18}	316.12	0.36	0.12	0.12	3.14	2.15	3.61	1.17	1.65	2.81	41.6	58.4	- 16.8
n-C_{19}	329.7	0.25	0.07	0.09	2.19	1.26	2.96	0.68	1.35	2.03	33.5	66.5	- 33.0
n-C_{20}	342.7	0.19	0.05	0.07	1.66	0.90	2.30	0.49	1.05	1.54	31.8	68.2	- 36.4
n-C_{21}	356.5	0.15	0.04	0.06	1.31	0.72	1.97	0.39	0.90	1.29	30.2	69.8	- 39.6
n-C_{22}	368.6	0.10	0.02	0.06	0.88	0.36	1.97	0.20	0.90	1.10	18.2	81.8	- 63.6
n-C_{23}	380.2	0.08	0.02	0.04	0.70	0.36	1.31	0.20	0.60	0.80	25.0	75.0	- 50.0
n-C_{24}	391.3	0.07	0.00	0.05	0.61	0.00	1.64	0.00	0.75	0.75	0.0	100.0	- 100.0
Other Compounds		4.89	2.36	1.22									
TOTAL		11.41	5.57	3.05									

TABLE 8. QUANTITATIVE DETERMINATIONS OF n-PARAFFINS IN THE ORIGINAL REDUCED CRUDE OIL AND IN THE FILTRATE AND RESIDUE LAYERS OF SAMPLE RATIO OF CRUDE OIL TO ACETONE: 1/4

n-PARAFFINS	B.P. (°C)	RELATIVE VALUES			WEIGHT PERCENTS			Wt. % x YIELD FACTORS		SUM OF ACTUAL Wt. in FILTRATE AND RESIDUE	Wt. % SEPARATION OF EACH n-PARAFFIN		Wt. % INCREASE in FILTRATE
		in ORIGINAL	in FILTRATE	in RESIDUE	in ORIGINAL	in FILTRATE	in RESIDUE	Absolute Wt. in FILTRATE (.828)	Absolute Wt. in RESIDUE (.172)		in FILTRATE	in RESIDUE	
n-C_7	98.43	0.40	0.10	0.020	3.50	3.24	4.70	2.68	0.81	3.49	72.0	23.0	+49.0
n-C_8	125.66	0.52	0.15	0.010	4.55	4.86	2.35	4.02	0.41	4.43	91.0	9.0	+82.0
n-C_9	150.81	0.56	0.17	0.010	4.89	5.50	2.35	4.55	0.41	4.96	92.0	8.0	+84.0
n-C_{10}	174.12	0.59	0.17	0.020	5.16	5.50	4.70	4.55	0.81	5.36	85.0	15.0	+70.0
n-C_{11}	195.89	0.52	0.13	0.030	4.55	4.21	7.05	3.49	1.22	4.71	74.1	25.9	+45.8
n-C_{12}	216.28	0.42	0.10	0.030	3.67	3.24	7.05	2.68	1.22	3.90	69.0	31.0	+38.0
n-C_{13}	235.44	0.45	0.09	0.030	3.93	2.91	7.05	2.41	1.22	3.63	66.5	32.5	+34.0
n-C_{14}	253.57	0.51	0.12	0.030	4.46	3.88	7.05	3.22	1.22	4.44	72.9	27.1	+45.8
n-C_{15}	270.34	0.48	0.11	0.030	4.20	3.56	7.05	2.95	1.22	4.17	71.0	29.0	+42.0
n-C_{16}	286.79	0.45	0.11	0.030	3.93	3.56	7.05	2.95	1.22	4.17	71.0	29.0	+42.0
n-C_{17}	301.82	0.42	0.10	0.030	3.67	3.24	7.05	2.68	1.22	3.90	69.0	31.0	+38.0
n-C_{18}	316.12	0.36	0.09	0.025	3.14	2.92	5.89	2.42	1.01	3.43	70.5	29.5	+41.0
n-C_{19}	329.70	0.25	0.06	0.020	2.19	1.94	4.70	1.61	0.81	2.42	66.5	33.5	+33.0
n-C_{20}	342.7	0.19	0.04	0.020	1.66	1.29	4.70	1.07	0.81	1.88	57.4	42.6	+14.8
n-C_{21}	356.5	0.15	0.03	0.015	1.31	0.97	3.53	0.81	0.60	1.41	57.4	42.6	+14.8
n-C_{22}	368.6	0.10	0.02	0.015	0.88	0.64	3.53	0.54	0.60	1.14	47.4	52.6	- 5.2
n-C_{23}	380.2	0.08	0.01	0.010	0.70	0.32	2.35	0.27	0.41	0.68	40.0	60.0	- 20.0
n-C_{24}	391.3	0.07	0.0	0.010	0.61	0.0	2.35	0.0	0.41	0.41	0.0	100.0	- 100.0
Other compounds		4.89	1.49	0.040									
TOTAL		11.41	3.09	0.425									

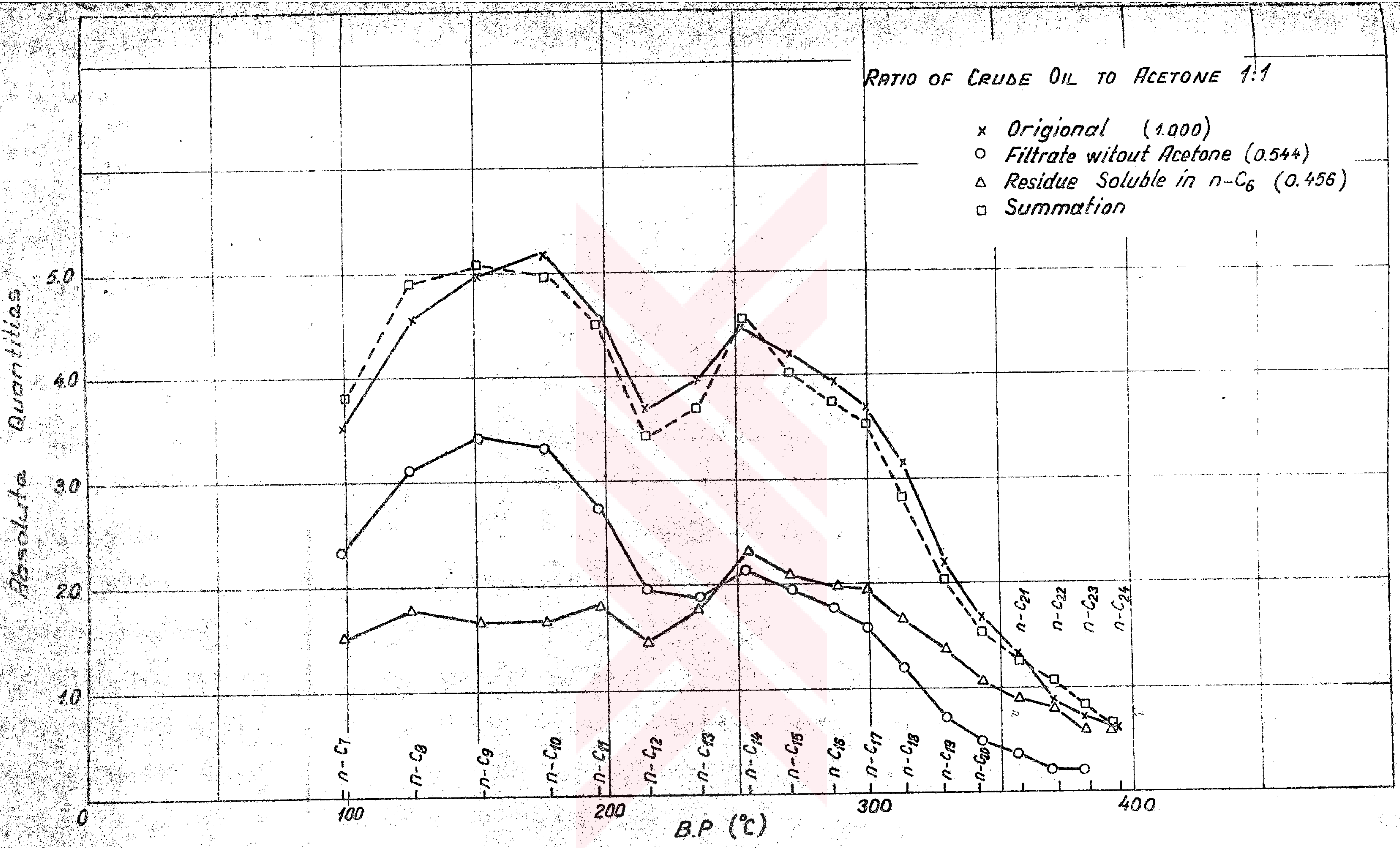


FIG. 16 DISTRIBUTION OF ABSOLUTE QUANTITIES OF n- PARAFFINS

(wt.% of n-Paraffins X Yield Factors.)

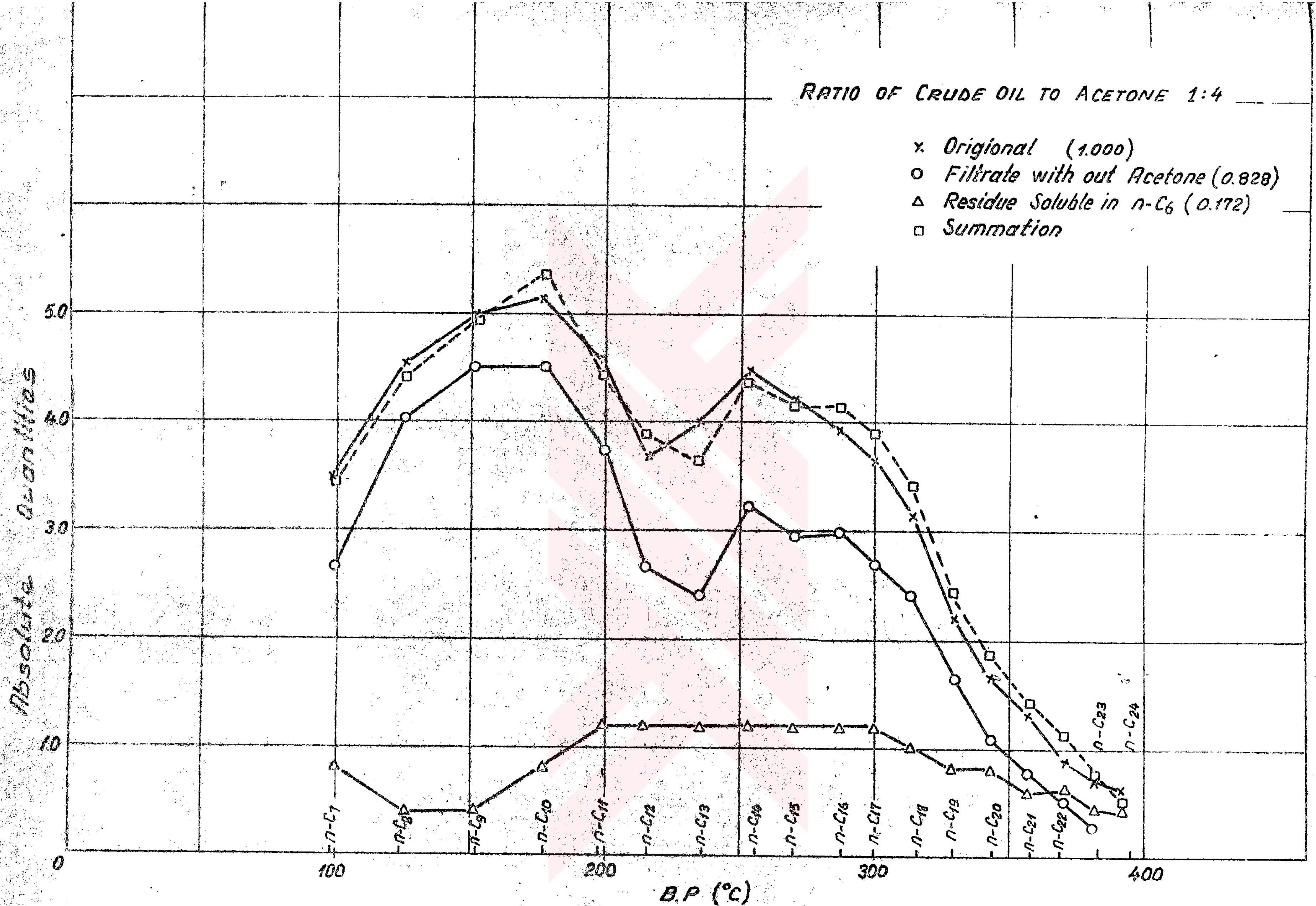


FIG. 17 DISTRIBUTION OF ABSOLUTE QUANTITIES OF n-PARAFFINS (wt.% of Paraffins × Yield Factors)

9.4.2. Enrichment and Group Separation of n-paraffins.

From the quantitative evaluation of the data presented in Table 7 in 9.4.1 it could be seen that within the range of n-C_7 to n-C_{13} an enrichment of 61.0 and 51.5 weight percents respectively has taken place in the filtrate, of 1:1 ratio sample. On the other hand in the remaining range between n-C_{14} and n-C_{24} an enrichment of 52.6 and 100 per cents in the residue layer of the same sample was determined, by taking the percentage as hundred os each n-paraffin in the reduced crude oil. See also Figure: 18, stage one in this Section.

In the 1:4 ratio sample an enrichment of almost all n-paraffins except n-C_{23} and n-C_{24} was observed in the filtrate layer. The corresponding data is presented in Table 8 in 9.4.1 and in Figure 19 in this Section.

From this data it is resulted that lower molecular n-paraffins are more soluble in acetone than the higher molecular n-paraffins, but the solubility of larger molecular n-paraffins is depending on the acetone concantration. Thus it is practical to use acetone treatment of the Garzan Crude Oil for the objective to enrich the lower n-paraffins up to n-C_{13}, using ratios of 1:1 and less. The use of higher ratios would more and more dissolve the higher n-paraffins until practically no paraffinic residue would remain. Such case had been made obvious by calculating a four stage extraction process with be ratio 1:1 in each stage based on the measured distribution in the first stage which was identical in the 1:1 ratio sample. See Figure 18 in this

Section. The results of calculations of four stage extraction are presented in Table 12, in the Appendix A, taking 1000 tons reduced crude oil as basis.

In order to achieve a group separation of n-paraffins, low ratios of acetone should be used. The limit of separation in the experiment, 1:1 ratio, is at n-C_{13}, but by increasing the solvent ratio, either in experiament 1:4 ratio, or in the four stage succesive extraction of the residue of sample, 1:1 ratio, the limit of separation has shifted to the higher molecular side. This limit is at n-C_{22} in the 1:4 ratio which is almost identical with the second stage of the succesive extraction calculations. Fora better idea compare Figures 18 and 19. The group separation of n-paraffins in experiment, 1:1 ratio, is more obvious in Figure 20.

In order to obtain the n-paraffins in a pure form, either molecular sieve treatment or Urea treatment could be used, which are well known refinery techniques, work with higher efficiencies in the presence of higher concentrated product.

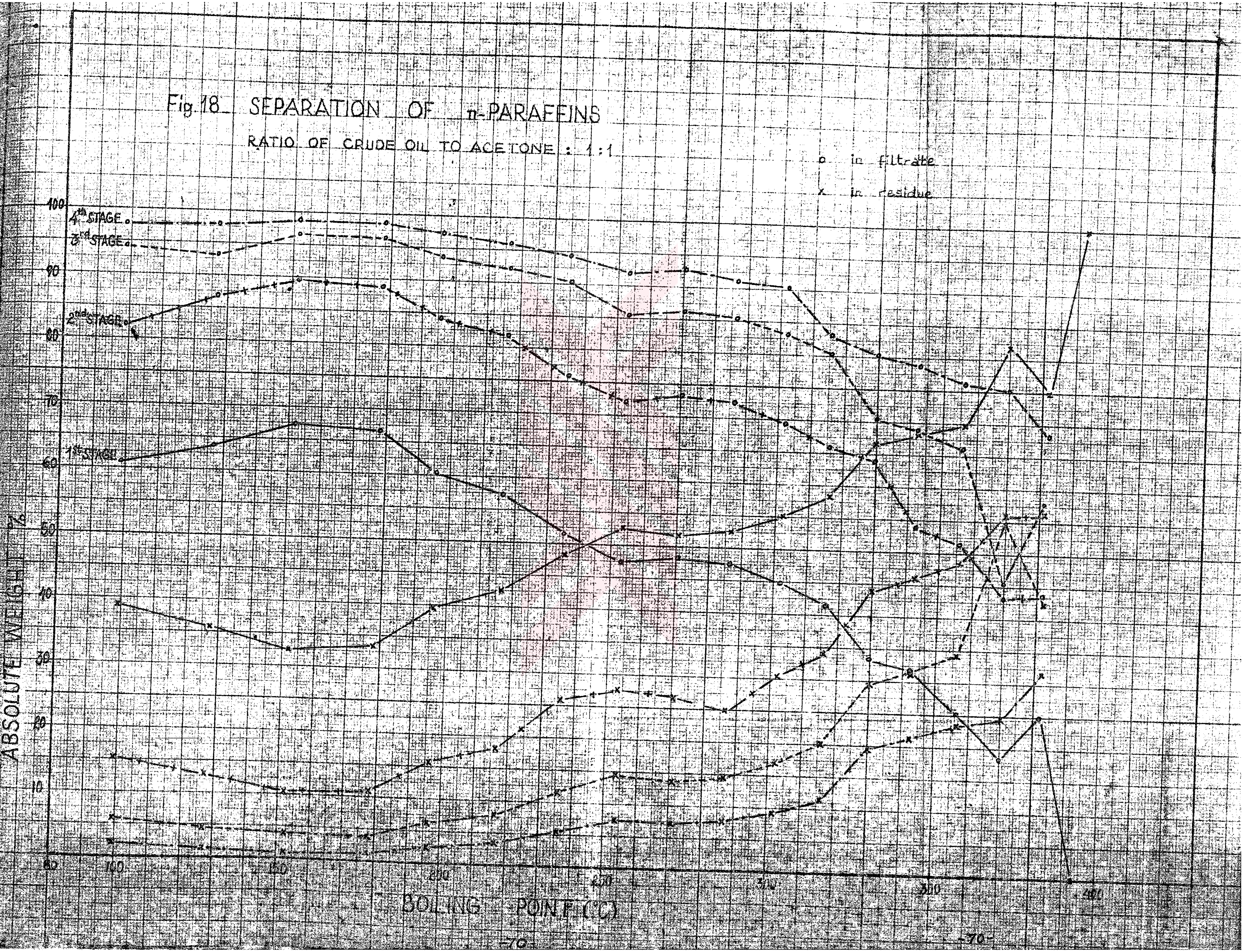


Fig. 18 SEPARATION OF n-PARAFFINS

RATIO OF CRUDE OIL TO ACETONE : 1:1

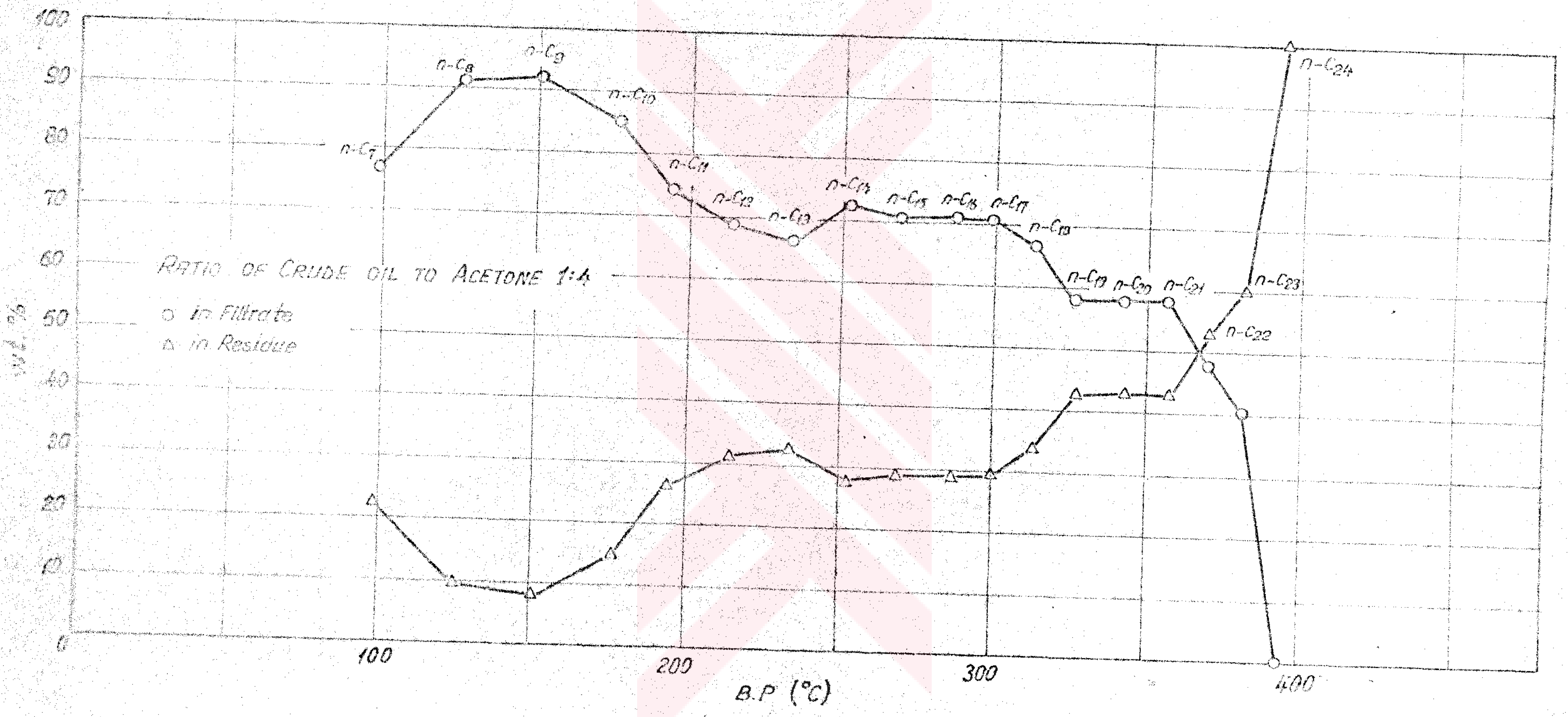


FIG. 19 SEPARATION OF n- PARAFFINS

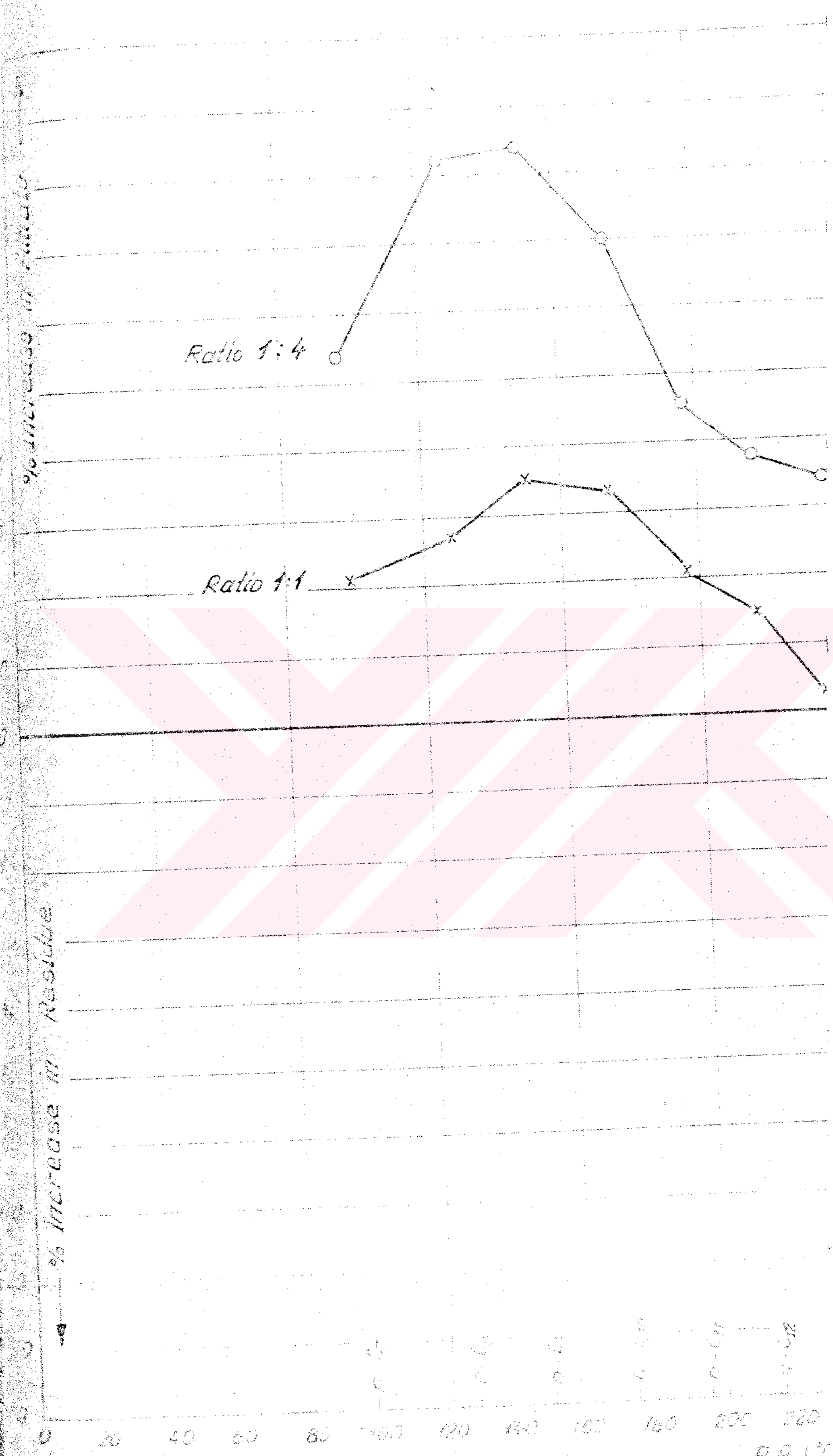


Fig. 20 wt % Increase of n-Paraff
Layers of Acetone treate

2.4.3. Quantitative Analysis of Larger Compounds Other than n-Paraffins.

While the redistribution of n-paraffins in the acetone treatment was quite obvious, a redistribution of other components could be determined by again evaluating the peak areas together with mass balance data. The results of larger compounds are presented in Table; 9, on the following page.

It was resulted that the groups, of the compounds which were taken into consideration, were enriched in the filtrate layer of the sample having the ratio of crude oil to acetone 1:1. About 60 wt. % of each group was in the filtrate layer.

TABLE [illegible]

1:1
RATIO

PEAK NO.	RELATIVE [illegible] in ORIGINAL	RELATIVE [illegible] in FILTRATE	RELATIVE [illegible] in RESIDUE	WEIGHT [illegible] in ORIGINAL	WEIGHT [illegible] in FILTRATE	WEIGHT [illegible] in RESIDUE	Actual [illegible] in FILTRATE	[illegible] in RESIDUE	ACTUAL WEIGHT in [illegible]	in FILTRATE	in RESIDUE	[illegible]	IDENTIFICIONS
15;16	0.44	0.27	0.05	3.86	4.84	[illegible]	[illegible]	1.75	3.06	66.10	33.90	+32.20	[illegible]-cyclo-C5; 3-Me-3 ethyl-C5; 3 ethyl-C6
20	0.34	0.13	0.06	2.10	2.35	1.97	1.27	0.89	2.16	58.80	41.20	+17.60	2,2,3,4-tetra-Me-C5; 2,4-di-Me-C7
22;23, 24;25	0.54	0.31	0.12	4.74	5.56	3.94	3.01	[illegible]	4.80	62.60	37.40	+25.20	m-xylene; cis-1,1-tri-Me-cyclo-C6; 4-Me-C8; [illegible] 3 ethyl-C7; 2-Me-C8; 3-Me-C8, 3,3-di-ethyl-C5
29;30; 32;35	0.25	0.15	0.07	2.20	2.69	2.30	1.46	1.05	2.51	50.30	41.70	+16.60	n-Butyl-cyclo C5; n-propyl-cyclo-C6; 2,2,3,4 [illegible] n-propyl-Benz; 3,5-di-Me-C8; 3,4-di-ethyl-C6; 4-Me-[illegible] 3-Me-3 ethyl-C[illegible]
34;35; 36	0.33	0.18	0.08	2.90	3.23	2.52	1.75	1.15	2.90	60.50	39.50	+21.60	4-Me-C9; 2-Me ethyl-C7; 3,4-di-Me-C8; 2,2,3,3 2-Me-C9; di-propyl-3-Me-cyclo-C5; 3 ethyl-4-Me 4-ethyl-4-Me; tert-Butyl-Benz; 1,2,4-tri-[illegible]
39;40	0.30	0.15	0.06	2.64	2.69	1.47	1.46	0.89	2.35	62.10	37.90	+24.20	n-pentyl-cyclo C5; 1-Me-3 n-propyl-Benz; n-[illegible]
42;43	0.22	0.13	[illegible]	1.92	3.35	1.64	1.27	0.75	2.32	63.00	37.00	+26.00	3-Me-2-[illegible]-C4; 1,3-di-Me-4-ethyl-Benz; [illegible]

10. CONCLUSION.

Normal paraffins have decreasing solubilities in acetone by increasing molecular weights. Thus the use of the limited solubilities of higher molecular n-paraffins in acetone, a highly polaric solvent, would make it possible to achieve the group separation of n-paraffins by the direct application of the solvent on the origional crude oil itself.

It is observed that a marked separation or enrichment of normal paraffins can only be expected when rather low ratios of acetone to crude oil are employed.

11. RECOMMENDATIONS

1. The separation of short chain n-paraffins from those of longer chains by a polar solvent as acetone, methyl ethyl ketone, alcohols and esters may be achieved by taking a paraffinic type crude oil and trying different ratios of solvents to crude oil.

2. The gas chromatograhic investigation may be carried out through capillary tubes and using flame photometric detectors as an improvement in better separation of peaks.

12. APPENDIX.

APPENDIX A. TABLES

TABLE 10. QUANTITATIVE RESULTS OF EXPERIMENTS. (MASS BALANCE.)

B. Deasphalting of Garzan Crude Oil :

Origional Garzan Crude Oil Taken: 577 ml.

509.1.g.

N-Hexane 2.308 lit

Asphaltenes Separated: 93.0 ml.

Asphaltenes Separated: 64.49 g.

Weight % of Asphaltenes: 13.31 %

Total reduced Crude Oil + $n-C_6$: 11.410 lit.

Deasphalted Crude Oil: 0.484 lit

n-Hexane/Reduced Crude Oil 22.6/1.0

C.

Batch 1. Removal of Surplus $n-C_6$ From Reduced Crude Oil.

Reduced Crude Oil Taken 1300 ml.

n-Hexane distilled off 850 ml.

Deasphalted Oil in residue: 1300/23.6=56.4. ml.

n-Hexane in residue : 1300-(850+56.4)=393.6. ml.

n-Hexane/Deasp.Crude Oil : 7/1

The same procedure is repeated for the other batches presented in Table.3 in Section Vlll.

D. Samples Preparation for Gibb's Diagram Representation.

Reduced Crude Oil ($n-C_6$/reduced crude oil = 22.6) taken = 50 ml.

Deasphalted crude oil present = 2.12 ml.

n-C_6 present = 47.85 ml.

Pure acetone added = 50 ml.

Deasp.crude oil: n-Hexane:Acetone=0.0212:0.4788:0.5000

The same procedure has been followed for the preparation of the twenty one samples for Triangular Diagram Representation. See Table 5 in Section VIII.

E. Treatment of Garzan Crude Oil with Acetone.

Larger Sample Ratio 1:1

Total Sample (100cc.Acetone + 100cc Crude Oil)	166.7 g.
Filtrate Layer	116.4 g.
Acetone in the Sample	72.8 g.
Hydrocarbons Soluble in Acetone	43.6 g.
Residue Layer	50.5.g.
n-C_6 Mixed with Residue: (150 cc)	100.5 g.
n-C_6 + Soluble Hydrocarbons in n-C_6	137.5 g.
Hydrocarbons Dissolved in n-C_6	36.5 g.
n-C_6 added for Washing Asphaltenes (100cc).	66.5 g.
Total Washings	68.3 g.
Hydrocarbons Dissolved in n-C_6 Washing	1.8 g.
Dry Asphaltenes	12.2 g.

Yield Factors:

Hydrocarbons Soluble in Acetone 43.6/43.6+36.5= 0,544

Residue Soluble in n-C_6 36.5/43.6+36.5 = 0.456

Larger Sample, Ratio 4:1

Total Sample (400cc.Acetone+100cc.Crude Oil)	395.8 g.
Acetone in the Sample	289.6 g.
Filtrate Layer	366.2 g.
Hydrocarbons Soluble in Acetone	76.6 g.

Prepicitate	29.4 g.
Acetone for washing the Precipitate (150 cc)	109.2 g.
Acetone Washings	110.3 g.
Hydrocarbons in Acetone Washings	1.1 g.
n-Hexane Added to the Precipitate Layer(150cc)	100.5 g
n-C_6 + Soluble hydrocarbons in n-C_6 from the precipitate	116.4 g.
Hydrocarbons Dissolved in n-C_6	15.9 g.
n-C_6 used for Washing Asphaltenes :(200cc.)	134.6 g.
Washings	135.5 g.
Hydrocarbons in the n-C_6 Washings	0.9 g.
Dry Asphaltenes	12.0 g.

Yield Factors:

Hydrocarbons Soluble in Acetone 76.6/76.6+15.9=0.828

Hydrocarbons Soluble in n-C_6

from the Precipitate Layer: 15.9/76.6+15.9 = 0.172

TABLE [illegible] OF n-PARAFFINS IN ORIGINAL REDUCED [illegible]

[illegible] AND RESIDUE LAYERS, IN MOLS & MOL [illegible]

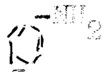
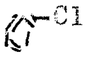
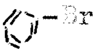
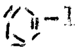
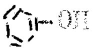
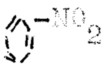
n-PARAFFINE	[illegible]	[illegible]	[illegible]	No. of mols in filtrate	% of mols in filtrate	No. of mols in Residue	% of Mols in Residue	No. of mols in Filtrate	% of Mols in Filtrate
				RATIO: 1/1				RAT[illegible]	
[illegible]	[illegible]	[illegible]	16	0.0254	12.60	0.0150	10.10	0.0268	10.50
n-C8	[illegible]	[illegible]	35	0.0275	14.80	0.0167	10.54	0.0353	[illegible]
n-C9	[illegible]	[illegible]	[illegible]	0.0267	14.40	0.0129	8.66	0.0356	[illegible]
n-C10	[illegible]	[illegible]	[illegible]	[illegible]	12.20	0.0116	7.80	0.0320	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0176	[illegible]	0.0115	7.70	0.0206	[illegible]
[illegible]	[illegible]	[illegible]	45	[illegible]	6.20	0.0086	5.76	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	40	0.0103	5.56	0.0097	6.50	0.0151	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0.0121	8.13	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0092	4.96	0.0099	6.63	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0077	[illegible]	0.0086	5.76	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0066	3.56	0.0081	5.44	0.0112	[illegible]
n-C18	[illegible]	[illegible]	[illegible]	0.0047	2.54	0.0065	4.56	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0025	1.35	0.0051	3.41	0.0060	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0017	[illegible]	0.0037	2.48	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	0.0015	[illegible]	0.0030	[illegible]	0.0027	[illegible]
n-C22	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	1.95	0.0017	[illegible]
n-C23	[illegible]	[illegible]	[illegible]	0.0006	0.31	0.0019	1.28	0.0016	[illegible]
n-C24	85-	[illegible]	54	0.00	0.0	0.0022	1.47	0.0	[illegible]
TOTAL		[illegible]	[illegible]	0.1955	100.00	0.1490	100.00	0.2589	[illegible]

	% in Filtrate	% in Residue	% in Filtrate	% in Residue	In Filtrate	In Residue	In Filtrate	In Residue	Crude Oil	Filtrate	In Residue	In Filtrate	In Residue	In Filtrate	In Resid.	Filtrate	Res
n-C7	61.0	39.0	84.65	15.35	98.58	1.42	97.69	2.31	35	21.35	13.65	29.62	5.38	32.93	2.07	34.2	0.8
n-C8	65.6	34.4	86.97	13.03	95.43	4.57	98.33	1.67	43.5	29.10	15.50	39.56	5.94	43.36	2.12	44.74	0.7
n-C9	67.5	32.5	89.45	10.55	96.57	3.43	98.88	1.12	48.9	33.00	15.90	43.75	5.15	47.22	1.68	48.35	0.5
n-C10	64.6	35.4	88.86	11.14	96.28	3.72	98.76	1.24	51.6	34.30	17.30	45.94	5.76	49.78	1.92	50.96	0.6
n-C11	60.4	39.6	84.31	15.69	93.78	6.22	97.54	2.46	45.5	27.45	19.05	38.36	7.14	42.67	2.83	44.38	1.1
n-C12	57.4	42.6	81.85	18.15	92.26	7.74	96.71	3.29	36.7	21.05	15.65	30.04	5.66	33.85	2.85	35.49	1.2
n-C13	51.5	48.5	76.44	23.55	88.58	11.42	94.94	5.06	37.3	20.22	19.08	30.04	9.26	34.81	4.49	37.12	2.1
n-C14	47.4	52.6	72.35	27.65	85.45	14.55	92.34	7.66	44.6	21.15	23.45	32.25	12.35	38.11	6.49	41.9	3.
n-C15	48.3	51.7	73.30	26.70	86.30	13.70	92.86	7.14	42.0	20.30	21.70	30.73	11.22	36.35	5.75	39.00	3.
n-C16	47.5	52.5	72.45	27.55	85.45	14.55	92.41	7.59	33.3	13.64	20.66	23.48	10.32	33.53	5.72	36.32	2.
n-C17	44.8	55.2	69.60	30.40	83.20	16.80	90.73	9.27	36.7	16.45	20.25	25.65	11.05	30.54	6.16	33.30	3.
n-C18	41.6	58.4	66.00	34.00	80.15	19.85	88.42	11.58	31.4	15.07	18.33	20.61	10.79	25.15	6.25	27.76	3.
n-C19	33.5	66.5	63.90	44.10	70.65	29.35	80.50	19.50	21.9	7.34	14.56	11.24	9.66	20.46	6.44	27.62	4.
n-C20	31.8	68.2	54.10	45.90	68.70	31.30	78.70	21.30	16.6	5.28	11.32	8.98	7.62	11.37	5.23	13.07	3
n-C21	30.2	69.8	51.40	48.60	66.10	33.90	76.40	23.60	13.1	3.96	9.14	6.74	6.36	8.65	4.45	12.17	0.9
n-C22	13.1	[illegible]	43.10	56.90	45.30	54.70	75.30	24.70	8.8	1.60	7.20	2.92	5.88	3.96	4.82	8.08	0.7
n-C23	25.[illegible]	[illegible]	44.70	56.30	57.80	42.20	68.40	31.60	7.7	1.75	5.35	3.66	3.74	4.04	2.46	6.45	0.5
n-C24	0.0	[illegible]	0.0	0.0	0.0	[illegible]	[illegible]	0.0	0.1	0.0	6.10	0.0	0.0	0.0	0.0	0.0	0.0

TABLE: 13

DIPOLE MOMENTS OF POLARIC SUBSTANCES AND POLARIC BONDS:

1 Deby Unit: 10^{-18} e.s.cm.

Substances	(D.U.)	Substances	(D.U.)	Substances	(D.U.)
HCl	+1.03		+1.56	P-$CH_3C_6H_4$- -NH_2	1.90
HBr	+0.78				
HI	+0.38	H–C*	+0.4		
NH_3	+1.46	C–O	+0.7		
H_2O	+1.84	C–Cl	+1.5		
H_2S	+1.10	H–O	+1.6		
HCN	+2.93	C=O	+2.3		
SO_2	+1.60	$\overset{H}{N-H}$	+1.5		
H_2O_2	+2.10	$\overset{O}{N=O}$	-3.9		
R–Cl	+2.05	C≡N	-3.8		
R–Br	+2.05	–O–H–	-1.7		
R–I	+1.90	–Cl	-1.5		
ROH	+1.70	H	0		
R–O–R	+1.15	$H-\overset{H}{C}-H$	0.4		
$R-\overset{O}{C}-R$	+2.70				
R–NO_2	+3.40	$CHCl_3$	1.05		
R–NH_2	+1.30	CH_3Cl	1.86		
	+1.73	$(C_2H_5)_2O$	1.20		
	+1.71	C_2H_5Cl	1.80		
	+1.20	CH_3NO_2	3.40		
	+1.70	C_6H_5Cl	1.7		
	+1.15	$C_6H_5NO_2$	4.20		
	+4.23	$C_6H_5NH_2$	1.50		

*The dipole moment of a molecule can be calculated by the vector addition of the dipole moments of the bonds,

$$\vec{\mu} = \vec{\mu}_1^2 + \vec{\mu}_2^2 + 2\vec{\mu}_1\vec{\mu}_2 \cos\theta$$

where θ is the angle between two polaric bonds.

TABLE: 14 . DATA ABOUT GARZAN CRUDE OIL:*

Physical Properties:

Gravity, API	26.7
Specific Gravity	0.894
Distillation, ASTM	**°F**
IBP	112
5	222
10	276
20	392
30	494
40	592
50	664
60	680
70	57 %
80	-
90	+
95	-
E.P	-
Recovery, % vol	-
Loss, % vol	-
Sulfur, % wt	2.16
Nitrogen, % wt	0.21
U.O.P characterization Factor	11.0
Asphaltene Content, % wt	8.4

* This data is provided by T.P.A.O. Batman Refinery.

APPENDIX: B

F. FORTRAN IV. COMPUT~~T~~ER PROGRAMME FOR THE CALCULATION OF BOILING POINTS, FOR QUALITATIVE ANALYSIS OF THE CHROMATOGRAMS:

Equation for each pair of n-paraffins is increasing number of carbon atoms.

$$\underline{\log(RT)} = \underline{\log A + m\log(BP)}$$

PROGRAMME:

```
       JOB ACA 025
       YUCEL DOLMACI CHEMICAL ENGINEERING 5
       ANALYSIS OF GARZAN CRUDE OIL
       DIMENSION BP(20), XLBP(20), RT(20), XLRT(20)
    10 DO 13 J: 1,2
       READ (1,101) RT(J), BP(J)
       1F (RT (J) 90,90,14
    14 XLRT (J)=ALOG 10(RT(J))
    13 XLBP(J)  ≠ ALOG 10(BP(J))
       XM=(XLRT(2)-XLRT(1)/(XLBP(2)-XLBP(1))
       XLA=XLRT(2)-XM*XLBP(2)
       READ(1,100) KM
       READ(1,102)(RT(K), K= 1,KM)
    11 DO 12 K=1,KM
       XLRT(K)=ALOG 10(RT(K))
       XLBP(K)=(XLRT(K)-XLA)/XM
    12 BP(K)=10.0 ** XLBP(K)
       WRITE (3,103) XLA,XM
       WRITE (3,104)
```

```
      WRITE (3,105) (RT(K), RP(K), K=1,KM)
      GO TO 10
 90   STOP
100   FORMAT (1X,13)
101   FORMAT (2(1X,F 6,4))
102   FORMAT (12 F 6.2)
103   FORMAT ( 11 8X, 5HLOGA =E 15,6,5X,2HM=E15.6)
104   FORMAT (11 12X, 2HRT, 16x, 2HRP1)
105   FORMAT (9X, 2F8.4,10x, F 8.3)
      END
```

APPENDIX: C

OTHER METHODS FOR QUALITATIVE AND QUANTITATIVE EVALUATION OF GAS CHROMATOGRAMS:

A. QUALITATIVE ANALYSIS:

1. The common and most accurate method the retention time technique has already been explained in the text.
Page: 25

The volume of carrier gas required to elute a compound from the G.C column is called the retention volume.
Page: 20.

This retention volume or time is characteristic of the sample and the liquid phase, and colum temperature.

2. Identification by Semi-log Plotting of (RT) of Homologous Series :

a. **Semi-log plotting:** If a sample containing several members of a homologous series is injected into a gas chromatograph, aplot of the log of the retention times is proportional to some increasing property of the homologous series. These property may be one of these; number of carbon atoms, number of methylene groups, boiling points e.t.c. This identification method has the advantageous in that only 2 or 3 compounds are needed to established the slope of a line this can be used to identify other members of the same series.

b. **Log-log Plotting:** When a plot is made of retention time on one liquid phase againts retention time on autober liquid phase of different polarity, straight lines are formed for each homologeous series. So by chromatographing a substance with two different columns it is possible to identify it by means of the graphs available.

3. Retention Index, 1

Peak identification can be confirmed by the use of the retention index, 1. (3)

$$I = 200\ \frac{\log \alpha\ (x)}{\log \alpha\ (P_Z + 2)} + 100\ Z$$

where: α = is the relative retention of the substance, x, reffered to a normal paraffin.

P_Z =containing an even number of carbon atoms.

$\alpha(P_Z + 2)$= is the relative retention of a normal paraffin, $(P_Z + 2)$, reffered to the normal paraffin, P_Z.

Z = The number of carbon atoms.

The retention indeces of the even-numbered paraffins are defined as 100 Z for every temperature and for every liquid phase.

Information on the structure of an unknown peak can be obtained from;

$I = I\ \text{polar} - I\text{nonpolar}$.

Where I= the difference between the retention index of a compound on a polar liquid and on a nonpolar liquid phases.

This system however, would have resulted in replacing the boiling point-method by Index, i.e. Number which refer to hydrocarbons, which are more specifically identified by their boiling points. Comparison of these indexes would have involved numerous calculations with practically the same results.

4. Identification by Relative Detector Response: (Dual Channel)

The comparison of response ratios of a given compound analyzed by two different detectors under fixed conditions is characteristic of that compound.

B. QUANTITATIVE ANALYSIS METHODS:

The determination of the peak height or the peak area with various methods would give the relative weights of the ingredients present in the mixture.

The peak height or the peak area produced is directly proportional to that substances, in weight % concentrations.

1. Peak Height Determination:

Peak height are generally used if samples are less than 10 g for peak columns and 0.1 g for capillary columns. Peak height is measured usually in mm., as the distance from the baseline to peak maxima. If the baseline drifts, the best line between start and finish of the peak is drawn.

2. Peak Areas Determination:

Peak areas are less dependant than peak height on operating conditions. They are certainly the most widely used at the present.

a. Planimetry: The peak is traced manually with a planimeter. It is an instrument which measures area by tracing the perimeter of the peak.

b. Height X Width at Half Height: The area is approximately calculated by multiplying the peak height with the width at half height. A rapid and simple technique which have good results with symmetrical peaks of reasonable width.

c. Triangulation: Height (H) is measured from the baseline to the intersection of the two tangents. The base (B) is taken as the intersection of the two tangents with the baseline. Areas is 1/2 BH. A time consuming but precise method for Gussian shaped peaks.

d. Cutting and Weighing: This is quite time consuming but precise, espesially for ansymmetrical peaks. A disadvantage is the chromatogram is destroyed. Thickness and moisture content of the peaks must be constant.

e. Disc Integrator: Manufactured by Disc Instrument Co. A precise and rapid method. The integrator pen is linked mechanically to the ball which rides on a rotating disc and the limit of precision is the mechanical performance of the recorder.

f. Electronic Digital Integrator: The chromatographic input signal is fed into a voltage to frequency convertor which generates an output pulse rate proportional to the peak area. These integrators have a wide linear range, a count rate and sensitive power detection.

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